A Study of Novel forms of Thermoluminescent Media for Clinical Dosimetry

Thesis

By

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Dedicated to My Parents and Children:

Hussain S. Alabdali & Alsamra U. Alabdali

Mayar, Odhai, Qusai and Raghad
Abstract

This work encompasses studies of two novel materials for radiation dosimetry as well establishment of a novel technique for dosimetry. Silica-based material and CNTs (carbon nanotubes) were used as passive radiation dosimeters. The atomic effective numbers ($Z_{\text{eff}}$) for the silica-based materials (glass beads and optical fibres) are similar to that for the bone tissue, while carbon nanotubes have effective atomic number ($Z_{\text{eff}}$) similar to that of human soft tissue. Present studies have been carried out seeking to improve upon the thermoluminescence (TL) yield of commercially produced small diameter telecommunication optical fibres as well as glass beads. Their small sizes make them of great interest as they can fulfil the Bragg–Gray cavity theory. In this thesis, demonstration is made of their utilities to measure the depth-dose profile for protons and neutrons at therapeutic energies range. In regard to carbon nanotubes, these were made in thin films (known as buckypaper) with various thickness ranging from ~10 to ~100 µm to fulfil two conditions; (i) satisfying the Bragg–Gray cavity theory, and; (ii) to present tissue equivalent material. The CNTs were examined in using conventional thermoluminescence technique. Then, a novel method of dosimetry was established by use of x-ray photoelectron spectroscopy (XPS).
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## Contents

List of Figures .............................................................................................................. XII  

Chapter 1 ......................................................................................................................... 1  

1 Introduction .................................................................................................................. 1  

Chapter 2 ......................................................................................................................... 3  

2 Brief overview of Radiation Interaction with Matter .................................................. 3  

2.1.1 Photoelectric Effect ............................................................................................... 4  

2.1.2 Compton Scattering .............................................................................................. 4  

2.1.3 Pair Production .................................................................................................... 5  

2.1.4 Beams Attenuation .............................................................................................. 7  

2.1.5 Electrons Stopping Power ................................................................................... 7  

Chapter 3 ......................................................................................................................... 9  

3 Radiation Therapy Dosimetry: Literature Review ..................................................... 9  

3.1.1 Introduction .......................................................................................................... 9  

3.2 The Bragg Cavity Theory and its validity ............................................................... 10  

3.3 Radiation Therapy ................................................................................................... 11  

3.4 Radiation Dosimeters: ............................................................................................ 12  

3.5 Application of Dosimeters: .................................................................................... 13
3.5.1 Types of Radiation Dosimeters: ................................................................. 13

3.6 Physical Principles of Radiation Dosimeters: ............................................. 19

3.6.1 Accuracy and Precision: ................................................................. 19

3.6.2 Linearity: ......................................................................................... 20

3.6.3 Dose Rate Dependence: ................................................................. 21

3.6.4 Energy Dependence: ......................................................................... 22

3.6.5 Directional Dependence: ................................................................. 22

3.6.6 Physical Size and Spatial Resolution: ............................................... 23

3.6.7 Readout Convenience: ....................................................................... 23

3.6.8 Convenience of Usage: ..................................................................... 24

3.7 Active and Passive Dosimeters: ............................................................. 24

3.7.1 Active Radiation Dosimeters: .......................................................... 25

3.7.2 Passive Radiation Dosimeters: ......................................................... 30

3.8 Thermoluminescence of Ge-doped SiO₂ Optical Fibres and Glass Beads .... 31

3.8.1 Introduction ....................................................................................... 31

3.8.2 The Ge-Doped SiO₂ Optical Fibres and Glass Beads ......................... 33

3.8.3 Advantages of Ge-Doped SiO₂ Optical Fibres and Glass Beads .......... 34

3.8.4 Limitations in Ge-Doped SiO₂ Optical Fibres and Glass Beads .......... 41

3.8.5 Conclusion in regard to doped silica media ....................................... 42
3.9 The Use of Carbon Nanotubes in Radiation Dosimetry and the Effect of Ionising Radiation on CNT Structure and Properties .......................................................... 43

3.9.1 Introduction ........................................................................................................... 43

3.9.2 Effect of Ionising Radiation Doses on their Structure and Properties .............. 43

3.9.3 Use of Carbon Nanotubes in Radiation Technology other than Dosimetry ...... 44

3.9.4 Effect of Ionising Radiation Doses on their Structure and Properties .............. 46

3.9.5 Conclusion in regard to CNT media ..................................................................... 53

3.10 Methods of Analysis .............................................................................................. 54

3.10.1 Introduction ......................................................................................................... 54

3.11 Analytical Methods ............................................................................................... 55

3.11.1 X-ray Photoelectron Spectroscopy ................................................................. 55

3.11.2 Thermal Gravimetric Analysis ......................................................................... 58

3.11.3 Energy Dispersive X-ray Analysis .................................................................. 59

Chapter 4 ...................................................................................................................... 63

4 Silica-Based material Studies ................................................................................... 63

4.1 Developments in Production of Silica-Based hermoluminescence Dosimeters .... 63

4.1.1 Introduction ......................................................................................................... 63

4.1.2 Silica production routes ..................................................................................... 67

4.1.3 Ge-doped optical fibre produced via MCVD technique .................................... 72
4.1.4 The sol-gel technique ........................................................................................................ 73
4.1.5 Ag-doped silica nanoparticles .............................................................................................. 74
4.1.6 Examples of fibre TL applications ........................................................................................ 78
4.1.7 Conclusions .......................................................................................................................... 83
4.2 Latest developments in silica-based thermoluminescence spectroscopy and dosimetry ........................................................................................................................................... 84
4.2.1 Introduction ........................................................................................................................... 84
4.2.2 Energy Band Diagram ........................................................................................................... 86
4.2.3 Energy Level of GeO₂-SiO₂ Glass ....................................................................................... 87
4.2.4 Sample Preparation .............................................................................................................. 88
4.2.5 Experimental Set-up for Conventional Glow Curves ............................................................. 88
4.2.6 The Experimental Set-Up for TL Emission Spectra ............................................................... 90
4.2.7 Peak Temperature ............................................................................................................... 91
4.2.8 Spectral Analysis ................................................................................................................. 92
4.2.9 Cases of Silica Beads Irradiated by an Am-Be Neutron Source ........................................... 96
4.2.10 Conclusion ......................................................................................................................... 99
4.3 Characterisation of an isotopic neutron source: A comparison of conventional neutron detectors and micro-silica glass bead thermoluminescent detectors .................................................................................................................... 100
4.3.1 Introduction ......................................................................................................................... 100
4.3.2 Surface Scan ................................................................. 103
4.3.3 Depth Measurement ....................................................... 104
4.3.4 Glass Beads .................................................................. 104
4.3.5 Calibration .................................................................... 105
4.3.6 Monte Carlo Simulation .................................................. 106
4.3.7 Results and Discussion .................................................. 106
4.3.8 Conclusion and Further Work ........................................ 109

Chapter 5 ............................................................................. 111
5 Carbon Nanotubes Buckypaper Radiation Studies for Medical Physics Applications . 111
5.1.1 Introduction ................................................................. 111
5.1.2 Carbon Nanotubes ....................................................... 111
5.1.3 Buckypaper Samples .................................................. 113
5.1.4 Thermogravimetric Analysis, TGA ................................. 116
5.1.5 Radiation Sources and System/Sample Set-up .................. 121
5.1.6 Results and discussion ............................................... 122
5.2 Conclusion ..................................................................... 129

Chapter 6 ............................................................................. 130
6 Lower Limits of Detection in using Carbon Nanotubes as Thermoluminescent Dosimeters of Beta Radiation ......................................................... 130
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1.1</td>
<td>Introduction</td>
<td>130</td>
</tr>
<tr>
<td>6.1.2</td>
<td>Strontium-90 source for Beta Irradiation of CNT Samples</td>
<td>132</td>
</tr>
<tr>
<td>6.1.3</td>
<td>Results and discussion</td>
<td>133</td>
</tr>
<tr>
<td>6.1.4</td>
<td>X-ray Photoelectron Spectroscopy</td>
<td>139</td>
</tr>
<tr>
<td>6.1.5</td>
<td>Conclusion</td>
<td>141</td>
</tr>
<tr>
<td>Chapter 7</td>
<td>Novel Dosimetric Study of sp2 to sp3 Irradiation hybridisation Ratio in Free –Standing CNTs</td>
<td>143</td>
</tr>
<tr>
<td>7.1.1</td>
<td>Introduction</td>
<td>143</td>
</tr>
<tr>
<td>7.1.2</td>
<td>Setup of the experiment</td>
<td>144</td>
</tr>
<tr>
<td>7.1.3</td>
<td>X-ray photoelectron spectroscopy (XPS)</td>
<td>144</td>
</tr>
<tr>
<td>7.1.4</td>
<td>Results</td>
<td>148</td>
</tr>
<tr>
<td>7.1.4.1</td>
<td>Raw single-wall carbon nanotubes samples</td>
<td>148</td>
</tr>
<tr>
<td>7.1.4.2</td>
<td>Pure single-wall carbon nanotubes</td>
<td>154</td>
</tr>
<tr>
<td>7.1.4.3</td>
<td>Super-pure single-wall carbon nanotubes samples</td>
<td>160</td>
</tr>
<tr>
<td>7.1.5</td>
<td>Discussion:</td>
<td>163</td>
</tr>
<tr>
<td>Chapter 8</td>
<td>Conclusion</td>
<td>169</td>
</tr>
<tr>
<td>8.1</td>
<td>Future Work</td>
<td>172</td>
</tr>
</tbody>
</table>
9  References.............................................................................................................. 175

10  Appendix........................................................................................................... 191
List of Figures

Figure 1: The range-energy dependence of product electrons in water, Source (Hendee et al., 2005).................................................................................................................................................................................. 3

Figure 2: The Photoelectric effect for high-energy photon interactions. ........................................ 4

Figure 3: The Compton scattering effect is energy dependent. ......................................................... 5

Figure 4: The Pair Production interaction mechanism........................................................................ 6

Figure 5: The relationship between the various primary photon interaction mechanisms as a function of photon energy and the atomic number (Z) of the absorber. From (Evans 1955) cited in (Knoll 2000). ......................................................................................................................................................................................... 6

Figure 6: Response characteristics of two dosimetry systems. Source: (Izewska and Rajan, 2005, p.75)................................................................................................................................................................................................................... 20

Figure 7: Design Characteristics of the 0.6 cm$^3$ Cylindrical Ionization Chamber. Source: (Izewska & Rajan, 2005, p.77). .................................................................................................................................................................................................................. 26

Figure 8: A Schematic Illustration of an XPS System........................................................................ 56

Figure 9: Typical TGA Instrumentation. Adopted from Duncan Price lecture notes (Price 2006). ................................................................................................................................................................................................................. 59

Figure 10: A Schematic Illustration of the Light Path Subsystem of an EDXRF Spectrometer ................................................................................................................................................................................................................ 61

Figure 11: (a) silica molecule; (b) 6-membered ring lattice of silica molecules (adapted from: http://www.iue.tuwien.ac.at/phd/filipovic/node26.html). ........................................................................................................ 68

Figure 12: Example XRD pattern of silica Nps, the broad peak indicating the silica nanoparticles to be in an amorphous state................................................................................................................. 75

Figure 13: XRD patterns for Ag-doped silica nanospheres, with crystalline peaks revealing AgNp within the structure of the pure silica base media. ......................................................................................... 75
Figure 14: Mass-normalised nanoparticles TL as a function of radiation dose, the table below (Table 6) providing information on particle size (Siti Shafiqah et al., 2015).

Figure 15: TL response of pure silica and Ag doped sample within dose range 1- 500 Gy. The variation in TL yield and error bars of relatively large magnitude are indicative of the control issues needing to be confronted in product generation.

Figure 16: Depth dose distribution of a modulated and un-modulated 62 MeV proton beam. The upper graph shows the outcome for an undmodulated beam, the parallel plate ion chamber achieving the predicted peak to plateau ratio of some 5:1 while the fibres approach a ratio of 4:1. The lower graph shows the outcome for a modulated beam, the fibres producing a range that closely agrees with parallel plate ion chamber measurements.

Figure 17: TL response of collapsed PCFs and phosphor TLDs subjected to 80 kVp X-ray irradiation. The inset depicts the TL response of the PCFs and TLD-100 in the absence of TL-200 data.

Figure 18: Mass normalized TL yield for collapsed PCFs and phosphor TLDs. R1 refers to the first sample collection (2 months post-burial) and R2 to the second sample collection (4 months post-burial). The five sampling locations, L1 to L5, are identified in Table 7.

Figure 19: The glow curve of PCFs obtained in burial at location L1 for the first sample collection (R1) and second sample collection (R2).

Figure 20: Energy band model illustrating the electronic transmissions associated with a TL material.

Figure 21: Modification of the energy band structure of silica by impurity atoms(Ge)or lattice irregularitiesinthesilicaglassthatcreatelocalizedelectronstates(energy values all in eV). This figure was constructed with the help of available literature (Randall, 1945; Skuja, 1992, 1998; Imai and Hirashim, 1994; Amossov and Ry-baltovsky, 1994), showing the various possible defect energy levels in Ge doped silica.
Figure 22: The In-house Experimental Setup for measuring emission spectra of the heated samples P1 and P2. 

Figure 23: Glow Curve Deconvolution Analysis for the Oxygen-Rich Sample (P1). 

Figure 24: Glow Curve Deconvolution Analysis for the Oxygen-Deficient Sample (P2). 

Figure 25: Results of the spectral analysis of samples P1 and P2. The figure illustrates the total intensity emitted from samples P1 and P2, Sample P2 is characterized by an additional peak at 5.4 eV. Furthermore, the intensity of P2 is about 12 times that of sample P1. 

Figure 26: Emission spectrum contour of plot sample P1. The right side of the figure shows the sample’s relative heat or its associated TL intensity. 

Figure 27: Emission Spectrum Contour plot of Sample P2. 

Figure 28: Depth-dose distribution in an Am-Be neutron source. (a) 1 mm spatial resolution depth dose distribution from the Am-Be neutron source; (b) A visual impression of the Monte Carlo simulation’s mathematical model; (c) Neutron source spectrum; (d) the MCNP Monte Carlo simulation’s 3 independent runs. 

Figure 29: Neutron tank setup and detectors positions for vertical measurement study. While both the glass beads and gas detectors were depicted in a similar position, their measurements were undertaken separately. 

Figure 30: Scans across the neutron tank’s surface with the gas detectors. The maximum intensity appears above the Am-Be source. 

Figure 31: individual hollow glass beads. 

Figure 32: Vertical Depth Measurements for the $^3$He Tube and the Glass Beads. 

Figure 33: Abridged TL Yield Associated with a Mixed Radiation Field. 

Figure 34: The structure of Single-Wall Carbon Nanotube, SWCNT, is displayed to the left-hand side while the Multi-Wall Carbon Nanotubes structure is displayed to the right (Choudhary and Gupta 2011). Licence: http://creativecommons.org/licenses/by-nc-sa/3.0/
Figure 35: Samples of Buckypaper of different thicknesses have been prepared and developed in the Nanomaterial and Structure Lab at the University of Surrey................................. 113

Figure 36: (a) A tip sonication, Branson – Sonifier 150, (b) Eppendorf Centrifuge 5702. .. 114

Figure 37: The preparation of buckypaper in the Material Processing Laboratory at the University of Surrey, (a) the mixture before dispersion takes place, (b) the glass stopcock, (c) the filtration system setup, (d) removal of the air bubbles from the solution. ............. 115

Figure 38: The Thermogravimetric Analysis Unit, (a) Cutting the Buckypaper to small pieces, (b) The small Pan ready to be loaded, (c) The cylindrical furnace and the pan. .............. 117

Figure 39: Thermogravimetric analysis diagram for Buckypaper made of Single-Wall Carbon Nanotubes................................................................. 118

Figure 40: Thermogravimetric Analysis graph for Triton, illustrating the change in mass when the temperature is increased from room temperature to 600 °C under the flow of nitrogen.................................................................................................................. 119

Figure 41: Thermogravimetric Analysis graph for Triton illustrating the change in mass when the temperature is increased from room temperature to 600 °C under the flow of air. ........ 120

Figure 42: Scheme of Strontium-90 decay (adopted from (Images SI Inc 2012)). ............ 121

Figure 43: Set-up for the beta irradiation source, 90Sr, the Buckypapers of size (5 × 5mm) and TLD-100 samples................................................................. 122

Figure 44: TL from Buckypaper (sample size 5 × 5 mm) raw SWCNT dispersed in 100 ml of deionized water using Triton X-100. The results show TL yield post pre-heat of 165 °C (Channel Number 0), the temperature subsequently ramping up at 6.5 °C per second to a maximum of 330 °C at channel Number 100................................................................. 123

Figure 45: The peak illustrates the TL yield from the raw SWCNT sample post-irradiation, while the lower line illustrates the TL from the unirradiated sample, post-annealing........ 124
Figure 46: The peak illustrates TL yield of raw SWCNT obtained following irradiation to a beta dose of 2 Gy, the lower line representing subsequent readout from the sample, demonstrating radical release of the trapped electron and lattice relaxation to have occurred.

Figure 47: TL from Buckypaper made of pure SWCNT dispersed in 100 ml of deionized water using Triton X-100 (sample size was 5 × 5mm).

Figure 48: The peak illustrates TL yield from pure SWCNT buckypaper irradiated to a dose of 2 Gy using a beta source 90Sr; the lower line illustrates the signal obtained on second reading.

Figure 49: TL yield, before irradiation, from buckypaper made of Super-Pure SWCNTs dispersed in 100ml of deionized water using Triton X-100, (sample size was 5 × 5mm).

Figure 50: The peak illustrates the TL yield from the super-pure SWCNT sample following exposure to a dose of 2 Gy using the 90Sr source, and the lower line illustrates the TL yield from second reading for the same sample.

Figure 51: TL yield from TLD-100 irradiated to a dose of 2 Gy using the 90Sr source.

Figure 52: Microscopic view of the Buckypaper sample made of single-wall CNTs. Obtained using accelerating potential energy of 20 kV, and magnification power of 50,000. The scale is shown in the form of the 100 nm white bar, provided in the lower part of the figure.

Figure 53: Microscope image of one of the buckypaper super-pure single-wall CNT samples, the image being obtained using an acceleration potential 20 kV and magnification 25x, the surface roughness being highlighted. A 1mm long scale is provided in the lower part of the figure.

Figure 54: The diagram shows the beta source irradiation set-up used to expose the CNT Buckypaper samples.
Figure 55: TL yield for the CNTs (the glow curve), encompassed within the temperature range 180–250 °C................................................................. 133

Figure 56: Comparison between the energy response for raw, pure, and super-pure (SP) SWCNTs. The TL yield divided by 1 million to normalize the numbers on the scale of Y-axis. The inset displays the hyper-sensitivity observed at low doses. ........................... 134

Figure 57: Energy Dispersive X-Ray Analysis (EDX), showing the various elements present in the raw SWCNT samples. ................................................................................. 135

Figure 58: TL yield for the CNTs (the glow curve), encompassed within the temperature range 180–250 °C......................................................................................... 136

Figure 59: Comparison between the energy response for raw, pure, and super-pure (SP) SWCNTs. The TL yield divided by 1 million to normalize the numbers on the scale of Y-axis. ......................................................................................... 137

Figure 60: X-ray Photoelectron Spectroscopy for the super-pure SWCNTs sample pre-irradiation, showing the separate sp² and sp³ peaks......................................................... 140

Figure 61: X-ray Photoelectron Spectroscopy for the super-pure SWCNTs sample post-irradiation. The peak of the sp² and sp³ are displayed......................................................... 140

Figure 62: Example for the first derivative for carbon KLL spectra was used to determine the distance “D” between the most positive maximum and most negative minimum for the raw sample A, in this case the D-value of 21.0 eV corresponds to the sample pre-irradiation. .. 145

Figure 63: Example for the first derivative for carbon KLL spectra was used to determine the distance “D” between the most positive maximum and most negative minimum for the raw sample A, in this case the D-value of 17.7eV for the A sample post irradiation, exposed to a dose 5.85 Gy. ........................................................................................................ 145
Figure 64: Hybridisation of orbital bonding, from sp2 to sp3; for sp2 the angle between the orbitals is 120° while for sp3 it is 109.5°. The sp2 to sp3 ratio has been observed to change systematically when the highly carbon-rich sample is exposed to ionising radiation. Figure 65: Examples of samples thickness variations. Figure 66: Relationship between deposited dose and change in D-value for raw sample A over the dose range zero to 5.85 Gy; the D-value shows exponential-like reduction with increase in dose. Figure 67: Display of the percentage sp2 associated with D values for raw sample A. Note that use has been made of two reference values, namely diamond (100% sp3) and graphite (100% sp2). Figure 68: Dose dependent D-values for raw sample D, made using 0.14 g of CNTs, 100 ml of DI-water and 1 g of Tx-100. Figure 69: Percentage sp2 associated with dose-dependent D values for raw sample D. Figure 70: Dose dependent D-values for raw sample H, made using 0.12 g of CNTs, with 100 ml of DI-water and 1 g of Tx-100. Figure 71: The percentage of sp2 associated with the D values for raw sample H. Figure 72: D-value vs dose for pure sample B1, prepared from 0.05 g CNTs, 100 ml DI-water and 0.5 g Tx-100. Figure 73: Percentages of sp2 associated with the D values for pure sample B1. Figure 74: D-value vs dose for pure sample B2, prepared using 0.05 g of CNTs, 100 ml DI-water and 0.5 g of Tx-100. Figure 75: The percentages of sp2 associated with the D values for pure sample B2. Figure 76: D-value vs dose for pure sample F, the D-value decreasing in an approximate linear fashion with dose. Figure 77: The percentages of sp2 associated with the D values for pure sample F.
Figure 78: D-value vs dose for super-pure sample G1, the D-value decreasing in a closely linear fashion with dose. .................................................................................................................................................................................. 161

Figure 79: The percentage sp\(^2\) associated with the D values for super-pure sample G1. ..... 161

Figure 80: D-value vs dose for super-pure sample G2. ............................................................................. 162

Figure 81: The percentage sp\(^2\) associated with the D values for super-pure sample G2. ..... 163

Figure 82: diagram illustrates the covalent and Van der Waals bonds in the graphite structure.
.................................................................................................................................................................................. 166
Chapter 1

1 Introduction

World-wide, there is on-going intensive research into the adaptation of carbon nanotubes (CNTs) for a wide variety of applications. Numerous studies have attempted to investigate different properties, including in photonics (Avouris et al., 2008) and radiation sensors (Ma et al., 2007a, Ma 2008). Of particular note for present interests is that the phenomenon of luminescence from CNTs has been observed during study of radiation defects on graphite, specifically by Bonard and his group (Bonard et al., 1998) in investigation of electron field emission. This has provoked further investigation into carbon structural material, examining defects induced by beta radiation in graphite and multi-wall carbon nanotubes, MWCNTs (Chruscinska et al., 2006). That said, the latter study focused almost entirely on defects in the graphite and multi-wall carbon nanotubes, not considering the potential use of both materials in radiation physics as a passive radiation dosimeter material. Since it is apparent that very little research is known to exist in this area of endeavour, representing a potential gap in knowledge, it is the intention of present work to study the dosimetric characteristics of such carbon based material, making comparison with other perhaps competitive media.

In the primary investigation, various samples of CNTs are to be irradiated using a range of sources of ionizing radiation. The thermoluminescence (TL) signal is intended to be detected from the samples, establishing at the outset the extent to which electron trapping centres exist in the media types, expected to be of interest given that to-date there have been no known efforts towards identification of the trapping centres in such media in the literature. The study aims to further ascertain the radiation sensitivity of CNTs, produced in the form of buckypaper. Here it is to be mentioned that buckypaper is a network of SWCNT fibres that form a thin membrane (Wang et al., 2004). By so doing, one wishes to establish baseline data for applications of buckypaper as a radiation dosimeter media, with potential outlook for buckypaper-based ion chamber walls and gas sensor devices (Ma et al., 2007b, Modi et al., 2003). Understanding the effect of radiation on CNTs can help to estimate the limitations on the sensitivity and precision of any such ion chamber and quality control applications of such devices.
Fundamental understanding of the radiation effect can facilitate optimal implementation of CNTs in many applications, such as light-weight and strong materials for space applications, in satellites, aircraft and spacecraft exposed to cosmic radiation. Irradiation-modified thermo conductivity, electric conductivity and stress-strain properties are of further interest, judged against a backdrop of pristine CNTs that offer performance rarely matched by other media. Therefore, the effect of radiation on these properties in CNTs will be also investigated.

Within the present study, and as previously mentioned, comparison will be made of the performance of CNTs against that of other potential novel competitor media. As an instance, it is immediately apparent that buckypaper has an effective atomic number \(Z_{\text{eff}}\) that is similar to that of soft human tissue, pointing to favourable measurement of dose deposited in the human body. Thus said, precision of measurement represents a considerable challenge that needs to be achieved in radiation dosimetry. In our primary investigation of the response of CNTs to ionising radiation it has become immediately clear that weight-for-weight it is not as sensitive as some known dosimeter materials such as the LiF based TLD-100. While this may appear to be a setback, the lack of sensitivity could well point to favourable application of CNTs in dosimetry in cases of elevated doses, such as might be experienced in space missions, high-energy gamma radiations and heavy particles that need to be contended with (Parker 2005). In comparing with other novel media, the study will also focus on the TL of silica fibres (with \(Z_{\text{eff}}\) approaching that of calcified tissues, bone primarily), directly comparing dose profiles from different radiotherapy systems that place great demand on spatial resolution to well below 1 mm. The fibres, purchased from CorActive (Canada), offer spatial resolution ~ 120 \(\mu\)m, with a doped-core diameter of 50 \(\mu\)m, and a cladding diameter of 123-127 \(\mu\)m. The dimensions and constitution of such media provide the opportunity for \textit{in vivo} dosimetry, presently at unprecedented spatial resolution, to be compared against the buckypaper fabricated down to thicknesses of some few microns, comparable with a fraction of a cell layer in the human body.

In what is to follow, a brief overview of radiation interaction with matter is first provided. A more detailed introduction for both materials is then included in the materials and sample preparations section, forming part of the methodology section. The irradiation methods, radiotherapy systems used and samples preparation will also be discussed in the same section. Following that will be an overview of the results obtained to-date, including discussion of these. Conclusions and prospects for future work will form the last two sections of this thesis.
Chapter 2

2 Brief overview of Radiation Interaction with Matter

There are number of possibilities that can occur when ionization radiation interacts with matter. The result of the interaction can be determined through knowledge of a number of key parameters that include the energy of the photons (photons being the major source type of interest herein) and the atomic number of the targeted material. Three main interactions can occur with photons: the photoelectric effect, Compton scattering and pair production. The results of these interactions are likely to produce scattered photons, photoelectrons, Compton electrons, Auger electrons and fluorescence photons and electron-positron pairs.

At the atomic level, dose deposition occurs through the slowing down of electrons. As an example, the range in µm for electrons of different keV energies travelling through water is displayed in Figure 1, the range increasing with electron energy, albeit in a non-linear fashion (Hendee et al., 2004).

![Figure 1: The range-energy dependence of product electrons in water, Source (Hendee et al., 2005).](image)

In regard to the primary processes for electron production from photon interactions, these are as discussed below.
2.1.1 Photoelectric Effect

The probability of a photoelectric effect event is directly proportional to some relatively high power of the atomic number of the medium ($\sim Z^3$ to $Z^4$) and inversely proportional to a power of the energy of the incident photons (typically quoted as $E^3$). In such an interaction, a photon of ionising energy is absorbed by an electron, the net result being ejection of the electron as illustrated in figure 2 for an inner-shell electron, the kinetic energy of the ejected photoelectron being calculated from the equation below;

$$E_k = h\nu - E_{binding} \quad \ldots (1)$$

Where $h\nu$ is the energy of the incident photon, $E_k$ is the energy of the recoil electron, and $E_{binding}$ is the binding energy of the electron to the nucleus (Turner 2008).

2.1.2 Compton Scattering

The probability of Compton scattering depends on the number of electrons available, increasing directly with the atomic number and Archimedian density. The energy of the photons is the main factor in determining the distribution of scattering angles. Figure 3 displays the Compton interaction mechanism.
Moreover, the probability of Compton scattering decreases with photon energy, but not as intensely as the photoelectric effect. Compton interactions may contribute a significant fraction of the total deposited dose for photons energies up to a few MeV (Hendee et al., 2004).

### 2.1.3 Pair Production

A photon in the Coulomb field of the nucleus may be annihilated converting its energy to the production of a positron-electron pair, as illustrated in figure 4. This process is called “Pair Production”. In this interaction, all of the photon energy is converting into the production of the pair with an extremely small amount going to the recoil of the nucleus. The equivalent energy of each electron mass is 0.511 MeV - thus the threshold for the pair production mechanism is 1.022 MeV. Any further energy is equally divided between the kinetic energy of the positron and electron. Both particles of the pair will lose energy by atomic ionisation and excitation as they travel from the point of origin.
Ultimately the positron interacts with an electron and the two particles annihilate due to the different polarity, with their mass energy being transformed into two 0.511 MeV photons emitted in opposite directions (Turner 2008).

Figure 5: The relationship between the various primary photon interaction mechanisms as a function of photon energy and the atomic number ($Z$) of the absorber. From (Evans 1955) cited in (Knoll 2000).
Figure 5 shows the probability relationship between the various primary photon interactions as a function of the photon energy and the atomic number of the absorber. As can be seen, the main dominant interaction for photons in the keV energy range is the photoelectric effect, greater photon energies resulting in growth of interactions occurring in the Compton region. Beyond 6 MeV there will be a rapid increase in the Pair Production mechanism. In regard to medical applications of photons, specifically in radiation therapy, different ranges of photon energy are selected for use, depending on the location of the tumour. For superficial tumours the X-ray region is used for which the photoelectric effect is dominant, while for deeper tumours MeV photons are used for which the Compton effect and pair production become and start become dominant processes.

2.1.4 Beams Attenuation

As photons are electrically neutral the attenuation is typically characterised in terms of loss of intensity. In contrast with electrons, photons strongly transport through media while suffering attenuation, the attenuation for photons being dependent on the energy of the photons and the effective Z, which is the weight-averaged atomic number for the material. The attenuation for particular monoenergetic values in a good geometry situation can be calculated by knowing the linear attenuation coefficient, the thickness of the material, and the intensity of the incident photons:

\[ I(x) = I_0 e^{-\mu x} \quad \text{.... (2)} \]

where \( I(x) \) is the intensity of the transmitted photons and \( I_0 \) is the intensity of the incident photons. \( \mu \) is the linear attenuation coefficient and \( x \) is the thickness of the material.

In water, the Compton contribution to the attenuation coefficient becomes equal to the photoelectric contribution at about 25 keV. The Compton contribution to the attenuation coefficient becomes dominant when the energy of the photons exceeds 25 keV, until the pair production mechanism contribution overtakes that of the Compton process at about 30 MeV.

2.1.5 Electrons Stopping Power

When photons interact with matter they produce electrons with a range of energies depending on the energy of the incident photons and the effective Z of the material. A number of factors
dictate the different probability of interactions and thus the resulting electron energy, including the angle at which the incident photons interact with electrons and location of atoms within the target medium. Electrons at lower energies predominantly interact via inelastic collisions with other electrons. For electrons with energies from 10 eV to 10 keV the major loss mechanism at low effective Z would be by scattering from valence band electrons. As an instance, for energies from 1 keV to 10 keV the core level contribution would be less than 10% to the electron interactions. Interactions between the resulting electrons and the other bound electrons or nuclei in the atom will cause the electrons to dissipate their energies by ionizing atoms and by bremsstrahlung radiation; consequently the electrons will eventually stop (Turner 2008).

The stopping power for electrons is different for each material and is energy dependent, hence S(E). It can be simply defined as the average energy loss per unit path length due to inelastic collisions with the nucleus or bound electrons of the medium, typically measured in units of keV \( \mu m^{-1} \):

\[
S(E) = -\frac{dE}{dx} \quad \ldots \ (3)
\]

By taking density into account, the stopping power can be re-written as:

\[
S'(E) = -\frac{dE}{\rho dx} \quad \ldots \ (4)
\]

With units typically quoted in MeV cm\(^2\)/g. As mentioned, for media of low effective Z, electrons with energies from 10 eV to 100 keV will dissipate their energy rapidly, the stopping power being relatively large, in the range 3 to 17 MeV cm\(^2\)/g (Berger et al., 2011). Conversely, electrons with energies from 0.1 to 6 MeV would travel further in the medium, with stopping powers in the range 1 to 3 MeV cm\(^2\)/g. For high Z media (eg gold, Z = 79) the stopping power for electrons from 10 eV to 100 keV, is also relatively large, within the range to 1 to 9 MeV cm\(^2\)/g, while at higher energies, 0.1 to 10 MeV, the electrons will travel further with stopping powers is in the range 0.1 to 1 MeV cm\(^2\)/g (Berger et al., 2011).
Chapter 3

3 Radiation Therapy Dosimetry: Literature Review

3.1.1 Introduction

According to the International Atomic Energy Agency (IAEA) among numerous other notables, precision and accuracy are critical elements in atomic science, especially when measuring invisible phenomena such as ionizing radiation (IAEA 2016). In radiation therapy (i.e. radiotherapy), ionizing radiation is used in the treatment of cancer patients by destroying harmful cancerous cells (Zhuang et al., 2016). In the course of radiation therapy treatment, cancer patients receive extremely specific and targeted quantity/dose of ionizing radiation for purposes of destroying the harmful cancerous cells (IAEA 2016). Delivering too much or too little radiation to the targeted cells can have an adverse effect on the cancer patient. In this regard, the accuracy of predicting and measuring the dose that the whole volume being irradiated receives thus plays a critical determining role on “the quality of the delivery of radiation therapy treatment” (Zhuang et al., 2016, p.2). Therefore, the need for enhanced accuracy and precision in the measurement and delivery of the necessary radiation dose to the cells has prompted the need for the design and development of in-vivo radiation devices that ensure the accurate and precise measurement of the radiation dose and its delivery to targeted tumour cells without occasioning adverse effect on the normal cells (Zhuang et al., 2016). Radiation dosimetry entails quantitative methods employed in determining the energy dumped in a medium by projected ionizing radiations (Attix 1986).

The devices that are most commonly employed in radiation dosimetry are the ionization chamber (IC). However, whereas the IC dosimeter has been regarded as the ‘gold standard’ device for Quality Assurance (QA) in radiation therapy, numerous investigations of the dosimeters report that these devices utilize relatively high voltages (i.e. several tens of volts
or more) to generate the requisite Electric Field (EF) for detecting the ionizing radiation, a phenomenon that compromises their compatibility and efficiency in in-vivo radiation dosimetry (Zhuang et al., 2016). In addition, the ICs rely on the “deployment of dose ionization conversion factors” (Zhuang et al., 2016, p.3), a feature that is largely dependent on the electron beam dose-rate. Therefore, in view of the foregoing, and given the significance of the dosimeter in radiation dosimetry, this review explores radiation dosimetry, with a particular focus on radiation therapy, radiation detectors (i.e. dosimeters), as well as whether the dosimeter is fulfilling Bragg-Gray Cavity Theory or not (see below). In the next section, the review provides a brief overview of the concept of radiation therapy.

### 3.2 The Bragg Cavity Theory and its validity

The Bragg-Gray theory gives route to the determination of absorbed dose in water from a measurement made in another medium, that of the detector, provided that the following so-called Bragg-Gray conditions are fulfilled:

1) The cavity (the spatial dimension of the dosimeter) must be small compared to the range of incident charged particles such that the electron fluence is not perturbed;

2) The absorbed dose in the cavity is deposited solely by the crossing electrons (photon interactions in the cavity otherwise being considered negligible).

If the cavity does not change the number and energy distribution of crossing electrons in the irradiated medium, exclusively depositing energy in the cavity, then the following relationship applies:

$$E_v = J_v W \rho \quad \ldots \quad (5)$$
where $E_\nu$ is the energy absorbed per unit volume of the medium. $J_\nu$ is the ionization per unit volume produced in the cavity. $W$ is the average energy lost by the secondary electrons per pair of ions formed in the cavity, and $\rho$ is the ratio of stopping power of the medium and the cavity for the secondary electrons. Thus for example, using the NIST ESTAR tabulations for electrons of energy 60 keV and 200 keV in graphite (density of 1.7 g cm$^{-3}$), the respective ranges (using the Completely Slowing Down Approximation, CSDA) are 39 µm and 300 µm.

### 3.3 Radiation Therapy

Radiation therapy, also known as radiotherapy, x-ray therapy, or irradiation, is one of the methods commonly adopted by oncologists for the treatment of cancer. Other cancer treatment methods in contemporary medicine, as outlined by (Delwiche 2013), include chemotherapy and surgery. Radiation therapy can be undertaken alone or administered together with the other two treatment methods - chemotherapy and surgery. According to the American Cancer Society (ACS), radiotherapy mainly relies on high-energy particles/waves, including x-rays, protons, or electron beams to kill tumour cells or cancer cells (ACS 2015). Treatment of cancer through radiation therapy entails giving the cancer patient specific, accurate, precise, and targeted doses of radiation. In order to ensure such precision and accuracy, a dosimeter is placed within a radiation beam, which generates an electrical charge within the dosimeter (IAEA 2017). Based on the magnitude of current or electric charge, typically using ICs, radiation therapists are able to determine the corresponding quantity of deposited energy that is received by the dosimeter (IAEA 2017). The electrical quantity received by the dosimeter is then converted into a radiation dose through the application of a calibration coefficient, which is a number that signifies the amount of radiation on the basis of corresponding electrical quantity (IAEA 2017).
However, the accuracy and precision attributed to the measurement of the electrical quantity is dependent on a number of factors, including the radiation beam in which the dosimeter is placed (i.e. electrons, protons etc), the material the dosimeter is made of, as well as the environmental conditions (temperature, pressure and humidity) at the time of measuring the electrical quantity (IAEA 2017). Therefore, considering its significance in radiation dosimetry, especially in radiation therapy, what are the various types of radiation dosimeters employed in radiation therapy? What are the physical principles of the dosimeter(s)? What are its applications in radiation dosimetry? What advantages and disadvantages characterize the dosimeter(s) with respect to its application in radiation dosimetry? Is the dosimeter soft or calcified tissue equivalent? Is the dosimeter fulfilling the Bragg-Gray Cavity Theory? The next sections of the review thus attempt to answer these questions.

### 3.4 Radiation Dosimeters:

(Izewska and Rajan 2005) described a radiation dosimeter as a medical device that is used by radiation therapists or oncologists to measure and/or evaluate the quantities of the absorbed or equivalent dose, or the dose rates, or relative amounts of ionizing radiation. The radiation dosimeter is complemented with a reader, and together these constitute a dosimetry system (Izewska and Rajan, 2005). The dosimetry system is employed in the experimental determination of the dosimetric quantity, the value of which is the outcome of the measurement and which is “expressed as the product of a numerical value and an appropriate unit” (Izewska and Rajan, 2005, p.71). The dosimeters are applicable in a number of areas as explored in the following subsection.
3.5 Application of Dosimeters:

Generally, dosimeters can be applied in a number of fields, including diagnostic, radiology, radiation therapy, etc. The application of dosimeters is dealt with in-depth later in the course of the review.

3.5.1 Types of Radiation Dosimeters:

A number of radiation dosimeters have been developed, tested, and used in radiation dosimetry for purposes of radiation therapy. Notable examples include thermoluminescent dosimeters (TLDs), radiochromic films, optical fibres or silica fibres, silicon diodes, ionization chambers (ICs), and metal-oxide field-effect transistors (MOSFETs) (Hyer et al., 2009, Lambert et al., 2007, Zhuang et al., 2016). The purposes of this review, radiation dosimeters are classified into two main techniques namely: active radiation dosimeters/active radiation detection device and passive detectors (typically integrating dosimeters). The active radiation dosimeters include ICs, semiconductor diodes, and water-equivalent plastic scintillation detectors. Passive detectors on the other hand include radiochromic films, phosphor-based TLDs, Silica-based TLDs and Silica-based fibres. An in-depth review of these classifications together with their respective medical applications as well as advantages and disadvantages is presented in the course of this review.

According to Zhuang et al. (2016), the TLD detectors exist in chip, cube or rod types. Pending treatment, the TLDs can be positioned externally on the body of the patient. In the subsequent radiation therapy, the TLD detector devices are then able to absorb energy, ionizations occurring throughout the bulk device (Jarnet et al., 2004). The subsequent readout requires the heating up of the TLD detector, with consequent emission of visible light from the typically crystalline medium making up the TLD detector device (Kirby et al., 1986). The amount of light emitted from the dosimeter medium is most often proportionate to the amount
of radiation the TLD device receives during radiation therapy (Liuzzi et al., 2015). Studies by
(Yoshimura and Yukihara 2006); (uz Zaman et al., 2011); Liuzzi et al. (2015); and Zhuang et
al. (2016) have established that due to their smaller size, TLD detector devices such as
dysprosium-activated calcium fluoride (e.g. TLD-200) and lithium fluoride (e.g. TLD-100,
TLD-600, TLD-700) are able to provide dose data with relatively high spatial resolution.
However, Yoshimura and Yukihara (2006) note that the TLDs lack the ability to provide real-
time information regarding the delivered dose. Table 1 provides some of the existing multi-
element TLD card dosimeters available in the market and their relative specifications.

<table>
<thead>
<tr>
<th>No.</th>
<th>Example of TLD</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>TLD-100 Microcube</td>
<td>1 x 1 x 1mm</td>
</tr>
<tr>
<td>2.</td>
<td>TLD-100 Chip</td>
<td>3.2 x 3.2 x 0.15 mm</td>
</tr>
<tr>
<td>3.</td>
<td>TLD-100 Chip</td>
<td>3.2 x 3.2 x 0.38 mm</td>
</tr>
<tr>
<td>4.</td>
<td>TLD-100 Chip</td>
<td>3.2 x 3.2 x 0.89 mm</td>
</tr>
<tr>
<td>5.</td>
<td>TLD-100 Disk</td>
<td>Diameter: 3.6 x 0.25 mm</td>
</tr>
<tr>
<td>6.</td>
<td>TLD-100 Disk</td>
<td>Diameter: 3.6 x 0.38 mm</td>
</tr>
<tr>
<td>7.</td>
<td>TLD-100 Disk</td>
<td>Diameter: 4.5 x 0.6 mm</td>
</tr>
<tr>
<td>8.</td>
<td>TLD-100 Disk</td>
<td>Diameter: 4.5 x 0.89 mm</td>
</tr>
<tr>
<td>9.</td>
<td>TLD-100 Chip</td>
<td>Pelletized, 3.2 x 3.2 x 0.89 mm</td>
</tr>
<tr>
<td>10.</td>
<td>TLD-100 Disk</td>
<td>Diameter: 3 x 0.38 mm</td>
</tr>
<tr>
<td>11.</td>
<td>TLD-100 Rod</td>
<td>Diameter: 1 x 3 mm</td>
</tr>
<tr>
<td>12.</td>
<td>TLD-100 Rod</td>
<td>Diameter: 1 x 4 mm</td>
</tr>
<tr>
<td>13.</td>
<td>TLD-100 Chip</td>
<td>6.35 x 6.35 x 0.89 mm</td>
</tr>
<tr>
<td>14.</td>
<td>TLD-100 Rod</td>
<td>Diameter: 1 x 2 mm</td>
</tr>
<tr>
<td>15.</td>
<td>TLD-100 Square Rod</td>
<td>1 x 1 x 6 mm</td>
</tr>
</tbody>
</table>

The silica-based optical fibres function in a similar way. However, they have the ability to provide for much greater spatial resolution, in the range of about 0.1 mm (Bradley et al., 2017), making them among the smallest of TLDs, also demonstrating great performance and reliability; for more details see the reviews of David Bradley and group (Bradley et al., 2012b, Bradley et al., 2017).

In radiation dosimetry, the active silicon diodes are normally characterized by limited applicability because they are temperature dependent, are damaged by radiation and highly dependent on photon energy (Dixon and Ekstrand 1982), a phenomenon that (Smith et al., 1977) attributed to the physical size of the silicon diodes (the physical size of a typically available single diode is $1.5 \times 1.5 \times 0.425$ mm$^3$). Electronic semiconductor diodes do however offer certain advantages, given that they can be utilized directly for purposes of measuring radiation dose, without having to correct for depth dependence (Kinhikar et al., 2012). Radiochromic films, yet another of the passive dosimeter types, are on the other hand a radiation dosimeter that has the capacity to provide spatially extensive dimension measurements for 24-48 hours after radiation therapy (Devic 2011). The radiochromic thin film (a radiochromic dosimeter) has a dose range of 0.5-200 kGy. The FWT-60 series Radiochromic Dosimeters available in the market are FWT-60-00 (1 cm x 1 cm x 42-52 microns); FWT-60-20T (10 x 10 cm sheets); FWT-60-20F (15 x 15 cm); and FWT-60-20S (custom sizes to 45 x 15 cm). One of the disadvantages associated with the radiochromic films is ironically radiation damage, which leads to the generation of dose intensity dependence (Zhuang et al., 2016). Also, according to (Liu et al., 2015), the response of the radiochromic film is dependent on a range of environmental conditions, including temperature and humidity, all which can have an adverse effect on the dose-rate. Appropriate factors must therefore be adopted for purposes of correcting the radiochromic film response results (Zhuang et al., 2016). The MOSFETs, a silicon chip form, typically of dimension (2.5
mm × 8 mm × 1.3 mm thick) are on the other hand detectors that measure variations in voltage shift in the diode before and after exposure of the diode to ionizing radiation (Yoshizumi et al., 2007). Their small detector size allows pinpoint measurements. In addition to their small detector size, the MOSFETs are lightweight (minimising any discomfort to the patient), require minimal power, are easy to use and provide for online readout (Sun et al., 2017). However, the MOSFETs are known to suffer from an accumulating dose effect, a phenomenon that significantly limits the lifetime of these dosimeters (Benevides and Hintenlang, 2006). Studies by (Koivisto et al., 2014) and Sun et al. (2017) have also established that the MOSFETs lack sufficient sensitivity when positioned at distances beyond 10 cm from the radiation source, a phenomenon that limits their utility.

The ICs are often regarded by most authors to be the instruments of choice for measuring absolute radiation dose (Zhuang et al., 2016). The ICs provide a point-by-point measurement of radiation, depending on charge generation within an electric field (Zhuang et al., 2016). Despite being regarded in the practice of radiation therapy as the gold standard instrument for purposes of ensuring QA, the ICs are not devoid of shortcomings. For instance, a major disadvantage associated with the IC as a radiation measurement instrument is its dependence on relatively high voltages to generate the requisite electric field (EF) for the detection of radiation (Palmans et al., 2010). In this regard, Zhuang et al. (2016) consider the ICs completely incompatible for in-vivo uses. Another disadvantage associated with the ICs is that the use of these devices requires “deployment of dose ionization conversion factors” (Zhuang et al., 2016, p.3), a feature that Zhuang et al. (2016) further note displays an increasing dependence on electron beam dose-rate, as one example.

In view of the various shortcomings associated with the conventional dosimeters discussed above, Zhuang et al. (2016) in their study: Embedded Structure Fibre-optic Radiation Dosimeter for Radiotherapy Applications, presented a novel alternative method for
radiation monitoring using scintillators and based on an ordinary plastic optical fibre (POF) made of polymethyl methacrylate (PMMA). According to Zhuang et al. (2016) this alternative radiation monitoring approach is characterized by a wide range of advantages, including low mass, reproducibility, small dimensions, real-time operations, a longer operating length, continuous sensitivity, insensitivity to external electromagnetic fields, as well as dose linearity. In addition, Zhuang et al. (2016) note that the alternative radiation monitoring approach entails a radiation measuring system that is not only simple and robust, but also clinically compatible.

Scintillating materials used in radiation dosimetry can be classified into organic and inorganic (Qin et al., 2016). Organic scintillating materials comprise plastic scintillators (Zhuang et al., 2016). Radiation dosimeters that have been developed using scintillators are often characterized by a tip composed of a scintillating material that is optically coupled to an optical fibre end ( McCarthy et al., 2014). Exposure of the scintillator to ionizing radiation leads to the generation of an optical signal that is guided toward a remotely placed detecting device from the radiation zone by the optical fibre (Zhuang et al., 2016). Separate extensive literature reviews undertaken by different scholars (Beddar et al., 1992, Beddar et al., 2001, Clift et al., 2000, Clift et al., 2002) to compare plastic scintillator radiation dosimeters with traditional detector systems found that the former exhibited desirable dosimetric characteristics. However, despite their numerous advantages, Zhuang et al. (2016) point out that the plastic scintillator radiation dosimeters are also not devoid of shortcomings. For instance, the plastic scintillator radiation dosimeter is characterized by a low signal-to-noise ratio (SNR), which arises from the Cerenkov radiation emission (Zhuang et al., 2016). In order to overcome this shortcoming, a parallel-paired fibre light guide together with identical photomultiplier tubes (PMTs) are incorporated in the design of the plastic scintillator radiation dosimeter. This helps in subtracting the background signal occasioned by the
Cerenkov radiation emission. Nevertheless, Zhuang et al. (2016) contend that this approach to solving the problem of low SNR leads to a significant enlargement of the volume of the plastic scintillator radiation dosimeter.

Whereas the organic (i.e. plastic) scintillator radiation dosimeters are characterized by low SNR, those that are developed using inorganic scintillating materials exhibit high SNR. For instance, McCarthy et al. (2014) fabricated a radiation dosimeter by employing an extrinsic fibre optic sensor. The development of the dosimeter fabricated by McCarthy et al. (2014) entailed injection of a mixture of Gd$_2$O$_2$S:Tb (i.e. a scintillating phosphor material), hardener, and an epoxy resin onto an exposed PMMA optical fibre. Even though the fabricated dosimeter demonstrated clinical significance, its design occasioned a homogeneity shortcoming with “relatively low light efficiency” (cited in Zhuang et al., 2016, p.3), which consequently limited the dosimeter’s ability to display satisfactory response. Cognizant of the shortcoming(s) of the dosimeter fabricated by McCarthy et al. (2014), Zhuang et al. (2016) fabricated a new type of inorganic dosimeter using a novel structure to aid in the measurement of low-energy absorbed radiation dose from a clinical linear accelerator (CLINAC). Given its embedded structure, the new inorganic dosimeter by Zhuang et al. (2016) not only exhibited the advantages associated with inorganic dosimeters, but also demonstrated ability to overcome the homogenous and low coupling efficiency shortcomings associated with most dosimeters. An assessment of repeatability and linear response of the embedded inorganic dosimeter by Zhuang et al. (2016) in accordance with the dose rates of CLINAC produced a depth-dose curve for a 6 MV photon beam. Therefore, in view of the foregoing, what then constitute the physical principles of a good dosimeter? The next subsections of the review explore this important question.
3.6 Physical Principles of Radiation Dosimeters:

In order to effectively serve as an effective tool for radiation dosimetry, particularly for purposes of radiation therapy, the dosimeter is expected to exhibit a range of desirable characteristics and adhere to certain physical principles. For instance, the radiation dosimeter is expected to have the ability to accurately determine the exact quantity of absorbed dose to water at a specific point (Izewska and Rajan, 2005). In addition, Izewska and Rajan (2005) point out that the dosimeter must precisely derive the dose to the target organ within the patient, ideally in real-time. In line with the study conducted by Izewska and Rajan (2005), the physical principles of a radiation dosimeter in the context of this review are characterized by precision, accuracy, dose/dose-rate dependence, linearity, spatial resolution, energy response, as well as directional dependence. Nonetheless, it is important to note at this juncture that no single dosimeter can possess all the desirable characteristics. However, as pointed out by Bale (1960), the choice of the dosimetry system has to be made judiciously, taking cognizance of the characteristics of the measurement situation. For instance, for beam calibrations, radiation therapy ionization chambers are often considered appropriate for evaluating the dose distribution to the target organs as well as the verification of such dose (Verma et al., 2016). The following is an in-depth review of the physical principles of radiation dosimeters.

3.6.1 Accuracy and Precision:

The uncertainty associated with the measurement of radiation in radiotherapy is often expressed in terms of accuracy and precision, with the latter specifying the reproducibility of the radiation measurements under similar conditions (Izewska & Rajan, 2005). In radiotherapy, accuracy of dosimetric measurements implies the proximity of the expected dosimetric value to the “true/actual value” of the measured quantity of radiation (Horton,
Since the results of dosimetric measurements are not often absolutely accurate, the inaccuracy associated with such measurements is described as “uncertainty” (Izewska and Rajan, 2005, p.72). In radiotherapy dosimetry, dosimetric measurement uncertainties are evaluated by using either Type A (statistical methods) or type B (scientific judgment using all of the relevant information available e.g. manufacture’s specifications, previous measurement data, etc), see Good Practice Guide No11 (Stephanie 2001).

### 3.6.2 Linearity:

In the ideal situation, the dosimetric quantity $Q$ and the dosimeter reading $M$ are expected to be linearly proportional (Izewska & Rajan, 2005). Nevertheless, a non-linear relationship between the values of $M$ and $Q$ are often witnessed beyond certain dose ranges (Attix, 1986). The linearity of the relationship between $Q$ and $M$ as well as the non-linearity behaviour of the values of $Q$ and $M$ are influenced by the type of radiation dosimeter used for the measurement as well as the physical characteristics of the dosimeter (Izewska & Rajan 2005). Figure 6 presents two typical examples of response characteristics of a dosimeter and its reader (i.e. the dosimetry system) as used by to explain Izewska and Rajan (2005) to demonstrate the linearity and non-linearity behavior.

![Response characteristics of two dosimetry systems](image)

*Figure 6: Response characteristics of two dosimetry systems. Source: (Izewska and Rajan, 2005, p.75).*
In the case of curve A, linearity with dose is first exhibited before supralinear behaviour is acquired, and a saturation point is then finally attained. This is different from the case of curve B where linearity is at first exhibited before saturation at high doses is attained (Izewska & Rajan, 2005). In view of the trends exhibited by the dosimetry system A, as shown in figure 6, there is need to correct nonlinear behaviour for the dosimetry systems. According to Izewska and Rajan (2005), even though a dosimeter and its reader may in certain circumstances display both linear and non-linear characteristics, the combined effect of the dosimetry system can sometimes result in linearity over wider ranges.

3.6.3 Dose Rate Dependence:

The principle of dose-rate dependence holds that for integrating systems such as the dosimetry systems of present interest, the measured dosimetric quantity and the rate of the dosimetric quantity are independent of each other (Sellakumar et al., 2010). In fact, in an ideal situation, the dosimetric response $M/Q$ (dosimeter reading “$M$”/dosimetric quantity “$Q$”) at two varying dose rates [i.e. $(dQ/dt)_1$ and $(dQ/dt)_2$] is expected to be a constant value (Izewska & Rajan, 2005). However, in practice, the ideal situation rarely exists, and the dosimeter reading are often influenced by the dose rate (Brualla-González et al., 2015). In this regard, Izewska and Rajan (2005) urged the need for undertaking appropriate corrections such as recombining ionization chambers in pulsed beams to establish the correction factors to account for the incomplete collection of ions at adequately high voltages. Recently, (Bruggmoser et al., 2006) published saturation coefficients for a different cylindrical chambers and plane parallel in pulsed electron and photon beams up to 42 mGy pulse$^{-1}$. 
3.6.4 Energy Dependence:

In radiotherapy dosimetry, the dosimetry system’s response $M/Q$ is basically determined by the quality of the radiation beam (the beam energy) in which the dosimeter is placed (Izewska and Rajan, 2005). Energy dependence refers to a change in instrument response with respect to the energy of radiation at a constant exposure or exposure rate. Normally, the calibration of the dosimetry system is intended for a specified radiation beam quality, and employed for relatively wider energy ranges (Looe et al., 2017). The dosimeter system’s response to radiation quality variation thus calls for correction (Izewska and Rajan, 2005). In ideal situations, the dosimetry system calibration is expected to be independent of energy. However, in reality, the determination of $Q$ for a number of radiation measurements entails the inclusion of the energy correction. The dose to water/tissue is normally the quantity of interest in the case of radiation therapy (Izewska and Rajan, 2005). Given that no single dosimeter employed in radiotherapy dosimetry is water/tissue equivalent for every radiation beam quantities involved, Izewska and Rajan (2005) identified the energy dependence principle as a critical aspect of the dosimetry system.

3.6.5 Directional Dependence:

The directional or angular dependence of a dosimeter refers to the variation in its response with the angle of incidence of radiation (Izewska and Rajan, 2005). Based on their constructional details, the energy of the incident radiation as well as their physical size, dosimeters often display directional dependence (Orita et al., 2015). The principle of directional dependence is an important dosimetric characteristic to consider when employing the dosimetry systems in in-vivo dosimetry, especially when semiconductor dosimeters are used (Izewska & Rajan, 2005).
3.6.6 Physical Size and Spatial Resolution:

Given the point-quantity nature of a dose, an effective dosimeter should allow the determination of such dose at nanoscale (Izewska and Rajan, 2005). The spatial location of a dose refers to the location of the point where the dose is determined. Therefore, the spatial location needs to be clearly defined within a reference coordinate system (Berg et al., 2013). The MOSFETs and commercial TLDs are examples of point dosimeters (i.e. are relatively small in dimensions) but so too are the optical fibres, developed with a range of diameters (0.1 mm to ~ 1 mm), also allowing for the approximation of point measurements (Bradley et al., 2017). Film dosimeters and gels have impressive 2-D and 3-D resolutions respectively, and it is ultimately the resolution of the evaluation system that limits the point resolutions in these dosimeters (Izewska & Rajan, 2005). However, for the ICs, their finite sizes limit their ability to deliver the requisite sensitivity, although this shortcoming has since been partially overcome by new generation of pinpoint microchambers (Berg et al., 2013). The original cylindrical IC (also known as a thimble chamber) was for instance of volume 0.6 cm³. Most cylindrical ICs have volumes ranging between 0.1 and 1 cm³.

3.6.7 Readout Convenience:

In radiation therapy dosimetry, direct reading dosimeters or active radiation dosimeters such as ICs are often considered more convenient than their passive counterparts such as the TLDs and film dosimeters. This is attributed to the fact that passive dosimeters are only readable upon due processing following the exposure (Izewska & Rajan, 2005). In addition, the ICs allow for measurement to be undertaken in both integral and differential modes as opposed to the TLDs and gels, which can only measure in integral mode (Izewska & Rajan, 2005).
3.6.8 Convenience of Usage:

Convenience of use is an important aspect of dosimetric utility in radiation therapy. Among the various dosimeters available for radiation dosimetry, the ICs are reusable, and such reusability has minimal or no effect on their sensitivity within their lifespan (Martin 2007). This is perhaps not true for the semiconductor dosimeters, which despite being reusable, lose their sensitivity gradually within their lifespan (Martin 2007). The films and gels are designed for measuring dose distribution in a single exposure (Izewska & Rajan, 2005). In terms of handling, the ICs are relatively rugged, and hence their sensitivity are little affected by handling. This is contrary to the TLDs, whose sensitivity is affected by handling (Izewska & Rajan, 2005).

3.7 Active and Passive Dosimeters:

In subsection 3.5.1 of this review, it had been stated that this review is essentially focused on two main classifications of radiation dosimeters, namely active and passive radiation dosimeters. Izewska and Rajan (2005) while exploring radiation dosimeters developed five categories of dosimetry systems, namely: (i) ionization chamber dosimetry systems; (ii) film dosimetry systems; (iii) luminescence dosimetry systems; (iv) semiconductor dosimetry systems; and (v) other dosimetry systems (e.g. plastic scintillator dosimetry systems, gel dosimetry systems, diamond dosimeters, etc). Therefore in this section, and while taking cognizance of the classifications by previous authors, the review provides an in-depth analysis of the various dosimeters, outlining their characteristics, applications, advantages, as well as disadvantages, with the ultimate goal of determining two essential principles; whether the dosimeter fulfills the Bragg-Gray Cavity Theory and whether is it tissue equivalent.
3.7.1 Active Radiation Dosimeters:

To reiterate, active radiation dosimeters are also known as active radiation detection devices. Under this classification, a number of radiation dosimeters exist, including dosimeters that belong to the ionization chamber dosimetry system (e.g. the ICs); the semiconductor dosimetry system (e.g. the semiconductor diodes); as well as other dosimetry systems such as the plastic scintillator dosimetry system (e.g. the water equivalent plastic scintillation detectors), gel dosimetry system, and diamond dosimeters. The following sections provide an in-depth review of the active radiation dosimeters.

3.7.1.1 Ionization Chamber Dosimetry:

The ionization chamber dosimetry system comprises chambers and electrometers, cylindrical (thimble type) ICs, parallel-plate (plane-parallel) ICs, brachytherapy chambers, as well as extrapolation chambers. The ICs are mainly employed in radiation therapy and diagnostic radiology for purposes of determining radiation dose (Sharifi et al., 2015). In radiation therapy, dose determination is often referred to as beam calibration (Izewska & Rajan, 2005). The ICs are designed with varying shapes and sizes to meet specific requirements. Nonetheless, the ICs are essentially designed with gas-filled cavities enclosed by a conductive outer and a centrally positioned collecting electrode, as shown in figure 7. A high quality insulator is used to separate the collecting electrode from the wall of the IC. The separation is necessary for reducing the leakage current when the chamber receives a polarizing voltage (Izewska and Rajan, 2005). The guard electrode is provided for purposes of reducing chamber leakage by intercepting leakage current and directing the flow of the current to the ground. Standard ICs are made of carbon-coated microfilms.
Figure 7: Design Characteristics of the 0.6 cm$^3$ Cylindrical Ionization Chamber. Source: (Izewska & Rajan, 2005, p.77).

In addition, the guard electrode also enhances field uniformity in the sensitive volume of the chamber, hence leading to increased charge collection (Izewska & Rajan, 2005). The cylindrical chambers are produced with active volumes typically ranging from 0.1 and 1 cm$^3$, typically with an internal length that is ≤ 25 mm and an internal diameter that is ≤ 7 mm (Izewska & Rajan, 2005). The IC’s wall material is tissue/air equivalent (i.e. of low atomic number Z). The aluminium central electrode of 1 mm in diameter helps in the fulfilment of the principle of flat energy dependence (Izewska & Rajan, 2005). Given their favourable physical and chemical properties such as that of surface charge, structure, size distribution, surface area, surface chemistry, purity of the samples, size distribution, as well as agglomeration, graphite and carbon have proven useful and promising in nanotechnology (Eatemadi et al., 2014). These chemical and physical properties have considerable impact on the reactivity of graphite and carbon nanotubes (Eatemadi et al., 2014).

Measurement of absorbed radiation dose and QA enhancement lies at the core of radiation therapy dosimetry (Funaro et al., 2013). The ICs are capable of high accuracy, being also practicable and reliable and are hence considered the most important dosimeter in radiation therapy dosimetry. In addition, these dosimeters are characterized by real-time read-out and a well-developed understanding of the necessary corrections. All these advantages
thus make the ICs suitable for beam calibration (Izewska & Rajan, 2005). However, their relatively large physical sizes (i.e. 0.1 and 1 cm$^3$) often limit their spatial resolution (Funaro et al., 2013). The relatively larger size of the ICs also implies that these dosimeters require a high bias voltage to attain the appropriate collection of charge, a phenomenon that compromises their use for in-vivo radiation therapy dosimetry (Zhuang et al., 2016). In addition, most ICs require connecting cables and a high voltage supply, as well as numerous corrections, especially for high energy beam dosimetry (Izewska & Rajan, 2005).

Graphite and carbon nanotubes are now being used in the development of ICs to allow for the development of miniaturized ICs. In addition, the use of graphite and carbon nanotubes helps in the improvement of IC performance, in terms of best charge collection efficiency as well as improved working, especially in lower bias voltages as well as zero volts (Funaro et al., 2013). This was confirmed in a study by Funaro et al. (2013) in which the researchers proposed novel real-time radiation ICs with collecting electrodes based on graphene or vertically aligned multiwall carbon nanotubes (MWCNTs). The results of the study showed that ICs developed based on graphene or carbon nanotubes provided best charge collection efficiency in addition to working effectively to lower bias voltages and zero volts (Funaro et al., 2013). In addition, the graphene or carbon nanotube-based ICs do indeed allow for miniaturization and hence have proved suitable for in-vivo applications (Funaro et al., 2013).

3.7.1.2 Semiconductor Dosimetry:

The silicon diode dosimeter, a p-n junction diode, is a member of the category of semiconductor dosimetry systems. For this dosimeter, the production of diodes entails counter-doping the surface of n-type or p-type to produce the opposite type material (Izewska and Rajan, 2005). The diodes produced in this manner are referred to in radiation dosimetry as $n$-Si or $p$-Si dosimeters, depending on the material whose surface is counter-doped.
Whereas both the $n$-$Si$ or $p$-$Si$ dosimeters are available in the market, only the $p$-$Si$ dosimeters are suitable for radiation therapy applications (Izewska & Rajan, 2005). This is because the $p$-$Si$ dosimeters are least affected by radiation damage. In addition, the $p$-$Si$ dosimeters are characterized by small dark current. As a result of irradiation, electron-hole (e-h) pairs and charges are produced in the dosimeter. The produced charges are then diffused into the depletion region from where they are dispersed due to the electric field created by the intrinsic potential. This movement leads to generation of current in the diode, but in the opposite direction (Izewska and Rajan, 2005).

The semiconductor diodes are suitable for short circuit mode, considering that this mode is characterized by a linear relationship between the dose and measured charge (Zhuang et al., 2016). In terms of advantages the diodes are small in size (a popular size is $1.5 \times 1.5 \times 0.425 \text{ mm}^3$) and more sensitive than ICs. However, unlike the ICs, the sensitivity of diodes changes when used, a result of radiation damage. The diodes are mostly suitable for measurements in nanofields employed in stereotactic radiosurgery. Contrary to ionization measured by the ICs, diodes allow for direct measurement of dose distribution when employed in the measurement of electron beam depth dose (Izewska and Rajan, 2005). These kinds of dosimeter are not suitable for long radiotherapy treatments because they exhibit variation in dose response with temperature (Zhuang et al., 2016).

### 3.7.1.3 Other Dosimetry Systems:

Examples of dosimeters in this category include water equivalent plastic scintillation dosimeters, diamond dosimeters and the gels. The plastic scintillators are somewhat new developments in radiation therapy dosimetry. One of the advantages of these dosimeters is that they can be miniaturized and still provide sufficient sensitivity for radiotherapy dosimetry. This therefore makes them suitable for use in cases involving high spatial resolution such as high dose gradient regions and/or interface regions (Izewska and Rajan,
In addition, plastic-based scintillation dosimeters have impressive reproducibility and long-term stability, since they are not significantly affected by radiation damage (Zhuang et al., 2016). Moreover, these dosimeters are not dependent on dose-rate, and hence are suitable for use ranging between 10 µGy/min and 10Gy/min (Izewska and Rajan, 2005). Furthermore, the plastic-based scintillation dosimeters besides not requiring pressure and ambient temperature, are not characterized by significant directional dependence.

The gels are considered as the only real 3-D dosimeters appropriate for the measurement of relative dose (Izewska and Rajan, 2005). Apart from being a dosimeter, Izewska and Rajan (2005) note that the gel is a phantom that has the ability to measure absorbed dose distribution in a full 3-D geometry. The gels are closely tissue equivalent and can be fashioned to any desired form and shape. This therefore makes them appropriate for in-vivo applications (Zhuang et al., 2016). The gel dosimetry can be classified as Fricke MRI gel and polymer gels. The Fricke MRI gel is based on the Fricke dosimetry, and involves the dispersal of Fe\(^{2+}\) ions contained in SO\(_4\) solution throughout gelatin, PVA matrix, or agarose (Izewska and Rajan, 2005). The continuous post-irradiation diffusion of Fe\(^{2+}\) ions is regarded as a major limitation of the Fricke MRI gel (Zhuang et al., 2016). Polymer gel on the other hand involves dispersal of monomers such as acrylamide in a gelatine or agarose matrix. Such monomers then undergo a polymerization reaction, giving rise to a 3-D polymer gel matrix, which can be evaluated using ultrasound or optical tomography (Izewska and Rajan, 2005). Polymer gels are almost water equivalent due to the large portion of water that characterizes them. The gel dosimetry is a relatively promising technique in automatically shaped phantoms as well as complex clinical circumstances.
3.7.2 Passive Radiation Dosimeters:

Passive radiation dosimeters are also typically known as integrating dosimeters, and include dosimeters within the film dosimetry system (e.g. the radiochromic films) and the luminescence dosimetry system (e.g. the phosphor-based TLDs and silica-based TLDs). These dosimeters are discussed in depth in the following sections:

3.7.2.1 The Film Dosimetry System:

The film dosimetry systems are dominated by silver halide radiographic films and also radiochromic films. Radiographic x-ray films continue to be applied in radiation therapy, diagnostic radiology, as well as radiation protection (Devic 2011). A radiographic x-ray film can serve four important functions in radiation dosimetry, including detecting radiation, acting as a relative dosimeter, as well as acting as a display device and an archival medium (Izewska and Rajan, 2005). A number of radiographic x-ray films are available for applications in radiation therapy dosimetry, including phosphor screen radiographic x-ray films, which serve as simulators (Izewska and Rajan, 2005). Thus said, as a recording medium in imaging they are rapidly being replaced by digital imaging devices.

Conversely, the radiochromic systems are novel types of film in radiation therapy dosimetry and are commonly employed as GafChromic films (Liu et al., 2015). These films are fitted with a special dye, which become polymerized when exposed to light. One of the advantages of the radiochromic films is that they are self-developing, and hence require no fixer or developer (Izewska and Rajan, 2005). In addition, given their grainless nature, these types of dosimeters are characterized by extremely high resolution and are hence suitable for high dose gradient regions. Unlike the radiographic films, the radiochromic films are easy to use, do not require darkroom facilities or film cassettes, are dose-rate independent, and possess better energy characteristics (Izewska and Rajan, 2005).
3.7.2.2 Luminescence Dosimetry System:

Certain materials retain part of the absorbed radiation (energy) in metastable states, to be subsequently released in various forms, including infrared/visible light or ultraviolet (UV) light (Izewska and Rajan, 2005). This phenomenon is known as luminescence. This category of dosimetry comprises fluorescence and phosphorescence, both of which are dependent on time delay between stimulation and light emission (Jarnet et al., 2004), albeit with completely different time signatures; the phosphorescent emission has particularly long-lived decay duration. TLDs are thermoluminescent materials, which are applied purposefully for dosimetry. The TLDs that are commonly employed for medical applications include LiF:Mg,Ti, Li₂B₄O₇:Mn and LiF:Mg,Cu,P (Izewska and Rajan, 2005). The suitability of these TLDs for medical applications is attributed to their tissue equivalence and high sensitivity. Annealing a basic TLD before using it is necessary for the purpose of erasing the residual signal (Zaman et al., 2011). When used in radiation therapy, a typical commercially-available well-prescribed TLD will produce a linear dose response over a wide range of dose. In terms of applications, the TLDs are suitable for in-vivo dosimetry, dosimetry audits, treatment verification in different phantoms, as well as comparisons among hospitals (Izewska and Rajan, 2005), otherwise known as audits.

3.8 Thermoluminescence of Ge-doped SiO₂ Optical Fibres and Glass Beads

3.8.1 Introduction

Radiation dosimetry, construed in the fields of medical physics and health physics to be the measurement and assessment of the amount of radiation dose the human body receives, has gained significant interest among medical and health physics professionals, underpinning as it does diagnosis and, for present interests, effective treatment of cancer
patients. The current major approach to cancer treatment by radiotherapy tends to be utilisation of high-energy electromagnetic waves such as x-rays, gamma-rays (Nawi, Siti Nurasiah Binti Mat et al., 2015) and also electrons (Murthy et al., 2015, Salguero et al., 2010, Shen et al., 2015), with at the present time the use of ion-beam therapy and neutrons being much less prevalent (Ohno 2013, Sulaiman et al., 2014, Takagi et al., 2013). In such treatment the intent is clearly to massively eradicate the viability of the cells of a localised tumour (in as far as is possible, killing the greater fraction of the cancerous cells in a tumour, seeking to enhance the so-called local tumour control probability, TCP) while minimising cell death in surrounding normal tissues, a quest defined in terms of this therapeutic ratio (ACS 2015).

The treatment situations referred to above call for the observance of a high degree of quality assurance in efforts to help ensure effective radiotherapy, radiation being a two-edged sword, being able to kill cancer cells but also being a potential carcinogenic factor, the risk increasing with dose (a concern in regard to the irradiation of healthy tissue surrounding the target volume). A major part of such endeavours involves the use of dosimeters, often typically being active devices but also sometimes being devices that are passive, placed in beams that are most often generated by tube x-ray devices or nowadays more usually by linear accelerators (IAEA 2016). As has been previously mentioned, a radiation dosimeter is a device that measures and leads to assessment of the amount of absorbed radiation dose received by the body. Various dosimeters currently exist in the market. One such example, as discussed above, are thermoluminescent dosimeters (TLD), a passive form of dosimeter, measuring exposure from ionising radiation (IR) in a multi-step process, in this case in two-steps, irradiation and subsequent readout. To-date such TLDs have typically comprised a crystalline medium suitably doped to provide for a required level of sensitivity, two examples of which are based on calcium sulphate: CaSO$_4$:Dy and CaSO$_4$:Tm, providing for trapping of
electrons when irradiated and emitting light (detected by a photomultiplier tube most typically) when exposed to a controlled level of heat (Carnicer et al., 2011).

Other than conventional TLDs, one further example of which is LiF:Mg,Ti, Ge-doped SiO₂ optical fibres and variously doped glass beads are being developed at the University of Surrey as well as elsewhere as novel forms of thermoluminescent (TL) dosimeter. There are now numerous empirical investigations that have been undertaken of these (Benabdesselam et al., 2013, Bradley et al., 2014, Jafari et al., 2014a, Nawi et al., 2015), seeking to establish their potential for in vivo and/or small-field radiation therapy dosimetry, as well as in brachytherapy. This review is therefore intended to examine the basis of the thermoluminescence of Ge-doped SiO₂ optical fibres and glass beads, with a view to establishing their advantages for radiation therapy dosimetry as well as their limitations. In so doing, the review examines the molecular structure of the Ge-doped SiO₂ optical fibres and glass beads, their associated trapping centres and activation energy and annealing process, also applications to-date, including why and how they are used.

3.8.2 The Ge-Doped SiO₂ Optical Fibres and Glass Beads

Optical fibres have, for decades, commonly been associated with the telecommunications industry. However, as pointed out by (Fadzil et al., 2017), recent innovations in optical fibre technology has seen the use of germanium (Ge)-doped silicon dioxide (SiO₂) fibres in the manufacture of thermoluminescent dosimeters (TLDs). A review conducted by (Bradley et al., 2012a) to understand the thermoluminescence characteristics of doped silica optical fibres and their potential applications in radiotherapy dosimetry established that the suitability of doped silica optical fibre as a TLD is attributed to its characteristically good spatial resolution and ability to yield the necessary sufficient thermoluminescence in meeting the sensitivity needs of a TLD for radiotherapy. The next
subsection therefore reviews existing empirical evidence for the advantages of Ge-doped SiO₂ optical fibres and glass beads, as TLDs.

3.8.3 Advantages of Ge-Doped SiO₂ Optical Fibres and Glass Beads

Unlike the commercial phosphor-based TLDs, which are associated with limited spatial resolution of a few mm, (Rahman et al., 2012a) have contended that commercially available Ge-doped SiO₂ optical fibres provide for the possibility of high spatial resolution thermoluminescence dosimetry, typically down to the order of 100 µm, as well as allowing for an appropriate Bragg-Gray cavity for essentially a non-tissue equivalent probe. A number of empirical studies have investigated the potential of Ge-doped SiO₂ optical fibres and glass beads for applications in small-field radiotherapy dosimetry (Rahman et al., 2012; Benabdesselam et al., 2013; Jafari et al., 2014; Bradley et al., 2017), reporting that they possess a number of suitable thermoluminescence characteristics, including being sensitive to dose over a wide range as well as offering dose stability and linearity of response. Among the instances, Rahman et al. (2012) investigated the thermoluminescence of Ge-doped SiO₂ optical fibres for such application in radiation therapy dosimetry, finding that at fixed dose-rate, the Ge-doped SiO₂ optical fibres generate a flat response against dose-rate to better than a mean thermoluminescence yield distribution of 4% (1 S.D). In terms of linearity, Rahman et al. (2012) noticed that up to a dose of 50 Gy for both electron and photon beams, the dosimeters exhibited good linearity of response ($r^2 = 0.998$). Results from an additional study of photo-electron dose enhancement in an iodinated medium (iodine has an atomic number of 53), modelled using Monte Carlo simulation (MCNPX v.2.6), indicated that in support of measurements the Ge-doped SiO₂ optical fibres yield thermoluminescence at a level approximately 60% greater than that generated by a non-iodinated medium (Rahman et al., 2012).
In a more recent study, investigating the dosimetric and thermoluminescence characteristics of Ge-doped fibres for varying germanium concentrations and outer diameter, (Noor et al., 2016) went beyond the scope of a number of previous works that have explored the basic dosimetric characteristics of the Ge-doped SiO₂ optical fibres (Bradley et al., 2014, Rahman et al., 2012a, Ramli et al., 2015), examining the suitability of Ge-doped SiO₂ optical fibres for interface radiation therapy dosimetry. Among the parameters studied were linearity of response, energy dependence, reproducibility, thermoluminescence signal loss (fading), as well as dose sensitivity. Using inter alia, two Ge-doped cylindrical silica fibres of differing outer diameters of 241 µm and 604 µm, and three varying germanium dopant concentrations of 6 mol%, 8 mol%, and 10 mol%, Noor et al. (2016) performed a range of experiments to determine the dosimetric suitability of Ge-doped SiO₂ optical fibres for such radiation therapy applications. The results of the experiments indicated that for both the 241 µm outer diameter and 604 µm outer diameter fibres, the thermoluminescence yield produced by the 6 mol% Ge-doped fibres was superior to those produced by the 8 mol% and 10 mol% Ge-doped fibres (Noor et al., 2016). In terms of reproducibility, the 6 mol% germanium dopant concentration was associated with a superior coefficient of variation (CV) compared to the 8 mol% and 10 mol% germanium dopant concentrations (Noor et al., 2016). Our present understanding is that with greater dopant concentrations, a greater degree of self-absorption is to be observed, reducing the TL yield accordingly. The results of the study by Noor et al. (2016) in respect of energy dependence of the Ge-doped fibres are presented in Table 2.
Table 2: A Summary of the Results of Energy Dependence (the greater the gradient value, the greater the energy dependency). The TL response was normalized to the response for 1.25 MeV.

<table>
<thead>
<tr>
<th>Dopant Concentrations</th>
<th>Outer Diameters</th>
<th>Gradient Values (MV⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 mol%</td>
<td>241 µm</td>
<td>0.341</td>
</tr>
<tr>
<td></td>
<td>604 µm</td>
<td>0.207</td>
</tr>
<tr>
<td>8 mol%</td>
<td>241 µm</td>
<td>0.237</td>
</tr>
<tr>
<td></td>
<td>604 µm</td>
<td>0.225</td>
</tr>
<tr>
<td>10 mol%</td>
<td>241 µm</td>
<td>0.364</td>
</tr>
<tr>
<td></td>
<td>604 µm</td>
<td>0.327</td>
</tr>
</tbody>
</table>

Source: (Noor et al., 2016, p.59)

As can be seen from Table 2, the 10 mol% Ge-doped cylindrical fibres provided the steepest slope (i.e. greatest gradient value, the greater the energy dependency) for the 241 µm outer diameter, followed by the 6 mol% Ge-doped cylindrical fibres, and the 8 mol% Ge-doped cylindrical fibres in that order (Noor et al., 2016). In the case of the 604 µm outer diameter, the results indicated that the 10 mol% Ge-doped fibres still produced the greatest gradient value, followed by the 8 mol% Ge-doped fibres and the 6 mol% Ge-doped fibres in that order (Noor et al., 2016). It is imperative to note that the greater the gradient value, the greater the energy dependency. Therefore, in view of the results summarised in Table 2, it can be concluded that the 10 mol% Ge-doped fibres were associated with the greatest energy dependency for both the 241 µm and 604 µm outer diameter cylindrical fibres.
Noor et al. (2016) also tested for the characteristic thermoluminescence signal loss (fading) of the Ge-doped cylindrical fibres for a period of 33 days, following irradiation. The results indicated that the 8 mol% Ge-doped fibres registered the greatest thermoluminescence signal loss, while the 6 mol% Ge-doped fibres registered the least thermoluminescence signal loss (Noor et al., 2016, p.59). In terms of dose sensitivity, Noor et al. (2016) found that the 6 mol% Ge-doped fibres were associated with the smallest minimum detectable dose (Gy). The results in respect of minimum detectable dose are summarised in Table 3.

Table 3: A Summary of the Results of Minimum Detectable Dose

<table>
<thead>
<tr>
<th>Dopant Concentrations (mol%)</th>
<th>Outer Diameters of Cylindrical Fibres (µm)</th>
<th>Minimum Detectable Dose (Gy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>241</td>
<td>0.126</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.027</td>
</tr>
<tr>
<td>8</td>
<td>241</td>
<td>0.188</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.058</td>
</tr>
<tr>
<td>10</td>
<td>241</td>
<td>0.203</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.061</td>
</tr>
</tbody>
</table>

Source: (Noor et al., 2016, p.60).

Overall, the 6 mol% Ge-doped optical fibres for both the 241 and 604 outer diameter cylindrical fibres exhibited superior thermoluminescence performance, in terms of linearity.
of response, sensitivity to dose, energy dependency, as well as fading rate. The foregoing results obtained by Noor et al. (2016) therefore demonstrate in particular the suitability of the 6 mol% Ge-doped SiO₂ optical fibres for development of novel high-performing TLDs.

Prior to the study by Noor et al. (2016), Jafari et al. (2014) had also investigated the potential of glass beads and optical fibres as novel TLDs for small-field radiotherapy dosimetry. In that study, Jafari et al. (2014) characterised commercially existing glass beads (1.5 mm diameter) and GeO₂-doped SiO₂ optical fibres (length = 5 mm length and diameter = 120 µm) as TLDs. After comparing the results against Monte-Carlo simulations with EBT3 GAFCHROMIC film and BEAMnrc/DOSXYZnrc, Jafari et al. (2014) found that both the glass beads and GeO₂-doped SiO₂ optical fibres exhibited suitable thermoluminescence (TL) properties for radiation therapy dosimetry applications.

Elsewhere, (Alalawi et al., 2014) measured small photon field doses using GeO₂-doped SiO₂ optical fibres and glass beads (GB), comparing them against GAFCHROMIC film, a small ionisation chamber (PK-018), a p-type silicon diode (SCANDITRONIX, FI356), as well as Monte Carlo simulations. The results of the study indicated that both the GeO₂-doped SiO₂ optical fibres and the GB were associated with impressive spatial resolution, with the optical fibres offering spatial resolution of approximately 120 µm and the GB offering spatial resolution of 2 mm (Alalawi et al. 2014). The optical fibres and GB were also characterised by large dynamic dose ranges (from tens of mGy up to many tens of Gy) (Alalawi et al. 2014).

In their recent study on doped silica fibre TL measurements on radiation dose in the utilisation of ²²³Ra for prostate cancer secondary bone sarcomas, Bradley et al. (2017) investigated the thermoluminescence yield associated with different forms of Ge-doped SiO₂ optical fibres, including flat and single-mode fibres as well as collapsed and uncollapsed photonic crystal fibres (PCFs). The results indicated the dosimeters to offer considerable
sensitivity and to provide an effective atomic number $Z_{\text{eff}}$ that approaches that of bone (Bradley et al., 2017). Importantly, Bradley et al. (2017) observed that the glass fibres offer an added advantage in terms of their ability to withstand direct placement into liquid. The findings by Bradley et al. (2017) thus demonstrated the potential of the Ge-doped SiO$_2$ optical fibres as versatile novel TLDs in a particularly harsh environment. Prior to Bradley et al. (2017), (Sani et al., 2017) had investigated thermoluminescence yields generated by different forms of Ge-doped SiO$_2$ optical fibres for in vitro dosimetry of $\alpha$-particles produced by the $^{223}$Ra decay series. After performing a series of irradiations, Sani et al. (2017) discovered that the Ge-doped SiO$_2$ optical fibres were associated with particular dosimetric advantages compared to their conventional counterparts, specifically in regard to the greater TL yield of flat- and photonic crystal fibres (FF and PCF). Similar to the findings of Bradley et al. (2017), Sani et al. (2017) found that the Ge-doped SiO$_2$ optical fibres provided a $Z_{\text{eff}}$ value that approach that of bone (with a range of from 11.6 to 13.8, depending upon composition). Sani et al. (2017) concluded that the dosimetric material in its various forms (i.e. Ge-doped FF, PCF and single mode fibres (SMF)) provide thermoluminescence responses favouring applications for radiation therapy dosimetry.

(Begum et al., 2015) attribute the promising thermoluminescence characteristics of silica optical fibre in radiation therapy dosimetry to its physical makeup, pointing out that the conventional cylindrical form (e.g. the single mode fibre [SMF] form) is characterised by two concentric layers (i.e. the “core” and “cladding”), characterised by varying index of refraction. Among others, (Rahman et al., 2011) have also described the SiO$_2$ optical fibres for TLD, characterised by structural defects that initiate a trapping process that produces the thermoluminescence properties associated with the SiO$_2$ optical fibres. Begum et al. (2015), also echo this, the thermoluminescence response of a dosimetric material being also affected by the nature and concentration of impurities present in the material. Studies by (Rahman et
al., 2010) and (Yaakob et al., 2011) have established that silica optical fibres possess unique properties (e.g. water resistance, high spatial resolution and low cost), overcoming a number of limitations associated with conventional thermoluminescent materials, Begum et al. (2015) also noting that such properties enhance their suitability as TLDs.

In a study using gamma radiation, investigating the photon dose response and fading, and also reproducibility for five different core-sized Ge-doped SiO$_2$ optical fibres, Begum et al. (2015) undertook a detailed examination of the Ge-doped SiO$_2$ optical fibres’ relative elemental composition. The characteristic background signal and low-temperature glow peaks of the silica optical fibres were manifestly reduced by taking all the five core-sized Ge-doped SiO$_2$ optical fibres through an annealing process, during which the dosimetric materials were kept in an aluminium container and annealed for one hour at 400°C (Begum et al., 2015). After irradiation and conducting a SEM-EDX analysis to map the inherent dopant concentration and the $Z_{\text{eff}}$ values of the optical fibres, Begum et al. (2015) found that the five fibres provided were characterised by elemental compositions in the range of 13.25 and 13.69, as shown in Table 4.

<table>
<thead>
<tr>
<th>Ge-doped SiO$_2$ Optical Fibre No.</th>
<th>Core/Cladding of Optical Fibre ($\mu$m)</th>
<th>Effective Atomic Number ($Z_{\text{eff}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100/604</td>
<td>13.25</td>
</tr>
<tr>
<td>2</td>
<td>80/483</td>
<td>13.69</td>
</tr>
<tr>
<td>3</td>
<td>60/362</td>
<td>13.57</td>
</tr>
<tr>
<td>4</td>
<td>40/241</td>
<td>13.40</td>
</tr>
<tr>
<td>5</td>
<td>20/120</td>
<td>13.43</td>
</tr>
</tbody>
</table>

*Source: (Begum et al., 2015, p.798).*

(Wagiran et al., 2011) and (Rahman et al., 2012b) record it to be conventional to seek a $Z_{\text{eff}}$ value that is ideally human soft-tissue equivalent (i.e. typically taken to be 7.42), with
Begum et al. (2015) going on to record that a $Z_{\text{eff}}$ value that is human tissue equivalent is dependent on the incident photon energy and its direct association with the degree (the probability) to which primary photon interactions take place within the detector medium. With tissue equivalency playing a critical role in radiation therapy dosimetry, it is notable for instance that the photoelectric interaction is dependent on something like the $3^{rd}$ power of the dosimetric material atomic number ($Z^3$). As can be seen in Table 4, the $Z_{\text{eff}}$ values of the five core-sized Ge-doped SiO$_2$ optical fibres (ranging from 13.25 to 13.69) are significantly greater than that of soft tissues (i.e. 7.42). Nonetheless, Begum et al. (2015) found that the $Z_{\text{eff}}$ values of the five optical fibres fall within the human-bones range of from 11.6 to 13.8 (p.799), in keeping with Sani et al. (2017), who also found that the Ge-doped SiO$_2$ optical fibres provided a $Z_{\text{eff}}$ value ranging from 11.6 to 13.8, making the doped silica useful as human-bone equivalent for dosimetric purposes.

3.8.4 Limitations in Ge-Doped SiO$_2$ Optical Fibres and Glass Beads

Despite their very promising thermoluminescence characteristics for applications in radiation therapy dosimetry applications, research has shown that the Ge-doped SiO$_2$ optical fibres and glass beads are not devoid of limitations. For instance, in a recent study of SiO$_2$ optical fibres as potential TLDs for radiotherapy dosimetry, (Rahim et al., 2017) examined the thermoluminescence dose response of flat optical fibres of differing dimensions (i.e. 270 $\times$ 60 $\mu$m; 360 $\times$ 73 $\mu$m; 100 $\times$ 510 $\mu$m; and 160 $\times$ 750 $\mu$m), characterising them in terms of their respective linearity, reproducibility, sensitivity to dose, as well as thermoluminescence signal loss (i.e. fading). It was found that the optical fibres thermoluminescence signal fading was approximately 20.4% 30 days post irradiation, with the loss being most rapid in the first seven days after irradiation (at approximately 17.8%). Therefore, despite their characteristic rate of loss of thermoluminescence response to fading, comparable to the conventional
dosimetric materials, previous investigators such as Rahim et al. (2017) suggest that the Ge-doped SiO$_2$ optical fibres are still characterised by limited capability, in terms of ensuring accurate determination and measurement of radiation dose, with a linear dose “response over wide range therapeutic dose” (Rahim et al., 2017). According to Rahim et al. (2017), this limitation in the Ge-doped SiO$_2$ optical fibres can be addressed by ensuring improved selection of the optical fibres for radiation therapy dosimetry applications.

3.8.5 Conclusion in regard to doped silica media

In view of the previous review, the Ge-doped SiO$_2$ optical fibres and glass beads exhibit a number of thermoluminescence characteristics (i.e. dose stability, sensitivity to dose, reproducibility, low energy dependency, linearity of response to dose, as well as a low rate of thermoluminescence signal loss), such that these facets render them highly promising for radiation therapy dosimetric applications but not comprehensively so. As has been established by various investigators, including Rahim et al. (2017), the Ge-doped SiO$_2$ optical fibres still lack the requisite capability to ensure that radiation dose is accurately determined and measured with a linear dose response over a wide range therapeutic dose, soft tissue equivalence being one marked issue. In this latter regard, there is need for further research to devise ways of addressing such limitation. In particular, there is need for a passive dosimeter of small dimensions, with facets similar to that of the silica media but that which in addition offer soft-tissue equivalence, pointing the way to for instance skin dosimetry.
3.9 The Use of Carbon Nanotubes in Radiation Dosimetry and the Effect of Ionising Radiation on CNT Structure and Properties

3.9.1 Introduction

This section reviews the uses of carbon nanotubes (CNTs) – single-walled or multi-walled CNTs as well as mixed-component or free-standing CNTs, as well as the effect of ionising radiation doses on CNT structure and properties. The review also discusses the molecular structure(s) of the CNTs, as well as how such structures interact with and are affected by radiations.

3.9.2 Effect of Ionising Radiation Doses on their Structure and Properties

Since their discovery in the early 1990s (Iijima 1991), carbon nanotubes (CNTs) have gained increasing popularity in the field of nanotechnology, with an increased interest in the exploitation of their novel properties (both electronic properties and mechanical properties). Given their advantageous properties - possession of effective atomic number ($Z_{\text{eff}}$ value) similar to that of adipose tissue, good conductivity, as well as low voltage demand in active devices (Chen et al., 2011), CNTs have become useful for medical physics applications as well as for other applications such as chemical sensors (Moradi et al., 2013); biosensors (Timur et al., 2007); field-emission displays (Saito 2010); memory storage (Lu and Dai 2006); as well as hydrogen storage (Yang et al., 2010). The increased interest in CNTs in radiation dosimetry is attributed to the fact that the atomic formation of CNTs are characterised by specific structures providing a range of interesting physical and chemical properties, including electric and thermo conductivity (Gojny et al., 2006). However, despite their usefulness in radiation therapy dosimetry, the properties and structure of CNTs are often affected by ionising radiation doses. The next subsections of this thesis therefore reviews the
uses of CNTs and the potential effect of ionising radiation doses on their structure and properties.

3.9.3 Use of Carbon Nanotubes in Radiation Technology other than Dosimetry

A number of previous attempts have been made to investigate the potential applications for CNTs in radiation technology. For instance, in a 2002 study, (Yue et al., 2002) demonstrated how a carbon nanotube (CNT)-based field-emission cathode can be used for the purposes of generating medical diagnostic x-ray radiation. Purified single-walled CNT (SWCNT) bundles, produced using the laser ablation method, were the emission material adopted by Yue et al. (2002). The researchers used electrophoretic deposition (EPD) to coat a uniform layer of SWCNTs onto a flat metal disc, EPD being a term used to describe various industrial processes, including anodic electrodeposition, electrophoretic painting, as well as cathodic electrodeposition.

The adhesion between SWCNTs and the substrate was enhanced by first depositing an iron layer on the substrate using an electrochemical plating method to provide for nanotube deposition (Yue et al., 2002). During the study, it was reported that the current, as well as the nanotube suspension concentration and deposition time, all acted as controls for the nanotube film thickness and packing density. With regard to measurements of the characteristics of the CNT, the group of Yue employed a hemispherical current collector to measure the SWCNT film current-voltage characteristics. The parallel-plate geometry was used to determine the total emission current generated by the 0.2 cm² macroscopic cathode. With the applied voltage being adjusted automatically and total emission current fixed at 6 mA, a significant improvement of the fluctuation and stability were ensured by incorporating a simple feedback loop.
Yue et al. (2002) went on to establish that a 0.2 cm$^2$ SWCNT film was able to generate a peak emission current of 28 mA at a rate of 140 mA/cm$^2$. According to their studies, an emission current of 28 mA, as witnessed with the 0.2 cm$^2$ SWCNT film, is a higher order of magnitude compared to the values of emission currents that have previously been generated by macroscopic cathodes. They further employed the triode geometry to test the potential of SWCNT film as an x-ray-generating cold-cathode. The viability of the SWCNT film as an x-ray source was demonstrated by them in their imaging of fish as well as of a humanoid hand, the images being recorded using Polaroid$^{TM}$ films located externally behind the x-ray chamber. After a series of such experiments, Yue et al. (2002) established that the SWCNT film generated high-intensity pulsed and high-frequency x-ray radiation, matters essential for both industrial and medical applications.

As noted by Yue et al. (2002), the CNT-based field emission cathode provides a novel opportunity for overcoming characteristic limitations of conventional x-ray tubes. For instance, the cold-cathode x-ray tube whose characteristics were investigated by the group allows for the elimination of the resistively heated filaments, hence significantly prolonging the x-ray tube life span (Yue et al., 2002). In addition, given its relatively smaller size and lower power supply demand, it was contended that the CNT-based field emission cathode provides an opportunity for producing portable and nano x-ray machines. Moreover, the CNT-based field emission cathode enhances the production of focused electron beams, which are characterised by a relatively smaller energy spread. This is critical in such radiation technology endeavours, as such energy spreads have the potential of enabling the production of high-resolution imaging x-ray tubes (Yue et al., 2002).
3.9.4 Effect of Ionising Radiation Doses on their Structure and Properties

As previously mentioned, CNT composites have a wide range of applications, including in optical sensor technology, nanotechnology engineering, manufacture of devices for shielding against electromagnetic interference, as well as in space environments where characteristically low-density structural materials are expected to withstand exposure to ionising radiation (Aryasomayajula and Wolter 2013, Jin et al., 2000, Star et al., 2001). However, empirical evidence from various research suggests that ionising radiation doses do have a significant effect on the structure and properties of CNTs.

One of the novel studies to have investigated and to have reported upon the effects of ionising radiation doses on the CNT composites was conducted by (Muisener et al., 2002). In that study, Muisener et al. employed differential scanning calorimetry to examine the effect of 0.26 wt% of SWCNT on the composite glass transition temperature before and after radiation. The CNT composite used in the study was poly(methyl methacrylate)/single-walled carbon nanotube (PMMA/SWCNT), which is a mixed-component CNT. The ionising radiation of choice in the study of the group of Muisener et al. was gamma radiation. For the purposes of allowing comparative investigation, the researchers adopted both polymer-wrapped SWCNT (PMMA/SWCNT) and pure PMMA for the experiment. The Young’s modulus of the composites (i.e. PMMA and PMMA/SWCNT) before and after exposure to the ionising radiation was determined through what Muisener et al. described as “dynamic mechanical analysis” (p.2508). It is worth noting that multi-walled carbon nanotubes (MWCNTs) are generally characterized by a “Young modulus of 200-4000 GPa, an estimated axial compression strength of 100 GPa, and a bending strength of 14 GPa” (Muisener et al., 2002, p.2507). In that study, Muisener et al. (2002) adopted dielectric analysis for the determination of the dielectric permittivity and the ionic conductance of the composites of CNT before and after exposure to the gamma radiation, the latter being the
choice of ionising radiation used in that study. With regard to gamma radiation-induced effects on the SWCNT morphology, the researchers documented such effects using “scanning electron microscopy (SEM)” (Muisener et al., 2002, p.2508).

Before carrying out the actual experiment, the researchers undertook a number of preparatory steps, including producing a composite comprising 0.26 wt% polymer-wrapped SWCNT for use in both the mechanical and thermal tests. The preparation of the 0.26 wt% polymer-wrapped SWCNT first involved use of a Branson Sonifier 450 to disperse the SWCNTs in N,N-dimethylformamide (DMF) for a duration of two hours. Methanol was then used to precipitate the heterogeneous mixture of the polymer-wrapped SWCNT composite obtained through the sonification process. The PMMA/SWCNT composite product of the precipitation process was then dried for two days at 110 °C. The dried PMMA/SWCNT composite was then reduced into pieces before these were then stacked between polished metal plates and compressed at about 20 MPa of pressure and at a temperature of 275 °C (Muisener et al., 2002). In order to allow for a well-supported comparison, the pure PMMA used in the study was also prepared in a similar manner to that for the PMMA/SWCNT composite.

The next step, conducted in air, was to expose the model samples and the nanotube paper to ionising radiation doses (5.9 Mrad doses, equivalent to 59 kGy) at a dose rate of 1.28 x 10^6 rad/h, equivalent to 12.8 kGy/h. The determination of glass transition temperature (T_g) was carried out using a TA Instruments 2920 Differential Scanning Calorimeter (DSC) (Muisener et al., 2002). In addition, the researchers erased annealing effects by taking the glass transition temperatures from the inflection of the second heat curve. Data regarding the effect of the ionising radiation doses on the mechanical properties of the PMMA/SWCNT composite was documented using a TA Instruments 2980 dynamic mechanical analyser (DMA) within a specified temperature range (-125 °C to 150 °C) and rate (4 °C/min). The
results of the study by Muisener et al. (2002), with respect to changes in the $T_g$ values of the composites are presented in table 5.

Table 5: A Summary of Tg Values of PMMA and PMMA/SWCNT

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$ Values Before Irradiation (Exposure to 5.9 Mrad of Gamma Radiation)</th>
<th>$T_g$ Values After Irradiation (Exposure to 5.9 Mrad of Gamma Radiation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>98 °C</td>
<td>94 °C</td>
</tr>
<tr>
<td>PMMA/SWCNT</td>
<td>112 °C</td>
<td>112 °C</td>
</tr>
</tbody>
</table>

Source: (Muisener et al., 2002, p.2509).

From the results presented in Table 5, it is evident that the pure PMMA $T_g$ value decreased by 4 °C, from 98 °C before irradiation to 94 °C after irradiation. The $T_g$ value of the PMMA/SWCNT composite on the other hand remained unchanged before and after irradiation, at 112 °C. Muisener et al. (2002) attributed the decrease in the neat (pure) PMMA $T_g$ value to the radiation induced scission reactions which the PMMA undergoes. According to the authors, the radiation induced scission reactions generate low molecular weight fragments, which are responsible for a reduction of the $T_g$ value of the polymer matrix. Since such an effect is not inherent in the PMMA/SWCNT composite, its value remains constant (at 112 °C) before and after irradiation (Muisener et al., 2002).

Muisener et al. (2002) provided three hypothetical explanations for the constant value of the PMMA/SWCNT composite before and after being exposed to doses of gamma radiation. The first hypothesis was that the dissolution of the irradiated samples in methylene chloride denied the nanotubes a chance to cross-link with the polymer matrix. Second, it was explained that the characteristic sensitivity to motion of the polymer matrix and degradation
products was decreased by the network of the nanotubes, which is a reinforcing agent. Finally, Muisener et al. (2002) posited that degradation of the nanotubes is impeded by the inherent $\pi$ electron clouds, which serve as radiation sinks. According to the authors, the radiation energy is localised by the inherent radiation-induced scission in the $\pi$ electron clouds, a phenomenon that inhibits the energy from migrating to more sensitive degradation-prone sites within the $\pi$ system. These results corroborated a study by (Clough et al., 1991).

The improved resistivity of the PMMA/SWCNT composite to the ionising radiation was confirmed by the results documented using the polydimethylsiloxane (DMS). For instance, the storage modulus of the neat PMMA decreased by 15% upon exposure to the ionising radiation. This reduction was significant given that the storage modulus of the PMMA/SWCNT composite registered a reduction of 3% upon exposure to similar radiation doses.

The results obtained by the group of O’Rourke have thus suggested that the storage modulus, hardness, as well as the $T_g$ value of PMMA increase with the addition of a 0.26 wt% SWCNTs. This was evident in the constant values of the $T_g$, Vickers hardness, and storage modulus for the PMMA/SWCNT composite, after irradiation. Morphological changes were also confirmed by the SEM characterisation of the nanotube paper.

The authors have also observed that the dielectric properties of CNTs are more prone to the effects of ionising radiation doses than their mechanical properties. In view of the foregoing, it is evident that addition of SWCNTs has a reinforcement effect on the degradation of the polymer matrix. Similar observations have also been made by Najafí and Shin (2005), who in their investigation of the degradation of poly(methyl methacrylate)-CNT nanocomposite thin films, established that the addition of 0.5 wt% CNT fillers generates a reinforcement effect on the extent of degradation occasioned by exposure of a polymer matrix to high-energy radiations (Najafí and Shin 2005). In that study it was also confirmed
that polymer-free radicals enhance the proliferation of degradation. In both studies conducted separately by Muisener et al. (2002) and Najafi and Shin (2005), it is evident that networks of CNTs play an effective role in dispersing the radiation damage.

In another similar study, (Vitusevich et al., 2010) investigated the effect of gamma radiation on transport properties of single-walled carbon nanotube (SWCNT)-based field-effect transistors (FETs) (SWCNT-FETs) using a standard source of the radionuclide $^{60}$Co. The $^{60}$Co source emitted characteristic 1.25 MeV mean energy gamma rays at the dose-rate of 1 Gy/s. The I-V characteristics of the FETs as well as the low-frequency noise spectra of the sample were determined via a 1 Hz-100Hz-frequency range before and after irradiation (Vitusevich et al., 2010). The CNTs used by Vitusevich et al. (2010) were grown for two minutes at a temperature of 900 °C, using methane, hydrogen, and ethylene flows at rates of 720 ml/min, 500 ml/min, and 12 ml/min respectively. The researchers controlled the orientation of growth using electric fields (1 V/µm). After measuring the diameters of the nanotubes using an atomic force microscope, they were found to be 1.3 nm. In addition, the documented images of the scanning electron beam microscope suggested alignment to the electric field’s direction, especially to the Mo electrode edges (Vitusevich et al., 2010).

The results of the investigation indicated effects upon the FET output characteristics following exposure to small doses of gamma radiation. A small dose of gamma radiation occasioned positive changes on the I-V characteristics of the FETs. Vitusevich et al. (2010) attributed the changes in the resistivity of the carbon nanotube. After being exposed to gamma radiation doses of $1 \times 10^4$ Gy and $2 \times 10^4$ Gy, Vitusevich et al. (2010) reported that the SWCNT-FET transconductance and noise level did not register significant changes. However, a decrease in the level of the current was evident. The difference in current was documented before irradiation ($I_{DSO}$) as well as after irradiation ($I_{DSR}$) (DSO and DSR refer to drain-source current before irradiation and drain-source current after irradiation respectively).
The variation of the two values (i.e. $I_{DSO}$ and $I_{DSR}$) was a linear function on the drain voltage (Vitusevich et al., 2010). This therefore confirms addition of certain linear resistance to the nanotubes. The linear function on the drain voltage could also be an indication that the process of irradiation removed a parallel resistance from the nanotubes (Vitusevich et al., 2010). In this study, the authors noticed that the CNT resistance registered a 25% increase after being exposed to a $1 \times 10^4$ Gy gamma radiation dose, a phenomenon that confirmed the effect of irradiation on the transport properties of the CNTs. The results of the study by the authors suggested that small doses of gamma radiation can improve the SWCNT-FET transport and noise properties.

Beside the use of gamma rays, as applied in the studies by Muisener et al. (2002) and Vitusevich et al. (2010) reviewed above, other researchers have opted for other ionising radiations (e.g. alpha-particles) in their analysis. For instance, in their study, Cress et al. (2010) investigated the effects of alpha-particles on high-purity freestanding SWCNTs. The researchers produced and purified (to > 99%) laser-synthesised SWCNTs (Cress et al., 2010a). A qualitative investigation of the high purity of the SWCNT sample was undertaken with the help of a scanning electron microscope (SEM), the research being conducted at 2 keV (Cress et al., 2010). A SWCNT paper (35 µm thick) was then prepared and dried for an hour at 250 °C. After being subjected to alpha-particles emitted isotropically via a thin Ni-Au coating, their effect on the sample temperature-independent conductivity was documented. The irradiation of the SWCNT papers was carried out in vacuo (at $< 5 \times 10^{-6}$ torr).

The results indicated that upon exposure to the alpha-particles, the SWCNT paper recorded a sustained decrease in the total conductivity with increasing fluence (Cress et al., 2010). The researchers noted significant changes in the temperature-dependent conductivity of the SWCNTs, a phenomenon that the authors attributed to the alpha-particles irradiation. According to the authors, the changes that characterised the SWCNT temperature-dependent
conductivity were occasioned by an increase in the number of barriers between the adjacent SWCNTs and the electronic wavefunction localisation. A calculation of the generated displacement damage dose profile within the SWCNT sample confirmed that the SWCNT paper received a uniform displacement damage dose from the environment (Cress et al., 2010). A nonlinear dependence of resistivity in nonionizing energy loss (NIEL) was observed when the rates of change in resistivity was performed for SWCNT papers exposed to two varying radiation doses (i.e. 23 MeV carbon ions and 2 MeV protons). This is a considerable distinction from the linear response associated with the bulk semiconductors and superconductors. The evidential implication of the findings of the study by Cress et al. (2010) is that a localised displacement damage dose imported to a SWCNT from the external environment has a significant damaging effect on the SWCNT’s conductivity compared to distributed point effects within the SWCNT exposed to similar total displacement damage doses (Cress et al., 2010).

In yet another study, (Lobez and Swager 2010) it was demonstrated how the electrical properties of a multi-walled carbon nanotube (MWCNT) are affected by gamma rays irradiation. In this study, the researchers had sought to showcase a novel approach to gamma rays detection that is not reliant upon charge generation or scintillation within semiconductors (Lobez and Swager, 2010). The composite adopted by Lobez and Swager (2010) for the study was polymer/MWCNT, which the researchers deemed capable of generating a real-time signal at room temperature. The polymer matrix underwent ionisation-induced depolarisation following the irradiation of the composite. Consequently, a lower resistance connection was created between the MWCNTs (Lobez and Swager, 2010). In addition, the depolarisation of the polymer matrix occasioned amplification and significant changes in the electrical properties of the composite. According to Lobez and Swager (2010), the depolymerisation-induced changes increased the conductivity of the composite, as detected through
amperometry. Amperometry is a method of measuring over time the current intensity (I) between two electrodes at a constant potential (V) (Lobez and Swager, 2010, p.1). The study thus demonstrated the extent of the effect of gamma rays on the electrical properties of a multiwalled carbon nanotube.

In another study, (Bardi et al., 2017a) quantitatively investigated the effects of X-ray radiation on both the physical and chemical properties of SWCNTs, with a particular focus on relatively low doses of 20 cGy and 45 cGy. Using different characterization techniques such as scanning electron microscopy and X-ray photoelectron spectroscopy (for a discussion of this technique see later) to quantify the effects of such radiation doses on the inherent properties of SWCNTs, Bardi et al. (2017) established that the X-ray irradiation of SWCNTs reduced the sp² of the SWCNT bond structure. In addition, Bardi et al. (2017) found that the electrical properties of SWCNTs were affected by X-ray irradiation, which also resulted in SWCNT of increased defect density.

3.9.5 Conclusion in regard to CNT media

In conclusion, with strong evidence of changes occurring in various material characteristics of CNTs as a function of dose, the indication is that the CNTs have the potential to play an important role in radiation dosimetry, and even more widely in radiation detection. To-date, the use of CNTs has been identified to overcome limitations (i.e. resistively heated filaments) associated with conventional x-ray tubes, allowing production of portable and nano x-ray machines due to their smaller sizes and lower energy dependency, as well as production of focused electron beams. The ability of CNTs to overcome the resistively heated filaments helps in prolonging the life span of the x-ray tube. In addition, the ability of CNTs to enhance the production of focused electron beams that are characterised by a relatively smaller energy spread is crucial in radiation delivery, in terms of generating high-resolution imaging x-ray tubes. However, as has been demonstrated in the above review, the
properties and structure of the CNTs can be significantly affected by ionising radiations, including as a result of exposure to gamma rays, x-rays, as well as alpha-particles. As evident in the studies reviewed herein, the ionising radiations can produce morphological changes in the CNTs and also alter their dielectric properties. Notably in this respect, the dielectric properties of the CNTs are more prone to the effects of the ionising radiation doses than their mechanical properties are. This review therefore provides useful insights for the future applications for CNTs. Indeed, it is apparent that CNTs can be made use of in the area of radiation dosimetry. As the literature shows there are defects and atomic displacements that occur and that can be assessed. These defects can be evaluated with respect to the deposited doses which make the material a potential candidate for use as a passive radiation dosimeter, while active devices are also open to development as seen in regard to FET related changes.

3.10 Methods of Analysis

3.10.1 Introduction

This section discusses the analytical methods applied in using carbon nanotubes (CNTs), seeking a firm basis for their application in radiation dosimetry. The section focuses in particular on how such methods work. Most specifically, in so-doing the section covers the characterisation of CNTs in terms of their mass loss during thermal treatment, analysed by thermogravimetric Analysis (TGA), also their elemental composition through use of Energy Dispersive X-ray Analysis (EDX), as well as the use of the X-ray Photon Spectroscopy (XPS) technique to elucidate how CNT bonding is modified as a result of irradiation. In regard to the latter, the section explores the use of XPS and the fitting of the C1s peak, also how sp² and sp³ are distinguished using peak fitting, energy windows, etc. Given the prominence of the XPS technique in the present work, this will be dealt with first, in subsection 3.11.1.
3.11 Analytical Methods

Within this section, the three analytical methods (XPS, TGA, and EDX) are described in detail.

3.11.1 X-ray Photoelectron Spectroscopy

Carbon spectroscopy is an important domain in surface science, more so in the study of novel carbon-based materials such as diamond-like carbon (DLC), nanotubes, carbides, graphene, as well as carbon nitride (Kaciulis 2012a). According to Kaciulis, identification of the bonds of diamond, amorphous phases of carbon and graphite is of the essence of carbon spectroscopy. In this regard, surface scientists often adopt electron spectroscopies such as X-ray Photoelectron Spectroscopy (XPS), Electron Energy Loss Spectroscopy (EELS), as well as Auger Electron Spectroscopy (AES), as analytical techniques for the identification (Kaciulis, 2012).

The XPS analytical technique is a surface-sensitive spectroscopic technique for the quantitative measurement of the elemental composition, chemical state, empirical formulation, as well as electronic state of the existing elements within a given material (Kim et al., 2007). The achievement of XPS spectra is done through irradiation of the material under investigation with a beam of x-rays, during which the kinetic energy and number of electrons escaping the top 0-10 nm of the surface of a material are measured and analysed simultaneously (Turner and Schreifels 1992). The recording of a photoelectron spectrum in XPS entails counting the ejected electrons over a range of electron kinetic energies (Sublemontier et al., 2014). The identification and quantification of the surface elements is aided by electron kinetic energies and the photoelectron peaks which feature in the spectrum. Figure 8 is schematic illustration of an XPS system.
As illustrated in figure 8, an XPS system comprises three fundamental components. The first component is the fixed-energy radiation source, which emits soft x-rays for the XPS. The second component is the electron energy analyser, which determines the emitted electrons in accordance with the relative kinetic energy. Consequently, the electron energy analyser is able to determine the flux of the emitted electrons of the x-ray radiation (energy). Lastly, the XPS system comprises a high vacuum environment, which allows for the efficient analysis of the emitted photoelectrons (Fadley 2010).

According to Susi et al. (2015), XPS is among the best quantitative techniques available for studying the chemical modification of surfaces, in terms of the distribution and bonding of hetero-atom dopants in carbon nanotubes. Graphitic carbon nanomaterials are characterised by carbon bonded through $sp^2/sp^3$ hybridised covalent bonds (Susi et al., 2015). The uniqueness of $sp^2/sp^3$ hybridisation leads to the formation of strong $\sigma$ bonds between carbon atoms in nanomaterials.

The XPS technique is typically regarded as the preferred method for studying individual atoms (Kaciulis 2012b), allowing those interested in surface science to obtain information regarding the distribution of for instance the various dopants that may be found
within a given sample. A number of studies have been carried out to demonstrate the role of
the XPS technique in surface investigation of CNTs. For instance, (Mezzi and Kaciulis 2010)
carried out a detailed spectroscopic investigation of two main allotropes of carbon - diamond
and graphite - using the XPS technique. They were able to characterise the carbon phase in
the samples of diamond and graphite by studying the relative photoemission peak spectrum
of each. In addition, these researchers determined the sp²/sp³ ratio from the first derivative of
the Auger line (C KLL) spectrum. Also in using the XPS technique, processing of the
spectroscopic data was enabled by using a spectrometer at 20 eV constant pass energy in
conjunction with CasaXPS v.2.2.84 software (Mezzi & Kaciulis, 2010).

The results obtained by Mezzi and Kaciulis (2010) indicated that the main peak of C
1s for the sp² and sp³ configurations had closely similar values of binding energy (BE)
(ranging from 284.4 eV to 284.5 eV). The analysis of the C KLL spectra proved more
diagnostic, allowing the researchers to determine the D-values for the allotropes of carbon
(graphite and diamond), the authors considering this as a fingerprint of carbon hybridization
(Mezzi & Kaciulis, 2010). The sp²/sp³ ratio in the materials under investigation was
calculated using a linear approximation between the D-values of the carbon allotropes.

In another study, Kaciulis (2012) demonstrated how the XPS technique can be
employed in characterising the sp²/sp³ ratio of CNTs, including fitting of the C 1s peak, as
well as distinguishing the sp² bonding from sp³ using peak fitting and energy windows. In
that study, Kaciulis (2012) found that there was linearity of the sp²/sp³ ratio in accord with
the D-value. Using the D-parameter approach, Kaciulis was able to characterise a series of
diamond-like carbon (DLC) media. (Kaciulis et al., 2014) have also confirmed in their
investigation the shape of the Auger C KVV signal (ejection of core shell electrons with
consequent valence to valence transitions) and the acquired relative D parameter such that the
diamond-like carbon (DLC) D-value can act as a fingerprint for recognising graphene. The
study also confirmed the potential of XPS in characterising CNTs. As such, the foregoing results have demonstrated the usefulness of the XPS technique in the fitting of C 1s peak as well as the use of D-values in calculating the $sp^2/sp^3$ ratio.

### 3.11.2 Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) or Thermogravimetric analysis is a thermo analytical technique for determining the chemical and physical properties of a nanomaterial, as a function of rising temperature and/or time (Acquah et al., 2017). Through TGA, see figure 9, one is able to characterise a material, in terms of its physical phenomena, including absorption, desorption, as well as vaporisation (Sergey 2012). Its underlying principle is the measurement of the amount and rate of the mass/weight change of a sample in relation to temperature or time in a controlled environment (Gabbott 2008). TGA is also useful for chemical characterisation of nanomaterials, in terms of chemisorption, decomposition, desolvation, and decomposition (Sergey 2012). In most cases TGA is employed in the determination of specific characteristics of materials that are characterised by mass gain or mass loss as a consequence of oxidation or decomposition (Acquah et al., 2017).

TGA has emerged as a useful tool in the research and development of a number of substances and engineering materials (both solid and liquid) – for purposes of gaining insight about their thermal characteristics, in terms of stability and composition (Loskyll et al., 2012). Some of the recent applications of TGA include quality control and assurance of raw materials, compositional analysis of rubber, evaporation loss associated with lubricating oils, as well as failure analysis of finished products – particularly in polymer processing (Loskyll et al., 2012, Maurer 1969).

In terms of measuring principle, TGA uses thermal analysis to determine the mass change of a given sample as a function of temperature or time, within a defined and
controlled environment in relation to gas atmosphere, crucible type, heating rate, among other factors (Gabbott 2008). As shown in figure 9, TGA instrumentation comprises three main components: a microgram balance, an auto sampler, and a thermocouple for controlling temperature (sample temperature and furnace temperature).

![TGA Instrumentation](image)

Figure 9: Typical TGA Instrumentation. Adopted from Duncan Price lecture notes (Price 2006).

### 3.11.3 Energy Dispersive X-ray Analysis

Energy-dispersive x-ray (EDX) analysis or energy-dispersive x-ray spectroscopy (EDS) or energy-dispersive X-ray fluorescence (EDXRF) is an x-ray technique for the identification of the elemental composition or chemical characterisation of materials. This is normally done using an energy dispersive X-ray spectrometer (Liu et al., 2015). The EDX technique is dependent on the interaction between the material under investigation and the
excitation of the sample resulting from irradiation by the x-ray source (Hotta et al., 2015).
The EDX characterisation is largely based on the principle that each material is defined by a
unique atomic structure, and thus permits a unique set of electromagnetic emission spectrum
peaks for the material (Ravisankar et al., 2014).

As discussed by Yao et al. (2015), EDX analysis of the X-ray fluorescence (XRF) spectrum is a quantitative approach premised on Moseley’s law, an empirical law relating to the characteristics of atoms-emitted X-rays. In 1913, Henry Moseley, an English physicist, conducted an experiment on the characteristics of X-ray, leading to the development of the concept of atomic number (i.e. number of protons). He later rearranged elements in the periodic table based on their atomic numbers and atomic weight, as had been the case previously. Moseley expressed his observations mathematically as shown in equation 6. The expression in equation (6) is referred to as Moseley’s law, which corresponds to Bohr’s atomic model.

\[ \sqrt{f} = k_1(Z - k_2) \quad \ldots (6) \]

Where: \( f \) is the frequency of the observed x-ray emission line

\( Z \) = atomic number; and

\( k_1 \) and \( k_2 \) = constants that depend on the type of line (K, L, etc. in x-ray notation)

Consequently, the design of the EDXRF spectrometer, as illustrated in figure 10 complies with the Moseley’s law, and comprises four main components namely: a power source, a subsystem that provides a path for light, a control circuit, and a personal computer (PC) (Yao et al., 2015). As demonstrated in figure 10, a primary X-ray is emitted by supplying high-voltage power to the X-ray tube. Once emitted, the primary X-ray irradiates the sample, which is consequently stimulated to emit XRF. The emitted XRF is then detected by an XRF detector (Yao et al., 2015). Upon receiving the emitted XRF, the XRF detector
classifies the received photons as per the relative energy. In addition, the XRF detector quantifies the number of photons that tally with various energy levels (Yao et al., 2015). Once the quantification of the photons is complete at the detector, the results are transmitted to the PC where the processes of quantitative and qualitative analyses are completed (Yao et al., 2015).

The light path subsystem of the EDXRF spectrometer comprises an X-ray tube, a collimator, charge-coupled device (CCD) camera and a detector, as shown in figure 10.

The responsibility of the light path subsystem of an EDXRF spectrometer is to emit, receive, and count the XRF photons. As shown in figure 10, the operation of the light path subsystem commences with a supply of high-voltage power, which consequently provides the X-ray
tube with high-voltage generated energy (Yao et al., 2015). As summarised before, the high-voltage energy stimulates the X-ray tube, which then emits a primary X-ray. The emitted primary X-ray is then transmitted through the Be window, filter, and collimator to irradiate the sample, stationed on the sample table as shown in figure 10. Once irradiated, the sample is stimulated and consequently emits XRF, which is then received by the detector. Once received by the detector, the emitted XRF is transformed into a low-voltage pulse by the amplifier (Yao et al., 2015). A pulse amplitude that is proportional to the energy of the XRF received by the detector is amplified further by the main amplifier. The amplified voltage is then transformed into a digital signal by the analogue-to-digital converter (Yao et al., 2015). The digital signal undergoes further transformation into a pulse counter. The transformed digital signal is stored in a mechanical analyser before being formatted to an XRF spectral line. The spectral information is then transmitted by the detector to the PC for qualitative and quantitative analyses via a USB hub (Yao et al., 2015). The qualitative analysis in XRF spectrometry is classified into peak location, peak recognition, and element determination.
Chapter 4

4 Silica-Based material Studies

4.1 Developments in Production of Silica-Based hermoluminescence Dosimeters

The content of the following section has been published in the journal “Radiation Physics and Chemistry”. D.A. Bradley, A.S. Siti Shafiqah, Z. Siti Rozaila, Siti Norbaini Sabtu, S. F. Abdul Sani, Abdulaziz Alanazi, S.M. Jafari, G. Amouzad Mahdiraji, F.R. Mahamd Adikan, M. J. Maah, A. N. Nisbet, N. Tamchek, H. A. Abdul Rashid, M. Alkhorayef, K. Alzimami. 2016. “Developments in Production of Silica-Based Thermoluminescence Dosimeters” Volume 137, Pages 37-44, (Appendix A). The right to include the article in any thesis or dissertation has been obtained during assignment of copyright with the publisher. Also, the right to include this work in this thesis has been obtained from the co-authors. My major role in this work centred around samples preparations for proton and neutron irradiation, results analysis together with participation in the interpretation of the results and writing of the manuscript.

4.1.1 Introduction

Over the past three years the University of Surrey radiation physics group have been exploring the association between design and performance of silica-based media, our interest being in the utility of the latter in sensing ionizing radiation and in radiation dosimetry. These efforts stem from earlier adventitious use of commercially available Ge-doped single mode telecommunication fibres (SMF) in such applications, the design of these being entirely unrelated to the needs to which the fibres were put. The SMFs, as well as other telecommunication fibres such as multi-mode fibres (MMF) and variants of these including
Bragg gratings, are fabricated from low-defect silica, as an example, very pure SiO$_2$ in the form of Suprasil F300, a product of Heraeus (Hanau, Germany). Doped fibre fabrication starts from a hollow capillary (of a few cm diameter), doped using the Modified Chemical Vapour Deposition (MCVD) process. This process requires the introduction of gases (typically germanium tetrachloride, GeCl$_4$, and silicon tetrachloride, SiCl$_4$) into a rotating hollow silica capillary, at the same time applying highly elevated temperatures, typically between 1800- and 2100°C, to allow a deformable material and the deposition on the inner walls of SiO$_2$ and Ge$_2$O$_3$. The preform resulting from this MCVD process can then be pulled into fine diameter (~ 0.1 mm) cylindrical fibres, a form typically used in telecommunications, again using elevated temperatures to soften the silica. The pulling requires use of a rig typically referred to as a pulling tower. For telecommunications the extrinsic dopant creates a change in refractive index between the boundary of the doped silica core and the silica cladding, light within a particular band of wavelengths suffering total internal refraction, transporting the light forward with very low losses from as low as 0.2 dB km$^{-1}$ to perhaps ~few dB km$^{-1}$.

The presence of defects extrinsically introduced into such silica-based insulator media provides for the trapping of electrons that have been excited by incident radiation, with these then being stored as a luminescence signal pending stimulated de-excitation. Storage of the trapped electrons in such media is typically good, providing integration of the irradiation-mediated signal, strongly preserved over a period many orders of magnitude greater than the duration of the exposure. The situation is imperfect, a fraction of the trapped electrons spontaneously relaxing, due to sources of ambient energy, a loss referred to as fading. The fractional loss of TL signal depends on the depth of traps, deep traps (~ few eV) suffering markedly less fading than more superficial traps. Practical systems of readout through stimulated de-trapping can either function through the application of heat, producing
thermoluminescence (TL), or exposure to a controlled source of light, producing optically stimulated luminescence, the emission spectrum that reflects the trapping levels being picked up by a photomultiplier tube. Such systems provide a passive form of detection, contrasting with active devices such as diodes or ionisation chambers.

Present interest is in TL, a less favourable practical feature of such systems is the lack of online monitoring capability. For a well-behaved TL medium, one that can be used for radiation dosimetry, it is desirable for the system to respond sensitively to the radiation levels of interest and to provide TL yield linear with radiation dose. The range over which this occurs is referred to as the dynamic range. A highly sensitive medium points to lower limits of detection, the tendency being for the available defects to become occupied at relatively low doses. Indeed, the study is currently pursuing doses down to a small fraction of a mGy as will be shown later. Conversely, the benefit of a less sensitive dosimeter for a particular source of radiation is that it can be used beyond the upper limit of linearity of the more sensitive dosimeters. As such, the question as to whether a dosimeter is considered good or poor is ultimately linked to the level of dose and range of dose that one wishes to detect, the arbiter of utility being whether it can be used as a monitor of environmental radioactivity, accumulating annual doses of as low as a few mGy, in dosimetry of synchrotron microbeam therapy beams delivering doses at a rate of the order of 10 kGy min\(^{-1}\) (Abdul Rahman et al., 2010), or applied to radiation processing facility dosimetry, with doses of 10s of kGy delivered over a period of an hour or less.

With this brief overview, it is perhaps clear that there exist a number of issues that need to be addressed in seeking high performance TL media. As an example, among the issues confronting use of commercially available fibres such as SMFs, are:
(i) undoped silica cladding, a low-defect unproductive component that also acts to attenuate the TL signal exiting the doped region, as indeed will the doped volume itself (Nawi et al., 2015);

(ii) dopant concentrations that yield sub-optimal TL levels;

(iii) geometric formation that offers sub-optimal net TL yield;

(iv) a potential inhomogeneously doped medium, with additional need to establish whether the fibres yield the designed-for dopant concentrations, measured using techniques such as refractive index profiling (RIP), scanning electron microscope energy-dispersive x-ray analysis (SEM-EDX) and also proton-induced x-ray emission/proton-induced gamma emission (PIXE/PIGE) techniques, the PIGE depending on nuclear reactions and their analysis;

(v) light transmitted through the cladding depending on the incident irradiation and spectra, trap depth also defining the net luminescence exiting the fibre;

(vi) recognition that the thermal conductivity of SiO$_2$, which while not small, is less than that of LiF, pointing to potential need for use of a temperature ramp-rate lower than that typically applied in use of phosphor dosimeters (LIF has a particularly high thermal conductivity).

In regard to (vi), with fibres popularly cut to 5 mm lengths for ease of handling, to-date the fibres have been read-out with their long dimension in contact with the planchet (the heating plate of the TL reader), not least allowing good thermal contact between the heating plate and TL medium. With TL light transporting preferentially along the fibre, normal to the photomultiplier tube, this sub-optimal readout situation has nevertheless been shown to offer excellent capability for radiotherapy applications (with doses from a fraction of a Gy to 10s
of Gy and beyond). A further issue in design of silica fibres is that the MCVD and fibre pulling facilities are expensive to establish and operate.

In what is to follow a review is given on the MCVD-based fabrication method and a wet-chemistry sol-gel nanoparticle approach that offers lower costs of fabrication, summarizing what is know from the characterization of defects and the radiation performance parameters. Example situations will then be provided.

### 4.1.2 Silica production routes

Understanding the origin of luminescence from the various silica fibres involves study of intrinsic defects in the starting material, as well as those that result from fabrication, eg strain-related defects and extrinsic doping, and those that arise from exposure to ionizing radiation, all existing in differing concentrations and charge states. As intimated, commercial optical telecommunication fibres can lead to a poorly posed situation, the fabrication parameters having been set up to provide for optimum telecommunications. As such, the primary intent of the present collaboration has been to work with preforms and fibres based on use of the MCVD process, in particular those that have been tailored towards radiation detection, contrasting this route towards production with the surface decorated nanoparticle sol-gel approach. The sol-gel route offers a very much cheaper processing technique for production of doped glass developed for TL purposes (T Rivera et al., 2007; Siti Shafiqah et al., 2015; Wang et al., 2012) but as with the MCVD product it provides a solution that is not entirely without issues, not least in seeking to obtain a closely similar quality product from each production batch. The variant of the sol gel technique of interest herein involves producing surface-decorated/surface-coated silica nanoparticles, the surface decoration/coating creating luminescence centres. Herein production of Ag-doped silica
nanoparticles is report. In this thesis the analytical approaches in investigating the utility of the two forms of doped silica media involve:

1. elemental composition and morphological studies, to-date the sol-gel media being limited to use of SEM-EDX and x-ray diffraction (XRD);
2. defects characterization via optical properties (UV-Vis, Raman spectroscopy, photoluminescence spectrometry, RIP and X-ray photo spectroscopy, XPS), to-date limited to the optical fibres;
3. dosimetric performance, for the MCVD fibres including the challenging situations of exposure to alpha particles and neutrons in aqueous environments.

SiO$_2$, be it crystalline (eg quartz, coesite, moganite) or amorphous (eg opal, hyalite, and silica glass, the latter being the main focus of our interest), is formed of a 3D network of four oxygen atoms surrounding each Si ion. The amorphous oxide lattice closely matches silicon in size, the tetrahedral structure bonding Si by sharing oxygen atoms in a six-membered ring (Fig. 11).

The physical properties of SiO$_2$ include:

i. high melting point, $\sim$1700 °C, the silicon-oxygen covalent bonds throughout the structure needing to be ruptured before melting occurs;
ii. being an insulator, with electrons tightly held between atoms;
iii. being insoluble in water and organics solvents, of particular interest for \textit{in vivo} applications and those involving aqueous environments.

Defects underpin the mechanism of TL, the electrons and holes released by radiation being trapped at defect sites, giving rise to optical absorption and luminescence (Chen & McKeever, 1997). Notwithstanding the many types of defects in silica, present interest concerns those causing significant TL, intrinsic and extrinsic. Prime examples of the intrinsic are the broken or dangling bond, the oxygen/silica deficient centre and the self-trapped exciton. The former are dangling orbitals populated by unpaired electrons, detectable through electron spin resonance (ESR) (Jafari et al., 2014). Non-bridging oxygen gives rise to oxygen dangling bonds (potential hole traps) and empty Si orbitals. The oxygen broken bonds have been identified to be the source of 7.6 eV absorption which, while too deep for direct TL readout, is nevertheless potentially accessible by photo-transferred TL, PTTL; (see Zulkepely et al., 2015). Expected to be present in as-grown materials, as in silica, the broken bonds are also readily created by ionizing radiation. In disrupted SiO$_2$ tetrahedra the absence of oxygen or silicon atoms creates oxygen deficient and silicon deficient defects. The oxygen-deficient centre (ODC), familiarly designated E’, is representative of $\equiv$Si-Si$\equiv$ with Si-Si indicating electron bonding in a chemical reaction. Analysis of the E’ centre indicates the presence of an unpaired spin, localized at the sp$^3$ orbital of the silicon atom, with orbital orientation towards the oxygen vacancy position (Silsbee, 1961). If two adjacent silicon atoms relax asymmetrically, the most likely occurrence in vitreous glass given its inherit asymmetry, then one electron can stabilize itself on one of the silicon atoms (Beall Fowler and Edwards, 1997). ESR studies in silica glass have shown the same E’ structure (Griscom, 1979). The Si-Si centre is capable of forming a hole–trap (Tsai et al., 1988). At annealing temperatures the E’ centre can transform into a Si-Si centre, while at even greater temperature the Si-Si centres
tend to transform into excess silicon atoms in $\text{SiO}_2$. These excess silicon atoms will then no longer produce luminescence (Rebohle et al., 1998).

In regard to the self-trapped exciton, when an electron is excited in a lattice it leaves a hole in the valence band. This electron will experience a Coulombic interaction with the hole, screened by ions and other electrons. The electron–hole pair, termed an exciton, can propagate through the crystal. In $\text{SiO}_2$, the electron-hole pair is strongly bound due to the low dielectric constant of the base compound. The presence of the self-trapped exciton in silica leads to energy levels inside of the normal bandgap. Tsai et al (1988) have estimated the exciton binding energy in $\text{SiO}_2$ to be about 1.3 eV. Further, the existence of a photoluminescence (PL) band at 440 nm in $\text{SiO}_2$ supports the suggestion that excitons are trapped in the $\text{SiO}_2$ matrix, a phenomenon absent in an ideal crystal. It is now accepted that the mechanism for this defect in silica is the motion of oxygen atoms in the crystal. The motion, first proposed by (Fisher et al., 1990) is an oxygen atom rotation about another Si-O bond of a neighboring silicon atom. This motion causes a lattice distortion that significantly changes the local energy level in the crystal.

In regard to extrinsic defects or impurity centres, when impurities are introduced into the $\text{SiO}_2$ substrate it involves a model in which the impurity centres become either substitutional atoms, interstitial atoms or an impurity-intrinsic complex, with any of these being present inside the material. Apart from the possibility of introducing a new luminescence band, impurity atoms might also change the number of electron or hole traps or else provide much deeper traps in the media. One of the main desirable properties involving Ge impurities is its photosensitivity. Much attention has been paid to the defect produced by the photosensitivity,
known as the germanium oxygen deficient centre (GODC). This defect is commonly considered to be responsible for the changes in the refractive index in germanosilicate glass (Dianov et al., 2000). Concerning the absorption optical activity of these germanium related defects, it has been observed to have a connection with the band peaks at 240 nm and 245 nm, referred to as the GODC and NOV (neutral oxygen vacancy) respectively. These two defects have sometimes been assigned to the wrong bond, such as Ge-Ge, Si-Ge, rather than the usual Si-O-Ge bond in Ge-doped-silica media. It is found that these defects can be bleached with UV irradiation, producing defects such as GeE’, Ge (1) and Ge (2). GeE’, Ge (1) and Ge (2) are the most common Ge related paramagnetic defects that can be detected by electron paramagnetic resonance (EPR) in irradiated Ge-doped silica media. The GeE’ is representative of (≡Ge•), associated with an absorption band at 6.2- 6.4 eV. The Ge (1) defect consists of an electron trapped at the site of a substitutional 4-fold coordinated Ge precursor (GeO₄)³⁻ (Chiodini et al., 1999; Neustruev, 1994; Pacchioni & Mazzeo, 2000), attributed to the absorption band at 4.4 – 4.6 eV. The Ge (2) defect is assigned as ionized twofold coordinated Ge (=Ge••). Based on EPR analysis, the presence of GeE, Ge (1) and Ge (2) are found to be in the region g = 1.9937, 1.9933 and 1.9866 respectively.

The photosensitivity of Ge-doped silica material is found to be correlated with a defect observed in the photoluminescence spectrum, known as the Ge Lone Pair Centre (GLPC) with microscopic structure that has been illustrated to be similar to the Ge (2) defect. This defect can be observed in two band peaks in the photoluminescence spectrum, at 3.2 eV and 4.3 eV, with the absorption band referred to as transitions from a point defect ground singlet state (S0) to the first single state (S1) (Hosono et al., 1992; Skuja, 1992).
4.1.3 Ge-doped optical fibre produced via MCVD technique

The fibres used in the current research in TL studies have employed the MCVD technique, produced in a high temperature environment using GeCl\(_4\) and SiCl\(_4\) as the precursor (Jacqueline et al., 2004; Liu et al., 1997; Mat-Sharif et al., 2013). The TL response of commercial SiO\(_2\) doped optical fibre has been investigated for photons (see for instance, Abdul Rahman et al., 2011; Youssef et al., 2001), electrons (eg Abdul Rahman et al., 2011; Hashim et al., 2009) and alphas (eg Ramli et al., 2009) in each case showing considerable potential in dosimetric applications. Abdulla et al. (2001) carried out a study on commercially available Ge-doped optical fibre using a gamma source, the response being found to be linear from 1-120 Gy. Under electron irradiations, the Ge-doped fibres were shown to have a TL response superior to that of Al doped optical fibre, with linearity over the range of doses 0.02-0.24 Gy (Yaakob et al., 2011), tying in with the fact that Ge in the core allows increase in the value of the refractive index due to the photosensitivity.

Developments beyond the commercially available telecommunication fibre, also obtained using the MCVD technique, have included fabrication of hollow cylindrical fibres, collapsed fibres, photonic crystal fibres and flat fibres, with various Ge dopant concentrations extrinsically introduced and with various dimensions. As an instance, Ghomeishi et al (2015) have investigated three types of Ge-doped optical fibres: conventional cylindrical fibre, capillary fibre, and flat fibre, all fabricated using the same optical fibre preform. For electron and photon irradiated fibres at doses from 0.5 to 8Gy, the results show for capillary fibre collapsed into a flat shape that the TL yield is increased by a factor of 5.5, also some 3.2 times that of the cylindrical fibre. This suggests a strain-generated means of production of suitably sensitive TLD for in-vivo dosimeter applications, with changes in the form of glow curve also being noted. Begum et al. (2015) have also been among those who have shown that the sensitivity of FF constructs can be made to be competitive with phosphor-based TLD,
in the particular case that of TLD-100 and TLD-700 (doped LiF). Further investigations have concentrated on novel microstructured fibres, one example being the photonic crystal fibre (PCF), produced by what is referred to as a stack and draw method (multiple doped fibres stacked together, as for example in a hexagonal array and then pulled into a fine fibre form), the TL arising from the dopant (Ge and B as an example) and induced strains (Dermosesian et al., 2015). Here, an interesting question concerns whether methods might be developed that could apportion the fractional TL yield due to the strain-related defects and extrinsic dopant(s). Glow curve analysis would seem to hold the key to this. The report of Dermosesian et al. shows that PCFs can markedly improve upon the sensitivity of an SMF, in one instance by a factor of ~ 30.

4.1.4 The sol-gel technique

Chemical precursors are applied in this low temperature technique, providing a means of producing ceramics and glasses with purity and homogeneity greater than that achievable using the conventional high temperature MCVD technique. The method has been used to produce a wide range of compositions, mostly oxides, in various forms including powders (Rivera et al., 2007b; Rivera et al., 2007c), fillers (Wen and Mark, 1994), coatings (Kurz et al., 2006; Natsume & Sakata, 2000) and thin films (Kajitvichyanukul et al., 2005; Marikkannan et al., 2015). The technique starts from mixtures of a chemical solution, the precursors acting as the source of elements to be incorporated into the final product. The most common precursor used for silica glass is tetraethylorthosilicate, Si(OC₂H₅)₄, commonly referred to as TEOS. The main chemicals in the mixture are then made to undergo chemical processes with the intent of forming a colloidal suspension known as sol. After going through a sequence of chemical reactions the sol stiffens to form a gel, subsequently heated and dried to form solid (sometimes as powders). In fabrication, Dabbaghian et al., (2010) found ethanol
co-solvent to have the most significant effect on particle size and size distribution of the synthesized silica nanoparticles. Park et al. (2002) reported that smaller sized silica particles can be obtained by employing a small ratio of ethanol in the mixture. The synthesis of mono-dispersed silica particles have been explained in detail by Bogush et al. (1988). To-date, most TLDs in nanoparticle form have been made of ceramics such as ZrO$_2$ and ZnS. Purpose-made for TLD studies, these have been demonstrated to have good performance under UV light (Azorin et al., 2005). Fewer studies have reported on the TL response of silica nanoparticles, Carvalho Jr et al. (2010) reporting on the TL response to gamma rays of natural quartz at nm particle size and Mendoza-Anaya et al. (2003) discussing the TL performance of pure silica nanoparticles, comparing these with Fe and Cu-doped material. Pandey et al. (2004) investigated TL from pure silica nanoparticles supported by results from photoluminescence spectroscopy for defect characterization.

4.1.5 Ag-doped silica nanoparticles

In the following section nanoparticles are abbreviated to Np and the focus is on Ag as the dopant of interest. Elsewhere, CdS and ZnS have been doped with Ag (Tiwari et al., 2014), the TL intensity increasing with increase in UV exposure time, indicative of TLD potential. The use of Ag nanoparticles in ZnO$_2$ has resulted in modification of the kinetic parameters, inducing a shift of the TL temperature towards higher values (Villa-Sanchéz et al., 2007), being of particular importance in ensuring a low fading rate of the stored TL signal.

One concern in introducing dopants into SiO$_2$ in the form of molten glass is the solubility. While in principle any element can mix with the SiO$_2$ precursor during the solution stage, the doping of Ag in SiO$_2$ is advantageous, SiO$_2$ reducing the tendency towards Ag Np agglomeration, important in achieving mono-dispersal of the AgNp. There is already a good deal of experience in working with Ag nanoparticles. As an example, coating of nanoparticles
of this metal with a SiO$_2$ shell has been studied in attempts to enhance colloidal and chemical stability (Niitsoo and Couzis, 2011). SiO$_2$ coatings have also been successfully produced in forming a controlled dielectric environment around the AgNp, improving precision in surface plasmon resonance (SPR) sensing. Ag-doped SiO$_2$ has also been applied in surface enhanced Raman scattering (SERS), with Ag as one of the plasmonic materials, light excitation enhancing the local electromagnetic field (Feng Xian Liu et al., 2001; Long et al., 2012). In Fig 12, the Cu K$\alpha$ XRD pattern shows a broad distribution peaking at $2\theta = 23^\circ$, indicating successful production of amorphous silica and agreeing with others (Gorji et al., 2012; Tabatabaei et al., 2006).

![Figure 12](image12.png)

**Figure 12:** Example XRD pattern of silica Nps, the broad peak indicating the silica nanoparticles to be in an amorphous state.

![Figure 13](image13.png)

**Figure 13:** XRD patterns for Ag-doped silica nanospheres, with crystalline peaks revealing AgNp within the structure of the pure silica base media.
The results of Figure 13 reveal crystalline peaks for the Ag-doped medium, at \(2\theta = 38.2, 44.4, 64.7\) and \(77.5\)°, confirming the presence of Ag nanoparticles in agreement with others (Hilonga et al., 2012; Mie et al., 2014; Torres et al., 2007).

Table 6: Mean particle size (\(\pm 1\sigma\)) silica nanoparticles (Siti Shafiqah et al., 2015)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E5</td>
<td>&lt;10</td>
</tr>
<tr>
<td>E10</td>
<td>80 ±18</td>
</tr>
<tr>
<td>E20</td>
<td>140 ±17</td>
</tr>
<tr>
<td>E30</td>
<td>550 ±9</td>
</tr>
</tbody>
</table>

In Figure 14, it is apparent that particle size manifestly influences the TL properties of the silica nanoparticles, smaller particles, with proportionately greater surface area, exhibiting the greater TL yield compared to that of larger samples (Siti Shafiqah et al., 2015). As such, there
are a proportionately greater number of light-emitting ions on the surface. The TL response of the nanoparticles increases with dose, pointing to the possibility of using silica nanoparticle powder as a dosimetric base-material. Mendoza-Anaya et al. (2003) report silica gel glow peaks to achieve an intensity maximum at much lower temperature compared to present results, indicative of a potential for enhanced TL performance in using present nanoparticle samples.

Figure 15: TL response of pure silica and Ag doped sample within dose range 1-500 Gy. The variation in TL yield and error bars of relatively large magnitude are indicative of the control issues needing to be confronted in product generation.

With Ag as the extrinsic impurity, effects are revealed in Figure 15 that contrast with the use of Ge, one similarity being that with both Ag- and Ge-dopants saturation appears at much greater dose, beyond 500 Gy, compared to that of pure silica samples. For the latter, saturation starts at around 300 Gy. For present samples the AgNps reduce the TL signal, with response less than that of the pure silica samples. Here the Ag multilayer coating the silica surface acts not only as a promoter of TL yield on the silica nanoparticles surface but also as an attenuator, absorbing and scattering a fraction of the incident radiation. Additionally, the layer acts as an inhibitor, reducing the efficiency for transport of TL from the silica nanoparticle surface. Thus said, a particularly attractive feature of the Ag is the extended dynamic range, providing greater versatility of the Ag-doped medium in radiation technology applications at elevated doses, as are found in radiation processing.
4.1.6 Examples of fibre TL applications

Here two situations were selected, the first being that of modulated and unmodulated proton beams, illustrating the considerable spatial resolution (0.1 mm) capability of fibres in making depthdose measurements, in this case of a 62 MeV proton beam. Use was made of commercial Ge-doped silica fibres, purchased from CorActive (Canada), the fibres having a core diameter of 50 μm and a cladding diameter of 125–127 μm. In order to use the fibres, the coating was first carefully removed through use of a fibre stripper (Miller, USA). The fibre was then cleaned to remove any residual polymer. The product was then cut into small fibre lengths of approximately 0.3 ± 0.1 cm, use being made of a scalpel.

The measurements (Fig. 16) were made in a thin window (0.1 mm mica) water phantom, the irradiations being carried out using the UK National Health Service Clatterbridge proton therapy facility. The results have been compared against gold standard parallel plate ionization chamber measurements. In measuring the Bragg peak, the commonly observed issue of a quenching effect is evident, with a decreased response with increasing ionization density of the radiation field. This dose underestimation in the Bragg peak of heavy charged-particles (Rah et al. 2012), also referred to as the quenching effect (Azangwe et al. 2014), has been reported most for chemical dosimeters such as film, polyacrylamide gels (PAG), Fricke gels, PRESAGEs, and alanine (Doran et al. 2015; Baldock et al. 2010 and Gustavsson et al. 2004). This phenomenon is not yet fully understood; high-dose saturation, ion-recombination and track structure theory are among the possible explanations, as discussed by Gustavsson et al. (2004); Jirasek and Duzenli (2002); Katz (1978); Zhao et al. (2012) and Gorjiara et al. (2012). More detailed investigations are ongoing, the present work simply being to illustrate the utility of the fibres. From this preliminary study it is evident that:

- Data for the profile can be obtained in a single exposure, saving considerable beam time, a matter contrary to the experience in making use of a parallel plate ionization
chamber for point-by-point measurements;

- Very high resolution range verification is to be had;
- The irradiated fibres show variations about the mean of up to ±10%, an outcome that is highly competitive with results obtainable using the well-established LiF:Mg, Ti (TLD-100) phosphor-based medium.

Figure 16: Depth dose distribution of a modulated and un-modulated 62 MeV proton beam. The upper graph shows the outcome for an undmodulated beam, the parallel plate ion chamber achieving the predicted peak to plateau ratio of some 5:1 while the fibres approach a a ratio of 4:1. The lower graph shows the outcome for a modulated beam, the fibres producing a range that closely agrees with parallel plate ion chamber measurements.
The graphed results of Figure 17, relate to the second set of situations, showing mass-normalised data from irradiations of fibres of various form and also of phosphor-based TLDs, obtained using a tube x-ray facility (model ERESCO 200 MF4-RW) located at the Physics Department of the University of Malaya. For present work the tube x-ray facility was operated at 80 kVp nominal tube potential, with doses to the samples ranging from 0.5 mGy to 10 mGy, verified through use of a calibrated ionisation chamber. The fibre results are for doped PCFs (Ge and B doped), PCFe_Ge and PCFe_B, the subscript c indicating that under the action of a vacuum, the fibres were collapsed down from hollow bores into a solid assembly (see for instance, Ghomeishi et al., 2015; Dermosesian et al., 2015), inducing strain-related defects and thus additional TL sensitivity. The inset shows the sensitivity of the PCFs to greatly exceed that of TLD-100 (a doped LiF medium) while the main figure illustrates the sensitivity of TLD-200 (CaF2:Dy) phosphor, a material notable for its ability to sense environmental levels. Under the well-controlled situation of x-ray irradiations, the sensitivity of TLD-200 is seen to out perform the present capability of our PCF media. It is to be noted that at calibrated doses the individual TLDs have been selected to provide uniform response to within ± 5% of the mean TL yield.
The various media under field conditions were subsequently tested, locating the media in glass containment in soil at a site marginally affected by technologically enhanced levels of naturally occurring radioactive material (TENORM). The dosimeters were buried in soil at 20 cm depth, as shown in Table 17 and left there for a period from two to four months. With mean above-ground dose-rates in air at 1 m of some 11 nGy/h, a dose corresponding to ~32 μGy over a four month period (Tikpangi Kolo et al, 2015). Samples of each type of TLD were collected 2 months after burial and 4 months after burial (with R1 representing the first sample collection and R2 the second sample collection).

<table>
<thead>
<tr>
<th>Sampling ID</th>
<th>Coordinates</th>
<th>Distance (in km) from Plant site</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>Latitude, N: 3⁰ 59' 52.4&quot;</td>
<td>Longitude, E: 103° 22' 26.3&quot;</td>
</tr>
<tr>
<td>L2</td>
<td>Latitude, N: 3⁰ 59' 50.1&quot;</td>
<td>Longitude, E: 103° 22' 25.6&quot;</td>
</tr>
</tbody>
</table>
Figure 18: Mass normalized TL yield for collapsed PCFs and phosphor TLDs. R1 refers to the first sample collection (2 months post-burial) and R2 to the second sample collection (4 months post-burial). The five sampling locations, L1 to L5, are identified in Table 7.

The results, in histogram form (Figure 18), are accompanied by glow curves for the various TL media (Figure 19), soils analysis at the five specific locations including high-resolution gamma-spectrometry using a shielded high-purity Ge (HPGe) detector. The choice of locations were guided by the gamma-spectrometry analysis and hand-held survey meter findings, obtained regularly over a two-year period, identifying potential elevations (of a factor of up to 2) of NORM over undisturbed soil values (sampling location L1, L2, L3 offering particular examples). For the second sample collection (R2), the TLD results are typically greater than those from first sample collection (R1). The PCFc_Ge samples offer greater TL yield compared to the PCFc_GeB, the converse of that found in using 80 kVp X-ray irradiations, a matter linked to the differing energy response of the two fibre types for the two very different spectral distributions (80 kVp x-rays and NORM). In line with the broad indication offered by the x-ray tube irradiations, TLD-100 offers a lesser response compared
to the PCFs, as expected, while the TLD-200 falls short of the indicative relative sensitivity recorded for the other media in use of 80 kVp calibrations. As expected, the PCF dosimeters provide sensitive measurement, unaffected by moisture, while the degraded in-field performance of the TLD-200 phosphor accords with evidence of moisture intrusion.

![Figure 19: The glow curve of PCFs obtained in burial at location L1 for the first sample collection (R1) and second sample collection (R2).](image)

In Figure 19, the glow curves for R2 for both PCFs are seen to be of manifestly greater intensity than R1 data. As further observed in the histogram of TL yields of for example the L1 sampling location, PCFc_Ge offers the greater TL yield compared to PCFc_GeB. For R2 data, the peak maximum is observed to occur between 255 to 260 °C for both PCFs. The glow curves for the PCFs show the beginning of a high temperature shoulder indicative of strain-related defects.

### 4.1.7 Conclusions

The collaboration whose work is represented herein have made progress towards understanding a number of the major issues guiding development of silica based media for TLD. Fabrication issues have been discussed and how these can influence defect types and concentrations.
4.2 Latest developments in silica-based thermoluminescence spectroscopy and dosimetry

The content of the following section has been published in the journal “Applied Radiation and Isotopes”: D.A. Bradley, S.M. Jafari, A.S. Siti Shafiqah, N. Tamcheck, A. Shutt, Z.Siti Rozaila, S.F. Abdul Sani, Siti Norbaini Sabtu, Abdulaziz Alanazi, G. Amouzad Mahdiraji, H.A. Abdul Rashid, and M.J. Maah. Volume 117, November 2016, Pages 128-134, “Latest developments in silica-based thermoluminescence spectroscopy and dosimetry” (Appendix B). The right to include the article in any thesis or dissertation has been obtained during assignment of copyright with the publisher. Also, the right to include this work in this thesis has been obtained from the co-authors. My major role in this work centred around samples preparations for proton and neutron irradiation, results analysis together with participation in the interpretation of the results and writing of the manuscript.

4.2.1 Introduction

The last three years has witnessed an increased desire to improve luminescence dosimetry through the development of GeO$_2$ doped SiO$_2$ fibres of fine diameter (0.1 mm – 1 mm). Our previous investigations of commercial jewelry beads have shown that such beads are characterized by additional benefits, in terms of robust utility and reduced cost. With both media (i.e. GeO$_2$ doped SiO$_2$ fibres and commercial jewelry beads) being silica-based, compositional investigations by previous researchers, including Jafari et al. (2014a), have established the presence and concentration of dopants in the silica, with the purpose of developing highly sensitive thermoluminescence dosimeters (TLDs).

Through the use of a custom-built spectrometer, this section presents first findings for emission wavelengths, which indicate a dominance of wavelengths towards the blue end of the visible spectrum. Our focus on thermoluminescence (TL) yield is aimed at defining the
optimal concentration of GeO₂ in the SiO₂ fibres, which currently ranges between the standard of 4 mol% up to 12 mol%. Whereas short-range SiO₂ network experiences minimal strain at low dopant concentrations, studies by Abdul Sani et al. (2015a, 2015b) have established that elevating Ge dopant concentrations above the standard 4 mol% lead to lower TL yield due to concentration quenching or “self-absorption. The present work thus predominantly investigates the preforms upon which the fibres are formed.

Given the current interest in Ge-doped silica preforms, this section attempted to determine changes in emission occasioned by changes in defect concentrations. To commence the study of the TL glow curve, a description of the standard energy levels for the inherent defects in the Ge-doped silica preforms media was undertaken as modeled in figure 1. The band model presented in figure 20 is characterized by different types of energy bands as demonstrated. $E_c$ is the activation energy or conduction energy, and is the least energy necessary for de-trapping.

![Figure 20: Energy band model illustrating the electronic transmissions associated with a TL material.](image)

$E_v$ refers to valence band energy, while $E_f$ is the Fermi energy. Electrons and holes are generated in the region $a$ of figure 20 while region $b$ allows for electron-hole trapping.
Thermal stimulation leads to the release of electrons in region $c$ while recombination occurs in region $d$ of figure 20.

### 4.2.2 Energy Band Diagram

The absorption and thermoluminescence process are the concerns of optical activity. The introduction of Ge atom into the glass-matrix lattice leads to the modification in the bond energy, as the Ge atoms move to take up interstitial or substitutional positions. Such modification occasions the free movement of the donor electrons from one ion to another. The energy gap between silica’s valence and conduction band widens at approximately 9 eV, as illustrated in figure 21.

![Energy Band Diagram](image)

**Figure 21**: Modification of the energy band structure of silica by impurity atoms (Ge) or lattice irregularities in the glass that create localized electron states (energy values all in eV). This figure was constructed with the help of available literature (Randall, 1945; Skuja, 1992, 1998; Imai and Hirashimi, 1994; Amossov and Rybaltovsky, 1994), showing the various possible defect energy levels in Ge doped silica.

The electrons can transition from ground energy to the conduction energy upon absorbing sufficiently greater light energy, and consequently, a current is produced. Trapping of the electrons by the Ge atoms (impurity atoms) in the silica glass can take place at intermediate energies, a phenomenon that leads to the creation of localized electron states which are often characterized by extremely narrow energy level, and can trap electrons longer (up to years). Such energies are released in the form of photons and are classified in accordance with typical time scales, as is the case in fluorescence ($10^{-7}$ s) as well as phosphorescence ($10^{2}$ s). The phosphorescence process has a range of applications. This photon forms our main interest in the current work. The localized energy states occasioned by impurity atoms such
as the Ge atoms, have been investigated by a number of researchers, including Randall (1945), Skuja (1998), Imai and Hirashim (1994), as well as Amossov and Rybaltovsky (1994). The results of these studies have provided for a comprehensive summary of the Ge-doped silica glass energy levels as shown in table 8.

<table>
<thead>
<tr>
<th>Acronym(s) of Defect</th>
<th>Proposed Structural Model(s)</th>
<th>Situation of Optical Absorption Band Peaks (eV)</th>
<th>PL Bands Peaks (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si ODC(II), Ge ODC(II)</td>
<td>Oxygen vacancy</td>
<td>6.8-7.0</td>
<td>4.2-4.3</td>
</tr>
<tr>
<td>B₂(Si),</td>
<td>Oxygen divacancy</td>
<td>4.95-5.05</td>
<td>4.3-4.4</td>
</tr>
<tr>
<td>B₂(Ge)</td>
<td>Oxygen divacancy</td>
<td>5.1-5.4</td>
<td>4.3-4.4</td>
</tr>
<tr>
<td>Si₂⁺</td>
<td>discoordinated Si/Ge</td>
<td>3.15</td>
<td>2.7-2.8</td>
</tr>
<tr>
<td>Ge₂⁺, Ge²⁺</td>
<td>Discoordinated Ge</td>
<td>3.7</td>
<td>3.0-3.2</td>
</tr>
<tr>
<td>Non-bridging-oxygen hole centre (NBOHC)</td>
<td>≡Si–O•</td>
<td>4.8</td>
<td>1.85-1.95</td>
</tr>
</tbody>
</table>

### 4.2.3 Energy Level of GeO₂-SiO₂ Glass

The production of the point defects in an insulator’s or semiconductor’s extrinsic doping adopts the form of a mixture of vacancies and interstitials, all which lead to the distortion of the structure plane, and thus occasioning the alteration of compactness and local charge as well as strain. Colour centres are produced by the point defects as a consequence of
the modification of electronic neutrality. The line defects and area defects emanate from
dislocations and instance grain boundaries respectively. The standard energy level description
of GeO$_2$-SiO$_2$, as shown in figure 21, provides a reflection of the defects, while table 8
summarizes the results of previous investigations of doped media such as silica doped by
GeO$_2$. In the current study, our focus is limited to the study of glow curves and emission
spectrum. In particular, an examination of two samples of GeO$_2$ doped silica proforms
namely: oxygen-rich Ge-doped silica preform and oxygen-deficient Ge-doped silica preform
was undertaken.

4.2.4 Sample Preparation

The approach taken in the present work has been that of developing the two preform
samples of oxygen-rich Ge-doped silica preform (P1) and oxygen-deficient Ge-doped silica
preform (P2). A description of the preparation these samples as well as their optical
spectroscopic characteristics have been provided by Tamchek et al. (2013) and Siti Shafiqah
et al. (2015).

4.2.5 Experimental Set-up for Conventional Glow Curves

In order to obtain the necessary glow curves, the University Malaya Radiation
Laboratory’s Harshaw Model 3500 Manual TLD reader was used. The two samples adopted
for the investigation (P1 and P2) had to undergo pre-heating up to a temperature of 80 °C so
as to get rid of the thermally unstable thermoluminescence component associated with the
glow curve. The pre-heated samples were then subjected to further heating to a temperature
of up to 400 °C at a rate of 10 °C/second. What followed then was the analysis and
deconvolving of the glow curves, beginning with Voigt profile, from which it was
demonstrated in the current work that the components peaks can be approximated by the
Gaussian function, which also allows the approximation of the peak central temperature and FWHM. Nevertheless, Alawiah et al. (2015) noted that this is a limited approach.

In the current case, the extremely smaller Lorentzian contribution to the Voigt profile was neglected while fitting the information to the Randall and Wilkins’ TL model. Figure 20 illustrates the activation energy ($E_c$) of the glow curves. A characteristic feature of the Randall and Wilkins’ TL model is that the peak positions remain fixed, while their heights are directly proportionate to the dose. The analysis of thermoluminescence emission spectra was performed using an in-house experimental setup (figure 22) as described in the following subsections.

Figure 22: The In-house Experimental Setup for measuring emission spectra of the heated samples P1 and P2.
4.2.6 The Experimental Set-Up for TL Emission Spectra

The experimental setup adopted for measuring the heated samples’ emission spectra is presented in figure 22. The entire system of the set-up (figure 22) comprises three main components namely: a heating chamber, the spectrograph, and a high sensitivity CCD array. The design of the system was intended to allow for the measurement of extremely low light intensities, given that the sample underwent heating over a pre-defined interval. A large diameter (24 mm) collimation lens, with a focal length of 35.4 mm was used to collect emission spectra from the heated samples. A Czerny-Turner spectrograph, utilizing a 600 µm core diameter was used for transferring the collected light. A grating groove of 150 g/mm to follow the dispersion of the spectra was used. The grating groove had the capability of producing a spectral bandwidth of 400 nm and spectral resolution of 0.4 nm. A high sensitivity cooled charge detector (CCD) of Andor Technology (Model iDUS DU401) was used to acquire the spectral information. The CCD was characterized by a pixel array of 1024 x 128, a pixel size of 26 x 26 µm, as well as a quantum efficiency above 95% within visible region (550 nm). The total dark current stands at 0.001 electrons/pixel/second, when the CCD is cooled to -80 °C. Our observation of the system light suggest that it can be compared to a conventional photomultiplier tube. A double layer copper cylinder, with a glass wood insulator, was used to shield the heater chamber was for purposes of reducing heat loss from the heater ceramic. The heater ceramic’s heat capacity and heat conductivity of 900 W and 100 W/(m K) respectively, allow maximum heat transfer to the sample. For purposes of ensuring accurate measurement of temperature, an external type K temperature probe fixed at the top of the sample was used. The sample’s and CCD’s temperatures sing a customized automation software were recorded and controlled, which was ran by a personal computer (PC) using LabView.
Both control and irradiated samples were placed in the heater and heater chamber in turns, with N\textsubscript{2} being used to purge the irradiated sample to rid it of water vapor as well as to prevent it from being oxidized. The samples were heated at a temperature rate of 1.5 °C/second, and record the emission spectra for a duration of 250 seconds. The CCD in the Photon Accounting mode was used, and accumulated the data at 5 x the shutter duration of 150 ms. In this regard, 1 sec/°C was not only the time that a single acquisition took, but also the time taken to stabilize the sample temperature. Correction of the emission spectra for background emission was obtained, ceramic heater blackbody radiation, as well as CCD quantum efficiency.

4.2.7 Peak Temperature

The results of the glow curve study for samples P1 and P2 are shown in figures 23 and 24 respectively. The deconvolved results for P1, as shown in figure 23, indicate that the sample is characterized by two peaks – the lower peak (peak 1) and the maximum peak (peak 2). The lower peak attains a maximum yield at a temperature of 234.8 °C, which matches the use of the Arrhenius equation with an $E_c$ of 0.4567 eV. The upper peak of P1 on the other hand attains maximum yield at a temperature of 328.5 °C, and which coincides with an $E_c$ of 0.5035 eV.
In the case of P2, the results shown in figure 24 suggest that the sample is characterized by a single peak, which attains a maximum yield at a temperature of 315.6 °C, and which coincides with an $E_c$ of 0.5377 eV. Figure 24 illustrates the results of sample P2.

4.2.8 Spectral Analysis

The preform samples (P1 and P2) were analyzed using the customized spectrograph. The results of the analysis are presented in figure 25.
Figure 25: Results of the spectral analysis of samples P1 and P2. The figure illustrates the total intensity emitted from samples P1 and P2. Sample P2 is characterized by an additional peak at 5.4 eV. Furthermore, the intensity of P2 is about 12 times that of sample P1.

The results indicate that sample P2 has an intensity that is about 12 times that of sample P1. It is possible to have a complete interpretation for purposes of calculating the defects concentration as shown in table 9.

<table>
<thead>
<tr>
<th>Sample/Preform</th>
<th>Peak Energy (eV)</th>
<th>Absorbance, $\alpha$ (cm$^{-1}$)</th>
<th>Full-wave-half maximum, W (eV)</th>
<th>Defect Concentration, $N_{def}$ (1 x 10$^{15}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>6.9</td>
<td>1.101</td>
<td>0.471</td>
<td>3.83</td>
</tr>
<tr>
<td>P2</td>
<td>5.1</td>
<td>3.492</td>
<td>0.565</td>
<td>14.63</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>2.174</td>
<td>0.844</td>
<td>13.61</td>
</tr>
</tbody>
</table>

The calculation of the defects concentration can be done using the Smakula formula (Smakula, 19930; Afanasyev-Charkin et al., 1999), and which holds as follows:

$$ N_{if} = 8.7 \times 10^{16} \frac{n}{(n^2+2)^2} \propto m \ U \quad \ldots \quad (7) $$
where, $N_i$ is number of defects, $f$ is the oscillator strength of the optical transition, $\eta$ is the refractive index of the sample, $\alpha$ is the height of absorption coefficient of the peak and $U$ is the band width (FWHM).

The results indicate that the TL yields and defect concentrations have a linear proportionate relationship, and thus occasions a prediction of an increase in the TL signal that is 3-4 fold. As evident in figure 25, the TL emission is characterized by a 4-4.5 eV energy level, indicating light whose wavelength is 290 nm, in accordance with the deep trapping levels presented in tables 8 and 10 as well as figure 21 (Khanlary et al., 1993).

Table 10: Some of the commonly reported luminescence bonds present in quartz and silica, as published by Khanlary et al. (1993). Potential defect models are indicated.

<table>
<thead>
<tr>
<th>Band (nm)</th>
<th>eV</th>
<th>Method†</th>
<th>Possible models for origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>4.77</td>
<td>CL</td>
<td>Oxygen vacancy</td>
</tr>
<tr>
<td>290</td>
<td>4.26</td>
<td>PL, CL</td>
<td>Oxygen vacancy</td>
</tr>
<tr>
<td>390</td>
<td>3.25</td>
<td>RL, CL</td>
<td>Aluminium impurity, an impurity</td>
</tr>
<tr>
<td>390</td>
<td>3.17</td>
<td>RL</td>
<td>$E_0$ intrinsic defects and Ge impurity</td>
</tr>
<tr>
<td>400</td>
<td>3.1</td>
<td>PL</td>
<td>$E_0$ intrinsic defects and Ge impurity</td>
</tr>
<tr>
<td>450-480</td>
<td>2.5-2.8</td>
<td>RL, CL</td>
<td>Recombination of self-trapped exciton</td>
</tr>
<tr>
<td>580</td>
<td>2.15</td>
<td>CL</td>
<td>Oxygen vacancy</td>
</tr>
<tr>
<td>640</td>
<td>1.9</td>
<td>IB1, CL</td>
<td>Oxygen vacancy and Na impurity</td>
</tr>
</tbody>
</table>

† CL, PL, RL are cathodo-, photo- and radioluminescence and as is ion beam implantation.

Figure 26 illustrates the TL emission spectrum of P1 as a contour plot of temperature, TL intensity, as well as energy.
Figure 26: Emission spectrum contour of plot sample P1. The right side of the figure shows the sample’s relative heat or its associated TL intensity.

As shown in figure 26, the emission maximum of the main dosimetric peak falls between 3.9 eV and 4.5 eV, with an additional evidence of the existence of several bands at energies beyond 6 eV. The results from the plot (figure 26) indicate that the peak maximum at the 3.90 eV energy level is commensurate with a sample temperature of 187.7 °C. An observation is also made of two more peaks whose intensities are lesser at energy levels of 4.37 eV and 4.60 eV. An observation of a continuous TL emission is made at the energy level of 4.20 eV, with temperatures exceeding that of the emission at a minimum of 187.7 °C and maximum of 400 °C. A defect analysis conducted by Skuja (1998) had identified the emission energies to have a relationship with the oxygen vacancy and divacancy, which are associated with Si ODC (II), Ge ODC (II), B₂(Si), and B₂(Si).

Figure 27 illustrates the results of the TL emission for sample P2, and indicate that emission spectrum associated with sample P2 ranges between energy levels 4.2 eV and 5.2 eV, with an extra high energy band at 6 eV.
The peak maximum form sample P2 was established at 4.94 eV. In addition, the intensity of P2 was found to be greater compared to that of P1. Nevertheless, important to note is that the peaks of sample P2 begin to emit at a temperature of 368 °C, which is relatively higher, and which corresponds that associated with the conventional glow curve measurement. Based on the results of defect analysis presented in Table 8, there is evidence to suggest that there is a relationship between this emission energy and the oxygen divacancy, which belongs to B$_{2}$(Si) and B$_{2}$(Ge).

4.2.9 Cases of Silica Beads Irradiated by an Am-Be Neutron Source

With the foregoing underpinning information, investigation of the potential of doped silica media for developing versatile thermoluminescence dosimeters continued, with a particular focus on neutron detection capability. In doing so, hollow silica beads, with a 1 mm diameter were adopted, and which have previously been adopted by Jafari et al. (2014a, 2014b, 2014c) for photon TL dosimetry. Figure 28 shows the preliminary depth-dose distributions that obtained from an Americium Beryllium (Am-Be) neutron source placed in a
water tank. While keeping the beads threaded onto a nylon filament, thin in size, the string of beads was suspended directly over the neutron source, whose activity was 17.6 GBq, and allowed a neutron emission rate of 62.6 n/s/MBq. The distance between the source surface and the nearest bead was kept at approximately 0.6 cm, with the rest of the 168 equi-spaced beads being placed at as far as approximately 20 cm away from the source surface. The exposure of the arrangement to the source lasted for a duration of 10 days, with beads undergoing sensitivity corrections from a photon irradiation to a standard dose. Detailed description of the calibration was produced in a previous publication (Jafari et al., 2014b). The utility of getting dense spatially resolved detection of the neutrons at unsurpassed spacing is demonstrated in figure 28. A general agreement was obtained in shape using the Monte Carlo simulation, as described by Yury Zevallos-Chavez and Bugno Zamboni (2005).

What seems to be an intriguing feature of our measurements, and that which is yet to be explored further, is the observed instances of variation in the otherwise uniform downward trend in the data. A prominent instance was the variation near a source to detector separation of a distance of 5 cm. Through the use of Monte Carlo simulation, sharp peaks are established, which are re-obtainable at similar points as those of the measured data, as indicated in figure 28.
Figure 28: Depth-dose distribution in an Am-Be neutron source. (a) 1 mm spatial resolution depth dose distribution from the Am-Be neutron source; (b) A visual impression of the Monte Carlo simulation’s mathematical model; (c) Neutron source spectrum; (d) the MCNP Monte Carlo simulation’s 3 independent runs.

Although further investigations are ongoing, it is worth noting that the particular MCNP code adopted for the simulation of our experiment did not factor in diffractional phenomena or take into account the 59.54 eV gamma rays that emanate from the $^{241}$Am source following alpha emission. The 59.54 eV gamma rays associated with the $^{241}$Am source contributed to the observed differences in intensity.
4.2.10 Conclusion

Using two samples of oxygen-rich (P1) and oxygen-deficient (P2) preforms, an in-depth overview of the physics upon which investigations of thermoluminescence of irradiated doped silica media are anchored has been produced. In particular, the band gap model and the defects that occasion the TL phenomenon are described in a detailed manner. The observations suggest the existence of a correspondence between the doped silica’s model system, as documented in literature, and our empirical measurements of the emission spectrum and glow curves from the doped silica preforms, as described in the current work. The scope of the current work is also extended to include a demonstration of the versatility of the silica media by taking TL measurements from a neutron source dipped in a water tank, with a view to establishing the unsurpassed spatial resolutions that can be obtained with such dosimeters.
4.3 Characterisation of an isotopic neutron source: A comparison of conventional neutron detectors and micro-silica glass bead thermoluminescent detectors

The content of the following section has been published in the journal “Radiation Physics and Chemistry” Y.M Abubakar et. al., M.P. Taggart, A. Alsubaie, A. Alanazi, A. Alyahyawi, A. Lohstroh, A. Shutt, S.M. Jafari, and D.A. Bradley. 2017. Volume 140, November 2017, Pages 497-501, “Characterisation of an isotopic neutron source: A comparison of conventional neutron detectors and micro-silica glass bead thermoluminescent detectors” (Appendix C). The right to include the article in any thesis or dissertation has been obtained during assignment of copyright with the publisher. Also, the right to include this work in this thesis has been obtained from the co-authors. My major role in this work centred around samples preparations for proton and neutron irradiation, results analysis together with participation in the interpretation of the results and writing of the manuscript.

4.3.1 Introduction

Achieving mm spatial resolution by mapping mixed radiation fields using conventional glass-based neutron detectors is a challenging undertaking. However, developing an in-depth knowledge of various radiation intensities as a consequent of the location of the environment enveloping neutron sources is of the essence if such sources are to be utilized as characterization tools. Therefore, in the present work, the potential of using thermoluminescence response of 1.1 mm diameter micro-silica glass beads for purposes of mapping the radiation field occasioned by an Am-Be neutron source dipped in a water tank was explored.
When convoluted through moderation and increasing of the distance from the source, Thompson and Tylor (1965); Anderson and Neff (1972); Lorch (1973); as well as Caeaho et al. (1989) have reported that the neutron emission energies occasion peaks in the distribution of the neutron capture cross section. In fact, this phenomenon has been corroborated by previous studies conducted by Mathews (1979); Nicolaou (1983); and Taggart (2007). As reported by Jafari et al. (2014a), a far finer ΔE (neutron) sensitivity is obtainable with the ~1 mm sized dosimeter than with alternative techniques. While the energy response of conventional gas detectors is properly documented in existing literature, Jafari et al. (2014c) have previously reported on that of glass beads.

Most of the previous work, including those by Chang and Timmerman (2007) and Teoh et al. (2011), have been focused on investigating the effectiveness of dosimeters for application in radiation dosimetry, and with a specific emphasis on the need to develop dosimeters with small dimensions vis-à-vis the radiation field dimension (Bjärngard et al., 1990; Higgins et al., 1995; Fracesco et al., 1998; Sauer and Wilbert, 2007; Aspradakis et al., 2010; Jafari et al., 2014a). However, most of the recent studies have shifted focus by investigating the potential of a mixed radiation field, as was the case in Bradley et al. (2016) as well as in the current study. The intention to observe this point is informed by the understanding that the glass beads’ response cannot be a function of neutron interactions per se, as a substantial gamma factor is expected to make a significant contribution to the TL yield, even though the γ efficiency remains extremely low for the comparative gas detectors as noted by Reilly et al. (1991) and Kouzes et al. (2009).

2. Experimental Setup

The experiments were undertaken using a mono 11 GBq Am-Be source (Ziegler, 2007), which was available at the University of Surrey, as described in figure 29.
Figure 29: Neutron tank setup and detectors positions for vertical measurement study. While both the glass beads and gas detectors were depicted in a similar position, their measurements were undertaken separately.

The glass beads were submerged in the water contained in the water tank. The vertical gas detectors (i.e. the $^3$H and boron trifluoride) on the other hand were enveloped within an air-tube. Instead of preferentially selecting fast neutrons by displacing the moderating water, the high-voltage supply was protected by raising the air-tube using the detector. The gas detector was powered with an Ortec 710 PSU, holding the $^3$He tube and the BF3 detector at 1200 V and 1800 V respectively. Respective detector outputs were led into an Ortec 142A preamplifier and an Ortec 672 spectroscopy amplifier was feted, with each tube being assigned a shaping time of 3 µs. The Ortec Maestro program (Ortec, 2016) provided online monitoring. Using the Root framework (Brun & Rademakers, 1997), a customized code, with which was performed offline analysis was built.
4.3.2 Surface Scan

The initial measurements were aimed at investigating the gas detectors scanning response across the neutron tank’s surface. As evident in figure 30, both detector systems are characterized by a similar response curve peaking regarding the source location.

![Graph showing scans across the neutron tank's surface with the gas detectors. The maximum intensity appears above the Am-Be source.](image)

However, the $^3$He tube provided a relatively greater neutron reaction, which permitted the generation of neutron count that proved more statistically reliable. Nevertheless, it was found both detectors to have comparatively poor spatial resolution, with the active volume of the $^3$H tube and the BF$_3$ being 76 cm$^3$ and 152 cm$^3$ respectively. These findings are commensurate with a spatial “bite” of approximately 2 cm within the horizontal surface plane. Besides performing detector measurements, data were repeatedly recorded set using a cadmium sheath, so as to reduce the effect of thermal neutrons. However, the cadmium sheath-based analysis proved statistically unsound in the case of the BF$_3$ detector, and hence the BF$_3$ results obtained through this analysis were excluded from this analysis.
4.3.3 Depth Measurement

The $^3$He detector was used to measure depth comparison. This was necessitated by the fact that the BF$_3$ tube is characterized by a limited resolution, and thus was not suitable for the depth comparison measurements. A substantial “energy bite” was observed for every data point, courtesy of the gas detector’s relatively large active area. The substantial “energy bite” observed in this experiment justifies the poor spatial resolution that characterizes the conventional neutron detectors. However, this confirmed the availability of spectroscopy in this instance. In addition, it was observed that measurements improved due to the significantly reduced gamma interaction component. Similarly, cadmium-sheathed have measurements were also undertaken on the surface measurements.

4.3.4 Glass Beads

Figure 31 shows a sample of the ~1.1 mm diameter glass beads were used in this study. Before irradiating the glass beads, preparation in accordance with the procedure outlined by Jafari et al. (2014b) was made.
The individual beads were subjected to annealation at 400 °C for a period of 1 hour with a ramp rate 10 °C/minute and a cool down rate of 1 °C/minute, so as to rid them of any historical record of irradiation, and thus ensure the provision of a clean dosimeter. The annealed samples were consequently maintained at 80°C for duration of 16 hours. In their previous measurements, Jafari et al. (2014b) had confirmed that annealation does not impact on the radiation response of the glass beads.

Three independent strings of glass beads were suspended directly above the neutron source as illustrated in figure 29, while ensuring a gap of approximately 31 mm between the glass beads at the bottom and the neutron source, with each of the three strings of beads containing a total of 370 individual hollow beads (see figure 31 for examples). The beads were threaded onto a nylon filament for an estimated length of 410 mm. Then irradiation of the glass bead samples using the 11 GBq Am-Be source for a period of 14 days was acquired. This corresponds to a neutron fluence of about 9.5 k neutrons per seconds per square centimeter for closer beads down to approximately 1.2 neutrons per seconds per square centimeter at the maximum length of the bead string.

A Toledo 654 TLD reader from the University of Surrey was used to measure the bead sets in the post-irradiation phase. The measurements in this regard were anchored on the technique provided by Jafari et al. (2014b). Before undertaking the measurement, the risk of the rapid fading of the TL material was eliminated by storing the irradiated glass beads in a dark environment as well as allowing the beads to undergo stabilization (Jafari et al., 2014c).

4.3.5 Calibration

A previous publication by Jafari et al. (2014b) has demonstrated that individual glass beads exhibit better uncertainty in response compared to other conventional TLD materials. According to Jafari et al. (2014b), and indeed as confirmed in by us, glass beads are
characterized by a variation of approximately 8%. This variability corresponds with the estimated 15% variability associated with the LiF TLDs, as reported by Jafari et al. (2015). Despite the current lack of absolute reference before performing the calibration, as suggested in the conclusion with respect to further work, it is worth pointing out that the data variation as illustrated in figure 33 concurs within uncertainty, and thus look forward to the same yields from the individual glass beads, with an exception of the peaks.

4.3.6 Monte Carlo Simulation

The Am-Be source’s mixed radiation field together with the dual neutron-gamma response of the dosimeter makes deconvolution of respective components a necessity. Using the general Monte Carlo N-Particle transport code, MVNPX proposed by Hendricks et al. (2008), a simulation was developed, during the modulation of the neutrons’ passage via the pure water shield. In a previous work by Bradley et al. (2016), this simulation procedure, which is based on preliminary mathematical model, had been discussed extensively. A number of assumptions were made regarding the Am-Be source, including a neutron energy spectrum being emitted by the Amersham source calibration data as well as the construction of an internal source based on an Am-Be layered structure.

4.3.7 Results and Discussion

As indicated in figure 30, the surface scanning measurements suggest slight variations in neutron yield over the water tank’s surface, with some greater than 20 cm being deemed necessary for exhibiting a two-fold reduction in count rate, which is not an unreasonable outcome, as far as classical trigonometry is concerned. As evident in figure 32, there is evidence of the vertical depth measurements in both the $^3$He tube and the glass beads.
These measurements indicate the cumulative effect of the geometric range of data as well as a reduction in the moderation of neutron. Measurements for the $^3\text{He}$ detector using a $\sim1.1$ mm-thick cadmium sheath were taken, the results which indicate a predicted fall in count rate as a result of the resonances associated with the neutron capture cross section as the energy range transit from the fast region and the neutrons undergo thermalization.

The vertical measurements presented in figure 32 suggest a similar trend of falling count rate with rising distance to the neutron source for every experimental data set and the simulation. However, it is possible to observe far finer structure courtesy of the glass beads greater spatial resolution. The energy regions that the numerous glass beads encounter are simultaneously integrated by the gas detectors. This therefore confirms the glass beads’ superior performance, in terms of providing greater spatial resolution.

In addition to the observed apparent energy sensitivity, further observations can be made through a closer examination of the glass bead data presented in figure 32 as well as the measurements of the additional bead string presented in figure 33. The glass bead dosimeters seem to exhibit an apparent lower level plateau region, a phenomenon that is not noticeable in
the case of the gas detectors. This therefore depicts a lower energy limit, and the glass beads may become insensitive when operated below such energy limit. It is found that such distance is commensurate with a distance of about 23 cm from the neutron source. The characteristic energy and dose limitations of the glass bead dosimeters have previously been described by Jafari et al. (2014c).

Figure 33: Abridged TL Yield Associated with a Mixed Radiation Field.

However, the quasi-regular spikes present in the TL intensity, and which are reproduced during the simulation, is perhaps the prominent feature of the glass bead spectra. The similarity observed between the TL intensity spikes attributed to the dosimetric data sets is not enough grounds to arrive at the conclusion that the peaks of the Am-Be neutron energy spectrum is the origin of the feature (Thomson & Taylor, 1965; Anderson & Neff, 1972; Lorch, 1973; Coehlo et al., 1989). Therefore, as noted by Lorch (1969) and Wright (1994), it must stated that some other phenomena are involved in determining the origin of the feature, or that such origin is potentially a function of a neutron-induced charged-particle reaction, such as \((n,\alpha)\) or \((n,p)\). In a previous discussion, Jafari et al. (2014c) had identified silicon
(33.62% by weight), oxygen (42.18% by weight), and Sodium (10.55% by weight) as the primary components of the elemental composition. Kim et al. (2013) had reported that the dominant neutron interaction associated with every element containing the glass beads is elastic scattering in nature, a phenomenon was observed in all the energy range investigated, and most of which corroborate the theory that the elastic scattering associated with the dominant neutron interaction is caused by high Q-values.

Before the Am-Be source adopted for our investigation was installed (Ziegler, 2007), Bradley et al. (2016) had carried out a similar measurement using two Am-Be sources placed approximately 20 cm apart, although with a relatively different configuration. Therefore, based on the previous studies, independent contribution from every individual source is expected. However, due to the lower spatial resolution (Nicolaou, 1983; Taggarat, 2007), the possibility of observing the spikes was less likely. The less likelihood of observing the spikes may also have been due to the potential effect of integrating contributions from the two neutron sources submerged in the water tank as reported by Bradley et al. (2016).

4.3.8 Conclusion and Further Work

Work is in progress to determine the potential of the commercial glass beads for dosimetric applications. However, with the little investigations so far, there has been evidence to suggest that these beads bear significant dosimetric features with regard to the neutron tank. Four areas that further work must address immediately with respect to this work were suggested. They include the following:

i. The need for secondary calibration through the Am-Be “halo”.

ii. The need to optimize the sophistication of Monte Carlo simulation.

iii. The need to evaluate the relative n/γ bead sensitivity by undertaking repeated measurements involving additional lead shielding.
iv. The need to evaluate the relative fast/thermal neutron sensitivity through cadmium shielding.

The “halo” configuration is intended to ensure a constant source-bead distance, and thus makes it possible for all the glass beads to receive the mixed radiation field dose in an equal manner. It is possible to uncover the possible source(s) of the “quasi-regular” spikes based on the experiments have been performed in the present study. For example, in instances of neutron-induced charged-particle reactions, a change in position regarding future simulation would be expected. Similarly, where a reaction is the source, the presence of the “halo” configuration spikes was predicted.

The following three chapters present a full study in radiation dosimetry. Single-wall carbon nanotubes (SWCNTs) were formed in a buckypaper to represent human tissue for radiation dosimetry application. The results show promising prospects on the novel methodology used that was applied on SWCNTs.
Chapter 5

5 Carbon Nanotubes Buckypaper Radiation Studies for Medical Physics Applications

Most of the content of this chapter has been published in the journal “Applied Radiation and Isotopes”: "Abdulaziz Alanazi et al., 2016. “Carbon Nanotubes Buckypaper Radiation Studies for Medical Physics Applications” Volume 117, November 2016, Pages 106-110, (Appendix D). The right to include the article in any thesis or dissertation has been obtained during assignment of copyright with the publisher.

5.1.1 Introduction

As discussed in the review of literature (see 3.9.5) passive dosimeters with a $Z_{\text{eff}}$ similar to tissue-equivalent are needed. In the following two chapters, the use of single-wall CNTs were made use of to demonstrate their ability to perform as a passive dosimeter with $Z_{\text{eff}}$ similar to soft tissue.

5.1.2 Carbon Nanotubes

Since CNTs were first reported upon by Iijima in the early 1990s (Iijima 1991), the properties of carbon nanotubes were investigated intensively and have been considered for many potential applications, such as chemical sensors (Kong et al., 2000, Moradi et al., 2013, Penza et al., 2010, Wongchoosuk et al., 2010, Zhao et al., 2005), biosensors (Balasubramanian and Burghard 2006, Koehne et al., 2004, Li et al., 2003, Timur et al., 2007, Wang 2005), field-emission displays (Choi et al., 1999, Kuznetzov et al., 2010, Lee et al., 2001, Saito 2010,
Talin et al., 2001), memory storage (Ganguly et al., 2005, Lu and Dai 2006) and hydrogen storage (Liu et al., 2010, Ranjbar et al., 2010, Yang et al., 2010). The specific structure of the atoms forming the carbon nanotubes gives interesting physical and chemical properties such as electric and thermo conductivity. Carbon nanotubes, CNTs, can be described as a beehive sheet bended to form a cylinder and the two ends of the cylinder are open or can be closed with a semicircle lid. This cylinder-like form can be shielded by other cylinders with open ends to form a multi-wall carbon nanotubes structure (MWCNTs). Figure 34 displays single and multi-wall carbon nanotubes with open ends. The dimensions of the structure, just described, are of the range of nanometers. The diameters range from a few nm to 30 nm and the length of the tubes can go up to ~ 1 µm (Iijima 1991). These dimensions can vary depending on the method of growth and the procedure parameters (Arjmand et al., 2016, Nihei et al., 2003, Yazyev and Pasquarello 2008).

Figure 34: The structure of Single-Wall Carbon Nanotube, SWCNT, is displayed to the left-hand side while the Multi-Wall Carbon Nanotubes structure is displayed to the right (Choudhary and Gupta 2011). Licence: http://creativecommons.org/licenses/by-nc-sa/3.0/
5.1.3 Buckypaper Samples

Carbon nanotubes are made from and provided in the form of powder. To enable them to be used as a passive radiation dosimeter, they need to be made in a way where they can be handled and used safely. To obtain that, a Buckypaper, can be made from the carbon nanotubes powder. The Buckypaper, illustrated in figure 35, can be handled and used as a paper. The size of the Buckypaper can be controlled depending on the application and the interest prompting dose measurements. The thickness of the Buckypaper can be varied from about 10 to 100 micrometres.

![Figure 35: Samples of Buckypaper of different thicknesses have been prepared and developed in the Nanomaterial and Structure Lab at the University of Surrey.](image)

Different qualities of single-wall carbon nanotubes, SWCNTs, were purchased from the company Unidym in the form of powder, Raw SWCNTs, Pure SWCNTs, and Super Pure SWCNTs. Triton X-100 has been used as a surfactant. A magnetic stirrer was used to maintain a suspension of the surfactant on the deionised water. The membrane filters, MCE MF-Millipore plain white, 0.22 µm pore size with diameter of 47 mm, were purchased from Fisher Scientific Company to filter and accumulate the CNTs. A tip sonication, Branson–Sonifier 150, was used for dispersion of the mixture.
5.1.3.1 Preparation of the Dispersion of SWCNTs and Buckypaper

As there were different purifications of SWCNTs, various concentrations of the surfactant and SWCNTs were used for each quality. Different concentrations of CNTs require different quantities of the surfactant. In this study the ratio by weight was the reference in the calculations. The optimum surfactant to CNT ratio was found to be 5:1 to 10:1 by weight (Islam et al., 2003). In this work 10:1 surfactant to CNT ratio was used to prepare all the samples and the amounts of CNT were from 0.03 g to 0.140 g depending on the purity of the CNTs.

Dispersion of Triton X-100 in deionised water was prepared to suspend the single wall carbon nanotubes homogeneously. Measured quantities of the Triton X-100 and deionised water were added to a flask and a magnetic stirrer was used to stir the mixture. The dispersant bottle was placed in a cold bath, at a temperature from 3 to 6 °C, and a tip sonication, Branson – Sonifier 150, illustrated in figure 36 (a), was used for 30 minutes with a power range from 17 to 20 watt to mix and disperse the solution.

Subsequent to the dispersion process a simple visual verification is conducted to check the homogeneity of the sample. If the sample is observed to include particle aggregation, further centrifugation can be applied, use being made of the Eppendorf Centrifuge 5702, illustrated in figure 36 (b).

Figure 36: (a) A tip sonication, Branson – Sonifier 150, (b) Eppendorf Centrifuge 5702.
in Figure 36 (b). The solution then can be filtered by the use of the filtration system as shown in figure 37. The resultant mixture, a black solution as illustrated in figure 37 (a), is poured into an open-ended flask that is closed by a glass stopcock. Use is made of a membrane filter, MCE MF-Millipore plain white, 0.22 µm pore size with diameter of 47mm, as illustrated in figure 37 (b, c, and d). The glass stopcock is linked to a vacuum pump to allow the solvent to be drained from the flask. This draining will lead to an accumulation of the carbon nanotubes suspended in the solution. This in turn enables the filter to form a disk-like membrane, the thickness of which depends on the concentration of carbon nanotubes in the mixture. The diameter depends on the membrane filter, which is 47 mm in our case.

a) The mixture before dispersion taken place   b) The glass stopcock

![Image](image1)

![Image](image2)

c) The filtration system setup.   d) Removal the air bubbles from the solution

![Image](image3)

![Image](image4)

**Figure 37:** The preparation of buckypaper in the Material Processing Laboratory at the University of Surrey. (a) the mixture before dispersion takes place, (b) the glass stopcock, (c) the filtration system setup, (d) removal of the air bubbles from the solution.
Before the vacuum pump can be turned on, the solution needs to be cleared of any air bubbles left in the solvent. Then the vacuum pump is turned on and the solvent takes up to several hours to be drained from the flask depending on the concentration of CNTs in the mixture. When all the solvent is drained, the membrane filter is removed from the system and left to dry. After the Buckypaper is dried, the accumulated carbon nanotubes (as illustrated in figure 35) can be peeled away from the membrane filter. The buckypaper now is ready to be used and can be cut into different sizes depending on the TLD Reader sample holder. In the current case, the sample holder can accommodate sample sizes of $5 \times 5$mm or less.

5.1.4 Thermogravimetric Analysis, TGA

During thermoluminescence readout both the CNTs and Silica Fibre undergo a heat cycle. As such a thermal stability test for the two materials is required. This can be conducted by use of the Thermogravimetric Analysis Unit at the University of Surrey Nanomaterials and Structures Lab. Thermogravimetric analysis (TGA) is an analytical technique that examines the change of material mass as a function of temperature. The TGA consists of a high precision balance that can detect mass change up to 0.1 µg. The temperature of the TGA furnace can reach up to 2000 °C and the ramp temperature can be controlled depending on the experiment requirement. The balance in the TGA consists of a small pan, figure 38 (b) which after being loaded is to be placed inside the cylindrical furnace. The pan can be loaded by a small amount of sample, about 1.0 g (Fig. 38a). The test can take a couple of hours depending on the temperature ramp and the maximum temperature that has been chosen.
The heating process in the furnace can take place either under a controlled flow of nitrogen or it can simply be run in air, depending on the experimental purpose and requirements. In our case both conditions have been applied. Of note is that the carbon nanotubes have high stability compared to many other materials when exposed to heat and can be heated up to 600 ºC in air without oxidation (Pang et al., 1993), and with no change in mass up to 1200 ºC under nitrogen flow. However, this is not the case when dealing with buckypaper as it consists of CNTs and surfactant, which in our case has been Triton X-100. The surfactant used to form the buckypaper is known to be affected by high temperatures. The diagram below, figure 39, shows the percentage change in weight when Raw-CNTs-Buckypaper has been exposed to temperatures up to 800 ºC.
Figure 39: Thermogravimetric analysis diagram for Buckypaper made of Single-Wall Carbon Nanotubes.

The blue line illustrates the change in mass when the sample is heated under nitrogen flow. The red line illustrates the change in mass when the sample is heated under air flow. As can be seen from figure 39, the change in mass starts at 100 °C, becoming pronounced after 200 °C, both with and without nitrogen. The mass of Single-Wall Carbon Nanotubes Buckypaper under the flow of air, depicted by the red line, shows a dramatic decline after 200 °C, about 68.94% of the mass being lost at 400 °C. Since as previously mentioned, CNTs are stable showing no loss of mass up to 600 °C in air (Pang et al., 1993), this decline cannot be attributed to the change of mass in CNTs, being only attributed to the loss of Triton X-100.

For increase in temperature of carbon nanotubes, the loss of weight from the sample is caused by oxidation of carbon into the gaseous phase, i.e. carbon dioxide. This can be noticed in the first stage of the graph. However, the graph shows a slight growth in weight above 450 °C, caused by oxidation of the remaining metallic catalyst into the phase of solid oxides.
The change in mass with increase in temperature is far less when nitrogen gas is applied to prevent oxidation. When applying nitrogen, as shown in the blue line, there is an observed loss of mass with increase in temperature from 200 to 400 °C, the mass then remaining steady up to 750 °C. The total loss of mass from the Buckypaper was measured to be 23.49% under the flow of nitrogen compared with 68.94% loss of mass under the flow of air. The loss from Buckypaper in both experiments can be attributed to oxidation of the Triton X-100. This has been confirmed by examining the TGA graph of Triton X-100 (Fig. 40).

![Graph showing the change in mass with increase in temperature under nitrogen flow.](image)

**Figure 40:** Thermogravimetric Analysis graph for Triton, illustrating the change in mass when the temperature is increased from room temperature to 600 °C under the flow of nitrogen.

As can be seen in the graph, the loss of mass as illustrated by the red line shows dramatic increase when the temperature increases from room temperature to 120 °C. The mass then remains constant from 120 °C to almost 300 °C. However, beyond 300 °C the loss of weight increases sharply, with less than 3% of the mass remaining in the pan when the temperature exceeds 400 °C.
Figure 41: Thermogravimetric Analysis graph for Triton illustrating the change in mass when the temperature is increased from room temperature to 600 ºC under the flow of air.

The TGA of figure 41 represents the situation for Triton in the absence of the nitrogen flow that would inhibit oxidation of the sample. The red line illustrates the decrease of mass when the temperature is increased from room temperature to 600 ºC. As can be seen, in air the Triton shows a gradual decrease in mass when the temperature increases from room temperature to 120 ºC. Beyond 120 ºC, up to 220 ºC the mass remains steady. However, beyond this the graph shows a rapid decrease in the mass when the temperature exceeds 250 ºC, with practically nothing left in the pan when the temperature reaches 500 ºC.

From the literature and from the experiments conducted in this study, the loss in mass from the Buckypaper samples when exposed to elevated temperatures can be estimated, up to 600 ºC, is due to the mass loss of the Triton X-100 surfactant used to disperse the CNTs in preparation of the Buckypaper samples. As such, in order to use Buckypaper for
thermoluminescence studies, the sample first needs to be exposed to such temperature elevations prior to irradiation. This will cleanse the sample of the Triton X-100.

5.1.5 Radiation Sources and System/Sample Set-up

A radioactive strontium-90 source, with a half-life of 28.8 years, decays by $\beta^-$ into yttrium-90, the latter having a half-life of 64 hours in decaying by $\beta^-$ into zirconium-90. The scheme in figure 42 illustrates the situation, including emission energies.

![Scheme of Strontium-90 decay](Images/SI%20Inc%202012.png)

**Figure 42: Scheme of Strontium-90 decay (adopted from (Images SI Inc 2012)).**

As shown above the maximum beta energy is 0.546 MeV for the strontium-90 decay into yttrium-90. The yttrium-90 will decay to zirconium-90 releasing beta particles with mean energy of 2.28 MeV (Browne 1997).

The various samples studied herein have been exposed to the strontium-90 source, as illustrated in figure 43. The source is retained within a plastic holder, contained within a leaded glass box to minimise the radiation hazard to users. CNTs and TLD-100 samples have
been placed in an aluminium tray. The aluminium tray is designed to hold samples of size $5 \times 5$ mm. As there are different concentrations and quality of CNTs in the Buckypaper, the edges of the tray are labelled by numbers and letters to help identify the samples.

Figure 43: Set-up for the beta irradiation source, 90Sr, the Buckypapers of size $(5 \times 5$mm) and TLD-100 samples. Different Buckypaper with different purities and concentration were irradiated in this experiment. Raw single-wall carbon nanotubes, pure single-wall carbon nanotubes, and super pure carbon nanotubes were used to form the various samples of Buckypaper. The concentration of the CNTs in the dispersion used to form the Buckypaper was 0.1, 0.1, and 0.05 gm for raw, pure, and super pure single-wall carbon nanotubes respectively. These quantities were dispersed in 100 ml of deionized water through the use of Triton X-100. The three samples received a dose of 2 Gy each.

5.1.6 Results and discussion

5.1.6.1 Raw Single-Wall Carbon Nanotubes

Figure 44 illustrates the thermoluminescence (TL) signal from the buckypaper prior to any treatment, it being noted that in this instance the Buckypaper was not annealed post-sample production, the background signal therefore representing inherent defect occupied as a result
of issues such as strain and lattice dislocations. A time-temperature profile has been selected for the TLD reader, the set-up chosen for present measurement providing a ramp-rate of 6.5 °C per second post pre-heat of 165 °C, with each channel number equivalent to a temperature increment above 165 °C of 1.65 °C.

![Figure 44](image)

**Figure 44:** TL from Buckypaper (sample size 5 x 5 mm) raw SWCNT dispersed in 100 ml of deionized water using Triton X-100. The results show TL yield post pre-heat of 165 °C (Channel Number 0), the temperature subsequently ramping up at 6.5 °C per second to a maximum of 330 °C at channel Number 100.

This measurement was required in order to enable comparison between the TL yield from a fresh unirradiated sample that had not been subject to any heat treatment and the TL yield from a sample treated with heat during an annealing or readout process. The sample consists of 0.1 g Buckypaper (sample size 5 x 5 mm) raw SWCNT dispersed in 100 ml of deionized water using Triton X-100. The multiple-peak signal profile is presumed to be a result of random defects created during the preparation of CNTs buckypaper samples, ranging from the superficial to deeper defects, reflected in the temperature required to enable release trapped electron and lattice relaxation. This is supported by the fact that following annealing of the sample, the signal profile changes dramatically, the TL yield reducing by a factor of 18 (Figure 45). The figure shows two profiles, one for the TL yield from an non-irradiated sample after annealing process (the lower line), and the other the TL yield (represented by the
prominent peak) from the sample following irradiation to a dose of 2 Gy, irradiated with the $^{90}$Sr beta source. The TL signal from the irradiated sample shows a pronounced TL response compared to that in the absence of irradiation. The TL signal was improved by a factor of $\sim 21$ over that of the unirradiated sample. The TL yield (the so-called glow curve) was found to be encompassed within the temperature range $180$ to $250 \, ^{\circ}C$.

![Graph showing TL yield vs. channel number](image)

**Figure 45:** The peak illustrates the TL yield from the raw SWCNT sample post-irradiation, while the lower line illustrates the TL from the unirradiated sample, post-annealing.

Another experiment was made in examining for the presence of any TL signal not released during the first readout procedure. Figure 46 shows two curves, the peak illustrating the first readout and the lower line illustrating the second readout for the same raw SWCNT sample. From this, it is apparent that one heating cycle is sufficient to provide for complete de-excitation of the irradiation sample.
Figure 46: The peak illustrates TL yield of raw SWCNT obtained following irradiation to a beta dose of 2 Gy, the lower line representing subsequent readout from the sample, demonstrating radical release of the trapped electron and lattice relaxation to have occurred.

5.1.6.2 Pure and super-pure Single-Wall Carbon Nanotubes

Similar measurements were conducted for the pure SWCNTs and super-pure SWCNTs. Figure 47 below illustrates the background reading for a fresh sample of the pure SWCNT that has not been exposed to radiation or heat treatment. The results are similar to that obtained for the raw SWCNT sample for both measurements, pre and post anneal. The TL yield from the annealed sample was practically identical to that provided by the raw SWCNT sample. However, comparing the irradiation raw and pure SWCNT samples, the magnitude of the TL signal for the same irradiation dose is lower for the pure SWCNT than that from the raw SWCNT.

This reduction in TL signal is expected as the former sample has been purified of iron and other elemental components. The absence of such impurity has a clear effect in the TL signal as can be seen in Figures 45 and 46, compared with the signal obtained from the pure SWCNT buckypaper sample shown in Figures 47.
Figure 47: TL from Buckypaper made of pure SWCNT dispersed in 100 ml of deionized water using Triton X-100 (sample size was 5 x 5mm).

Reduction in TL yield of some 3.8 was found for the irradiated pure SWCNT buckypaper in compared with that from the irradiated raw samples as in Fig. 45 and 46.

Figure 48: The peak illustrates TL yield from pure SWCNT buckypaper irradiated to a dose of 2 Gy using a beta source 90Sr; the lower line illustrates the signal obtained on second reading.

Figure 48 illustrates the first and second readings for the pure sample subsequent to irradiation to a dose of 2 Gy. The peak illustrates the result of the first reading cycle and the lower line illustrates that of the second read cycle, again supporting the previous sample
results indicating little necessity for annealing when the sample is exposed to a dose in the range of several Gy.

Figure 49 shows the TL yield for a fresh super-pure SWCNT Buckypaper sample. The sample consists of Buckypaper made of 0.05g of Super-Pure Single–Wall Carbon Nanotubes dispersed in 100 ml of deionized water through the use of Triton X-100. The sample size was again 5 × 5 mm and again the sample was irradiated to a dose of 2 Gy using the $^{90}\text{Sr}$ beta source. The graph is multi-peaked for the non-irradiated sample as obtained from raw and pure SWCNT Buckypapers. However, this sample provides a greater TL yield than the pure SWCNT sample, being similar to the TL yield obtained from the raw SWCNT sample. This was not expected as the sample is super purified from impurities. However, as nitrogen is used in the process of purification of the samples, this increase is thought to be due to contamination during that process, the nitrogen atoms potentially causing increase in the trap centres in the sample.

![Figure 49: TL yield, before irradiation, from buckypaper made of Super-Pure SWCNTs dispersed in 100ml of deionized water using Triton X-100, (sample size was 5 × 5mm).](image)

Figure 50 again shows two line profiles, the peak illustrating the TL yield from the super-pure SWCNT sample after exposure to 2 Gy using the $^{90}\text{Sr}$ source, and the lower line
illustrating the TL yield resulting from the second reading for the same sample. The TL yield from the super-pure sample is greater than the TL yield from the pure sample by factor of 2.2.

![Graph showing TL yield comparison](image)

**Figure 50:** The peak illustrates the TL yield from the super-pure SWCNT sample following exposure to a dose of 2 Gy using the $^{90}$Sr source, and the lower line illustrates the TL yield from second reading for the same sample.

### 5.1.6.3 TLD-100

The response of TLD-100 (doped lithium fluoride) has been obtained for the same beta dose as that used for the SWCNT buckypaper samples, residual clipping being observed even with a factor of $10^3$ increase in TLD reader sensitivity over that adopted for the SWCNT samples (see figure 51).
Figure 51: TL yield from TLD-100 irradiated to a dose of 2 Gy using the \(^{90}\)Sr source.

It does need to be observed that the SWCNT samples were of lower mass than that of the TLD-100 ranging from 2 to 10% of the TLD-100 mass. Thus the mass-normalised relative response of the SWCNTs to the TLD-100 was of the order of some 2%.

5.2 Conclusion

Three types of SWCNT buckypaper, each of different impurity, were prepared for irradiation using different sources. TLD-100 was used for comparison. The samples were irradiated using a \(^{90}\)Sr source. The TL yield from the CNT samples indicate considerable potential for these media, underlined by a fact that the response to varying purity would need to be calibrated for. While the response of the buckypaper is less than that obtained from TLD-100, the results do suggest that CNTs may accommodate higher levels of radiation dose, with potential for use in dosimetry as in radiation therapy, a matter requiring further investigation which has been further investigated in the following chapters.
Chapter 6

6 Lower Limits of Detection in using Carbon Nanotubes as Thermoluminescent Dosimeters of Beta Radiation

6.1.1 Introduction

Most of the content of this chapter has been published in the journal “Radiation Physics and Chemistry”: "Abdulaziz Alanazi et al., 2016. “Lower Limits of Detection in using Carbon Nanotubes as Thermoluminescent Dosimeters of Beta Radiation”, Volume 140, November 2017, Pages 87-91, (Appendix E). The right to include the article in any thesis or dissertation has been obtained during assignment of copyright with the publisher.

In the previous chapter (Chapter 5) the thermoluminescence signal was measured from samples of Single-Wall Carbon Nanotubes (SWCNTs) produced in the form of Buckypaper, the samples being of varying purity. The samples (raw SWCNTs, pure SWCNTs, and super-pure SWCNTs) were irradiated by a $^{90}\text{Sr}$ source to obtain various doses. In this chapter further investigations of the materials was conducted, seeking to obtain a measure of the lower limit of detection (LLD) for the particular samples and their associated production methods. The doses used were in the range of 35 mGy to 1.3 Gy, the response of the CNT Buckypaper against doses showed a trend towards linearity.

5.3 Methods of Sample preparation

The method of Buckypaper preparation was as discussed in section 5.1.3.1. The optimum surfactant to CNT ratio was found to be in the range 5:1 to 10:1 by weight (Islam et al., 2003). In this and previous work, a surfactant to CNT ratio of 10:1 was used to prepare the various samples. The concentration of the single-wall carbon nanotubes in the dispersion that
was used to form the buckypaper were 0.1, 0.1, and 0.05 gm for raw, pure, and super pure single-wall carbon nanotubes respectively. These quantities were dispersed in 100 ml of deionized water through the use of Triton X-100 as previously mentioned.

Figure 52: Microscopic view of the Buckypaper sample made of single-wall CNTs. Obtained using accelerating potential energy of 20 kV, and magnification power of 50,000. The scale is shown in the form of the 100 nm white bar, provided in the lower part of the figure.

Figure 53: Microscope image of one of the buckypaper super-pure single-wall CNT samples, the image being obtained using an acceleration potential 20 kV and magnification 25x, the surface roughness being highlighted. A 1mm long scale is provided in the lower part of the figure.
Surface roughness and variability in the buckypaper samples as shown in figure 54 indicate considerable variability in the amount of CNTs deposited in the surface of the Buckypaper (compare to figure 53). Normalization for surface roughness can be expected to lead to reduction in the variability in response to dose.

### 6.1.2 Strontium-90 source for Beta Irradiation of CNT Samples

Exposure of the CNTs samples was carried out in the radiation laboratory, University of Surrey. A $^{90}\text{Sr}$ beta source of approximate activity 95 MBq was used to irradiate the various CNTs samples, raw, pure, and super-pure. In order to minimise exposure to the user, the source was located within a box shielded by lead. The samples were positioned in a rotating disk that can accommodate 26 individual samples within it, each labelled to identify the individual samples. The set-up is as shown in Figure 54. The different qualities of single-wall carbon nanotubes have been exposed to the beta-ray emissions to provide doses of 0.02, 0.035, 0.627, 0.836, and 1.245 Gy.

![Irradiator Interior (side view)](image)

Figure 54: The diagram shows the beta source irradiation set-up used to expose the CNT Buckypaper samples.
6.1.3 Results and discussion

6.1.3.1 The glow curve

Figure 55: TL yield for the CNTs (the glow curve), encompassed within the temperature range 180–250 °C.

Figure 55 above shows the glow curves obtained for the irradiated CNT buckypaper samples for doses within the quoted range, the TL yields being observed to be encompassed within the temperature range 180–250 °C. The absence of noticeable differences in shape or distribution of TL yield with dose is indicative of an essentially identical trap centre activation energy distribution over the particular dose range. The temperatures have been made to ramp from room temperature to the maximum value of some 397 °C at a ramp rate at 6.5 deg C per second, leading to an ability to discern above-background glow curves for doses down to 35 mGy, extending to 1.3 Gy, allowing the samples to be considered to be of utility for radiotherapy dosimetric applications. Thus said, it was also observed that a hyperresponse at 0.2 Gy of the order of four times greater than that obtained at any other dose within the dose range which was explored, with further experiments subsequently carried out.
(in the subsequent subsection to this). The more general trend, in response to the various doses, in the absence of this hyper-response was found to be linear across the dose range (Figure 56). Note should be taken that each point in the graph is the mean of three measurements made on three individual samples irradiated under the same conditions.

6.1.3.2 Energy Response

![Comparison between different CNTs response to dose](image)

**Figure 56:** Comparison between the energy response for raw, pure, and super-pure (SP) SWCNTs. The TL yield divided by 1 million to normalize the numbers on the scale of Y-axis. The inset displays the hyper-sensitivity observed at low doses.

In figure 56 the lower line in the graph represents the dose response for the super-pure SWCNTs, that above it the dose response for the pure SWCNTs and the upper line represent the dose response for the raw SWCNTs. The inset to the figure displays the hyper response observed at 0.2 Gy. As can be seen in the graph the dose response is generally proportional with dose, trending toward linearity for the three samples, raw, pure, and super-pure single-wall CNTs. The raw sample provides the greatest response, a matter supported by Energy Dispersive X-Ray Analysis (EDX) examining the purity of samples provided by the manufacturer. Figure 57 shows EDX analysis for the raw SWCNTs, the Fe content in the raw sample being some 17.2 wt%, considerably greater than that for the pure and super-pure samples, at 11.7 and 7.6 wt% respectively. These quantities are a reflection of the number of
trapping centres within each sample. As such, the raw samples produce a commensurately large TL yield; conversely the super-pure samples, greatly purified from impurities, produces a commensurately low TL yield.

From EDX analysis for the raw, pure, and super-pure SWCNTs (figures 57 and table 11), the weight percentage of carbon were found to be 68.2%, 72.1%, 74.1% respectively. The remaining impurities are dominated by Fe and O₂. Fluorine, Al, SiO₂, and Ca were found in amounts of less than 1%. The oxygen weight percentage for the raw, pure, and SP SWCNTs were 13.5%, 15.1%, 15.5% respectively. These impurities contribute to the charge centres localization and induce the SP² to SP³ hybridization as mentioned earlier.

Figure 57: Energy Dispersive X-Ray Analysis (EDX), showing the various elements present in the raw SWCNT samples.

Table 11: Quantitative EDX Results for raw, pure and super-pure SWCNT, obtained using an accelerating potential of 15kV and magnification power of 50.

<table>
<thead>
<tr>
<th>Elements Line</th>
<th>Raw Sample</th>
<th>Pure Sample</th>
<th>Super-Pure sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Norm. Wt.%</td>
<td>Norm. Wt.%</td>
<td>Norm. Wt.%</td>
</tr>
<tr>
<td>CK</td>
<td>68.22 ± 0.35</td>
<td>72.14 ± 0.35</td>
<td>74.07 ± 0.35</td>
</tr>
<tr>
<td>OK</td>
<td>13.54 ± 0.28</td>
<td>15.51 ± 0.21</td>
<td>15.53 ± 0.27</td>
</tr>
<tr>
<td>AlK</td>
<td>0.16 ± 0.02</td>
<td>0.15 ± 0.02</td>
<td>2.36 ± 0.02</td>
</tr>
<tr>
<td>SiK</td>
<td>0.31 ± 0.02</td>
<td>0.18 ± 0.03</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>TiK</td>
<td>0.59 ± 0.04</td>
<td>0.31 ± 0.02</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td>FeK</td>
<td>17.18 ± 0.27</td>
<td>11.71 ± 0.26</td>
<td>7.63 ± 0.19</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Further investigation was conducted to examine the response at 0.2 Gy. Six repeat experiments were conducted, exposing the sample on each case to a dose of 0.2 Gy. The results of the focal study are shown in the following subsection.

6.1.3.3 Focal Study of TL Response at a Dose of 0.2 Gy

As mentioned in the previous study, a hyper sensitive response was observed at the low dose of 0.2 Gy. In this subsection, further more intensive study has been conducted to investigate in detail the response of the CNT Buckypaper at a dose of 0.2 Gy. Six repeat experiments were conducted, the glow curve and TL yield signal again being observed. An example of the typical TL response (fig. 58) has shown the TL yield data to now fit linearly with that of the other doses.

Figure 58: TL yield for the CNTs (the glow curve), encompassed within the temperature range 180–250 °C.
Figure 58 above shows the glow curves obtained for the irradiated SWCNT Buckypaper samples, presented as the average value for the several measurements conducted to examine the response of the samples. The behaviour of the glow curve is identical to that in figure 55, the only change being the magnitude of the TL yield at 0.2 Gy, encompassed within the same temperature range 180–250 °C. The TL reader has been set up to re-obtain the parameters used in the previous experiment; the temperatures have been made to ramp from room temperature to the maximum value of some 397 °C at a ramp rate at 6.5 deg C per second. The more general trend, in response to the various doses was found to be linear across the dose range (Figure 59). Note should be taken that for the doses other than that at 0.2 Gy, each point in the graph is the mean of three measurements made on three individual samples irradiated under the same conditions. It is possible that in previous measurement at 0.2 Gy use was made of a sample with an unusual localised density of CNTs, leading to the greater TL yield, a yield that was found to be reproducible.

![Graph: Comparison between different CNTs response to dose](image)

Figure 59: Comparison between the energy response for raw, pure, and super-pure (SP) SWCNTs. The TL yield divided by 1 million to normalize the numbers on the scale of Y-axis.
Figure 59 shows the response of SWCNTs samples (raw, pure and super-pure) for different doses. The lower line in the graph represents the dose response for the super-pure SWCNTs, above it the dose response for the pure SWCNTs and the upper line represent the dose response for the raw SWCNTs. As can be seen in the graph the dose response is generally proportional with dose, trending toward linearity for the three samples, raw, pure, and super-pure single-wall CNTs. The raw sample provides the greatest response, a matter supported by Energy Dispersive X-Ray Analysis (EDX) examining the purity of samples as discussed in the previous subsection. In the table below the results of 6 experiments conducted for dose 0.2 Gy. The TL yield of 6 measurements for the raw SWCNTs and the standard deviation for each sample response are presented in table 12.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experiment 1</th>
<th>Experiment 2</th>
<th>Experiment 3</th>
<th>Experiment 4</th>
<th>Experiment 5</th>
<th>Experiment 6</th>
<th>Average</th>
<th>Standard Deviations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A1</td>
<td>A2</td>
<td>A3</td>
<td>A1</td>
<td>A2</td>
<td>A3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment 1</td>
<td>302</td>
<td>341</td>
<td>313</td>
<td>300</td>
<td>318</td>
<td>361</td>
<td>319</td>
<td>19.2</td>
</tr>
<tr>
<td>Experiment 2</td>
<td>345</td>
<td>297</td>
<td>351</td>
<td>316</td>
<td>350</td>
<td>321</td>
<td></td>
<td>24.8</td>
</tr>
<tr>
<td>Experiment 3</td>
<td>314</td>
<td>346</td>
<td>319</td>
<td>341</td>
<td>366</td>
<td>351</td>
<td></td>
<td>20.4</td>
</tr>
<tr>
<td>Average</td>
<td>319</td>
<td>336</td>
<td>336</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The TL yield can be interpreted to result of hybridization between the carbon atoms themselves and between the carbon atoms with other atoms within the sample. Changes in the state of the electron orbitals, in particular sp² and sp³ bonds, cause the electron orbitals to change from sp² to sp³ hybridization, the latter having greater energy level. When there is sufficient energy to break this hybridization, photons will be released. In the coming subsection a pilot study of the hybridization change in the carbon atoms was conducted by the means of x-ray photoelectron spectroscopy.
6.1.4 X-ray Photoelectron Spectroscopy

To account for the change in the ratio of the \( \text{sp}^2 \) to \( \text{sp}^3 \) hybridization before and after irradiation, XPS (Beamson and Briggs 1992) analyses were performed on a ThermoFisher Scientific (East Grinstead, UK) Theta Probe spectrometer. XPS spectra were acquired using a monochromated Al K\( \alpha \) X-ray source (\( h\nu = 1486.6 \text{ eV} \)). An x-ray spot of \( \sim 400 \mu\text{m} \) radius was employed. Survey spectra were acquired employing a pass energy of 300 eV. High resolution, core level spectra for C1s and O1s were acquired with a pass energy of 50 eV. High resolution, core level spectra for Fe2p and Si2p were acquired with a pass energy of 50 eV. Quantitative surface chemical analyses were calculated from the high resolution, core level spectra following the removal of a non-linear (Shirley) background. The manufacturers Avantage software was used, incorporating the appropriate sensitivity factors also correcting for the electron energy analyser transmission function. The best fit C 1s (Kaciulis 2012c) was acquired with a centre peak binding energy for the \( \text{sp}^2 \) of 284.4 eV and with a shift of 0.4 eV. The \( \text{sp}^3 \) peak was located at binding energy 284.8 eV.

The results show an increase in the \( \text{sp}^3/\text{sp}^2 \) hybridization ratio for a sample exposed to a dose of some 0.4 Gy. As can be clearly seen in the displayed example of the peak fitted for C 1s for the super-pure SWCNTs sample, Figures 60 and 61 display the peak associated with the \( \text{sp}^3 \) and \( \text{sp}^2 \) hybridization, before irradiation (Fig. 60) and after irradiation (fig. 61). This increase in the \( \text{sp}^3 \) hybridization has been found in the pure and raw samples, with quantitative data provided in table 13 showing the increase in the \( \text{sp}^3/\text{sp}^2 \) hybridization ratio for the sample after irradiation.
Figure 60: X-ray Photoelectron Spectroscopy for the super-pure SWCNTs sample pre-irradiation, showing the separate $sp^2$ and $sp^3$ peaks.

Figure 61: X-ray Photoelectron Spectroscopy for the super-pure SWCNTs sample post-irradiation. The peak of the $sp^2$ and $sp^3$ are displayed.

From table 9, $sp^2/sp^3$ hybridization ratio pre-irradiation for the raw, pure, and super-pure SWCNT samples were 44%, 22%, and 25% respectively, increasing post-irradiation by factors of 1.8, 1.9, and 2.7 respectively.
This change in the orbitals within the carbon atoms leads to increased molecular strain, reflected in the molecular binding energy. With the sample heated to temperatures > 250 °C, sp³ hybridization can change to sp² hybridization, with energy release in the form of photons. This luminescence has been observed by the group of Chruścińska, referring to them as relaxoluminescence (Chruścińska et al., 2006). While this relaxoluminescence contributes to the thermoluminescence signal it remains apparent that greater contribution can be obtained through the addition of impurity to the samples, as clearly shown from the response of the raw SWCNT sample.

### 6.1.5 Conclusion

Three types of single-wall CNTs were formed into Buckypaper, with each of different impurity and prepared for irradiation using a $^{90}$Sr source. The samples, irradiated to different doses from 35 mGy to 1.245 Gy, show the TL yield from the single-wall CNT buckypaper samples to be generally proportional to the dose deposited in the sample. While sp³ to sp² hybridization in carbon provides a strain-related contribution to the TL signal from irradiated samples, the greater contribution to the overall TL signal can be obtained from impurity, in the present case predominantly from Fe. The general response indicates considerable potential for the raw CNT media to be used in radiotherapy dosimetric applications, although
there remains a need to develop means for control of surface roughness of the buckypaper CNTs in order to obtain more uniform response. The following chapter discusses the new technique developed using XPS to examine the change of hybridization (sp$^3$ to sp$^2$) with deposited doses and proposing this to be a new method of dosimetry.
Chapter 7

7 Novel Dosimetric Study of sp2 to sp3 Irradiation hybridisation Ratio in Free –Standing CNTs

7.1.1 Introduction

Most of the content of this chapter has been published in the journal “Radiation Physics and Chemistry”: "Abdulaziz Alanazi et al., 2016. “Novel dosimetric study of the sp² to sp³ hybridisation ratio in free–standing carbon nanotubes buckypaper", DOI: https://doi.org/10.1016/j.radphyschem.2018.02.006 , (Appendix F). The right to include the article in any thesis or dissertation has been obtained during assignment of copyright with the publisher.

As shown in section 6.1.3.3 (focusing on lower levels of detection), an apparent reproducible hypersensitivity has been observed at lower dose (by which for present purposes one understands this to mean a fraction of 1 Gy), in particular herein at about 0.2 Gy. While further investigation conducted using various CNT samples have not typically reproduced the deviation from linearity at the same low dose nevertheless, and much less frequently, the enhanced response has been obtained. This presents one with several possibilities as to influencing factors, including variation in buckypaper thickness at the effective point of measurement, also imperfect thermal contact across the sample, both exacerbated by the decreasing signal to noise ratio at low dose. In part, this suggests need for a microscopic investigation to enable better understanding of the effect of radiation dose on the CNTs. This chapter reports on use of x-ray photoelectron spectroscopy (XPS) in a surface analysis study exploring the CNTs pre and post irradiation.
7.1.2 Setup of the experiment

XPS analyses were performed using a Thermo Fisher Scientific Instruments (East Grinstead, UK) K-Alpha+ spectrometer. XPS spectra were acquired using a monochromated Al Kα X-ray source (\( h\nu = 1486.6 \text{ eV} \)). An X-ray spot of \(~400 \mu\text{m} \) radius was employed. Carbon KLL Auger peaks were acquired using a Pass Energy of 50 eV and the samples D parameter determined. Quantitative surface chemical analyses were calculated from the high resolution, core-level spectra following the removal of a non-linear (Shirley) background. The manufacturers’ Avantage software was used for analysis, incorporating the appropriate sensitivity factors and corrections for the electron energy analyser transmission function.

7.1.3 X-ray photoelectron spectroscopy (XPS)

Use of XPS enables exploration of the effects of ionising radiation on the structure of CNTs. In particular, XPS is a surface sensitive technique that provides quantitative spectroscopic measurements of elemental composition, also providing information on the chemical/electronic configurational state of the surface of the target medium. XPS spectra are acquired by exposure of the material to X-ray radiation, simultaneously measuring the kinetic energy and number of electrons that travel from the upper-most surface of the material (0 to 10 nm) via use of an electron energy analyser detector. The technique requires relatively high vacuum conditions (\(~ 1 \times 10^{-7} \text{ millibar} \)) and reference to the D parameter, the latter based on separation of the pair of maxima and minima observed in the X-ray excited carbon KLL transition (see figures 62 and 63). This has been used to estimate the hybridisation ratio (sp²/sp³), representing the change in orbital bonding with respect to dose received. Figure 64 illustrates the change in hybridisation of the carbon atom orbitals. The study has been carried out for three different purities of CNT sample, raw, pure and super-pure, each exposed to various doses.
Figure 62: Example for the first derivative for carbon KLL spectra was used to determine the distance “D” between the most positive maximum and most negative minimum for the raw sample A, in this case the D-value of 21.0 eV corresponds to the sample pre-irradiation.

Figure 63: Example for the first derivative for carbon KLL spectra was used to determine the distance “D” between the most positive maximum and most negative minimum for the raw sample A, in this case the D-value of 17.7 eV for the A sample post irradiation, exposed to a dose 5.85 Gy.
The XPS technique has been used to explore the surface structure samples of single-wall carbon nanotubes (SWCNTs) of various degrees of purity, raw, pure and super pure. In present investigations the buckypaper samples have been irradiated with beta-particle ionising radiation, use being made of a $^{90}$Sr irradiator. The rationale for this choice has been to ensure dose deposition throughout the buckypaper, the thickness of samples ranging from as low as 10 $\mu$m to as great as 100 $\mu$m (with a mean and standard deviation of 12.9 ± 1.7 $\mu$m for the most uniformly flat sample and 82.5 ± 26.4 $\mu$m for the least uniform sample, see histograms in figure 65 for sample thicknesses).
The stopping power of $^{90}$Sr/$^{90}$Y beta particles in graphite ($\rho = 1.7$ g cm$^{-3}$) is of the order of 0.3 keV μm$^{-1}$ [ESTAR (electron stopping power and range) database, (NIST 14 June 2017)], also noting that the maximum decay energy of the beta decay from $^{90}$Sr to $^{90}$Y is 0.546 MeV while that of the subsequent decay to $^{90}$Zr with a half-life of 64.1 h is 2.28 MeV. The short versus long half-life relationship between $^{90}$Y and $^{90}$Sr respectively provides the basis for secular equilibrium between the two radionuclides.

XPS analyses were performed using a Thermo Fisher Scientific Instruments K-Alpha$^+$ spectrometer (East Grinstead, UK). XPS spectra were acquired using a monochromated Al Kα X-ray source ($h\nu = 1486.6$ eV) and an x-ray spot size of radius ~ 400 μm. Carbon KLL Auger peaks were acquired using 50 eV Pass Energy and the sample D parameter was determined. With removal of a non-linear (Shirley) background, quantitative surface chemical analyses were obtained from the high resolution, core-level spectra. For analysis,
use was made of the manufacturers’ Avantage software, the latter incorporating the appropriate sensitivity factors and corrections for the electron energy analyser transmission function.

To observe dose-dependent change, the XPS technique was applied to samples pre- and post-irradiation, the source providing a dose-rate that allowed delivery of doses in the range 0.2 to 6 Gy in irradiation times of between 24 hours and 28 days. After each exposure the surface of the SWCNTs was examined through use of the XPS technique, the results giving information on the relative presence of the two carbon orbital forms, sp² and sp³, as discussed above. In so-doing, the investigation has concerned whether, as a result of deposited dose, the bonding in the surface structure changes in a proportionate and sensitive way.

7.1.4 Results

For all three qualities of CNT, the ratio sp²/sp³ shows an exponential-like dose-dependent response (see for example, Figure 66), the functional dependency differing from sample to sample, a reflection of sample variation, including level of impurity, thickness and surface roughness. Fitting by non-linear least-squares, carried out using the Python package SciPy data analysis toolkit (Jones, 2001), produced equations of the form:

\[ y = A \cdot e^{-b \cdot x} + c \quad \ldots \quad (8) \]

With \( y \) the D-value, \( x \) the dose and \( A, b, c \) constants for the particular sample and type (raw, pure or super-pure). Such exponential behaviour has also been reported by (McEnaney and Wickham 1996) in their study of degradation of nuclear graphite properties.

7.1.4.1 Raw single-wall carbon nanotubes samples

For preparation of raw sample A, use was made of 0.1 g of CNT, 80 ml of deionised (DI) water and 1 g of Triton X-100 (Tx-100) to act as surfactant, see section 5.1.3.1 for more details of the method of preparations. The curve fitting parameters were: \( [A = 3.5 \text{ eV}, b = \ldots] \)
0.38, $c = 17.5$ eV]. Each data point presented in Fig. 66 is the average of three separate measurements, the standard error in $D$ being 0.2 eV.

![Figure 66](image)

**Figure 66:** Relationship between deposited dose and change in $D$-value for raw sample A over the dose range zero to 5.85 Gy; the $D$-value shows exponential-like reduction with increase in dose.

![Figure 67](image)

**Figure 67:** Display of the percentage sp$^2$ associated with $D$ values for raw sample A. Note that use has been made of two reference values, namely diamond (100% sp$^3$) and graphite (100% sp$^3$).

The fractional change from sp$^2$ to sp$^3$, typically referred to as hybridisation, can be assessed using the plot of Fig. 67, showing the percentage sp$^2$ associated with each $D$-value. Here use has been made of the fact that graphite is 100% sp$^3$ while diamond is 100% sp$^3$, both used as reference values for the sp$^2$ and sp$^3$ ratio such that any $D$-value can then be measured accordingly. As can also be seen in fig. 67, measured $D$ values associated with given doses can be projected to calculate the sp$^2$ to sp$^3$ hybridisation. Table 14 shows the quantitative data...
for raw sample A, the change of hybridisation and D-values associated with the deposited doses being provided. The D-values for the sample at zero and at 5.85 Gy were 21.1 eV and 17.8 eV respectively.

Table 14: Quantitative results for raw sample A for different doses

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% sp²</th>
<th>% sp³</th>
<th>D-value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>84.1</td>
<td>15.9</td>
<td>21.1</td>
</tr>
<tr>
<td>0.21</td>
<td>80.1</td>
<td>19.9</td>
<td>20.8</td>
</tr>
<tr>
<td>0.63</td>
<td>74.5</td>
<td>25.5</td>
<td>20.3</td>
</tr>
<tr>
<td>1.05</td>
<td>68.9</td>
<td>31.1</td>
<td>19.8</td>
</tr>
<tr>
<td>3.50</td>
<td>55.7</td>
<td>44.3</td>
<td>18.6</td>
</tr>
<tr>
<td>5.85</td>
<td>46.8</td>
<td>53.2</td>
<td>17.8</td>
</tr>
</tbody>
</table>

Fig. 68 displays the D-value (D parameter) vs dose for raw sample D, being of the same purity category as that of sample A but differing in regard to the preparation process, with a greater quantity of SWCNTs being used; 0.14 g of CNTs, with 100 ml of DI-water and 1 g of Tx-100. The resulting equation fitting parameters were: \[A = 3.1 \text{ eV}, b = 0.53, c = 18.1 \text{ eV}\], with again each data point representing the average of three measurements and a standard error in D of 0.2 eV. The decrease in the value of D with dose is similar to that seen in raw sample A, indicative of a technique robust against such concentration variation. Fig. 69 exhibits the dose-dependent measured D values for raw sample D as a function of sp².
Figure 68: Dose dependent D-values for raw sample D, made using 0.14 g of CNTs, 100 ml of DI-water and 1 g of Tx-100.

Figure 69: Percentage sp² associated with dose-dependent D values for raw sample D.

Table 15 shows the quantitative data for raw sample D; at zero and at 5.85 Gy the D-values were 21.1- and 18.3 eV respectively.
Table 15: Quantitative results for raw sample D for different doses

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of sp² hybridisation</th>
<th>% of sp³ hybridisation</th>
<th>D-value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>83.7</td>
<td>16.3</td>
<td>21.1</td>
</tr>
<tr>
<td>0.21</td>
<td>82.8</td>
<td>17.2</td>
<td>21.0</td>
</tr>
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<td>75.1</td>
<td>24.9</td>
<td>20.3</td>
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<td>1.05</td>
<td>67.4</td>
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<td>19.6</td>
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<td>3.50</td>
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<td>43.2</td>
<td>18.7</td>
</tr>
<tr>
<td>5.85</td>
<td>52.5</td>
<td>47.5</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Fig. 71 shows the D-value vs dose for raw sample H, formed using 0.12 g of CNTs, 100 ml of DI-water, 1 g of Tx-100, with associated fitting parameters \[ A = 3.5 \text{ eV}, b = 0.59, c = 17.6 \text{ eV} \]. Again, each data point is the average of three measurements, the standard error again being 0.2 eV. The fitting parameter values lie between those of A and D as expected of a medium of intermediate concentration of SWCNTs. Fig. 72 displays the percentage sp² associated with each dose dependent D-value.

Figure 70: Dose dependent D-values for raw sample H, made using 0.12 g of CNTs, with 100 ml of DI-water and 1 g of Tx-100.
Figure 71: The percentage of sp² associated with D values for raw sample H.

Table 16 Quantitative data for raw sample H, with D-values at 0 and 5.85 Gy of 21.1- and 17.7 eV respectively.

Table 16: Quantitative results for raw sample H for different doses

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of sp² hybridisation</th>
<th>% of sp³ hybridisation</th>
<th>D-value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>84.1</td>
<td>15.9</td>
<td>21.1</td>
</tr>
<tr>
<td>0.21</td>
<td>78.4</td>
<td>21.6</td>
<td>20.6</td>
</tr>
<tr>
<td>0.63</td>
<td>71.6</td>
<td>28.4</td>
<td>20.0</td>
</tr>
<tr>
<td>1.05</td>
<td>64.8</td>
<td>35.2</td>
<td>19.4</td>
</tr>
<tr>
<td>3.50</td>
<td>50.0</td>
<td>50.0</td>
<td>18.1</td>
</tr>
<tr>
<td>5.85</td>
<td>45.5</td>
<td>54.5</td>
<td>17.7</td>
</tr>
</tbody>
</table>
7.1.4.2 Pure single-wall carbon nanotubes

Fig. 73 shows the D-value vs dose for pure sample B1, of comparative purity compared to that of pure and super-pure using the Energy Dispersive X-ray (EDX) facility of a Scanning Electron Microscope as in table 17 below.

Table 17: EDX analysis of raw, pure and super-pure SWCNT, using an SEM at 15kV and 50 × mag.

<table>
<thead>
<tr>
<th>Element/Line</th>
<th>Raw samples</th>
<th>Pure samples</th>
<th>Super-Pure samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>68.2 ± 0.4</td>
<td>72.1 ± 0.4</td>
<td>74.1 ± 0.4</td>
</tr>
<tr>
<td>O K</td>
<td>13.5 ± 0.3</td>
<td>15.5 ± 0.2</td>
<td>15.5 ± 0.3</td>
</tr>
<tr>
<td>Al K</td>
<td>0.16 ± 0.10</td>
<td>0.15 ± 0.10</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>Si K</td>
<td>0.31 ± 0.10</td>
<td>0.18 ± 0.10</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>Ti K</td>
<td>0.59 ± 0.10</td>
<td>0.31 ± 0.10</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td>Fe K</td>
<td>17.2 ± 0.3</td>
<td>11.7 ± 0.3</td>
<td>7.6 ± 0.2</td>
</tr>
</tbody>
</table>

For preparation of pure samples B1 use was made of 0.05 g of CNTs, 100 ml of DI-water and 0.5 g of Tx-100. With this change in preparation the resulting equation fitting parameters were: [A = 6.3 eV, b = 0.20, c = 14.9 eV], with each data point the average of three measurements and with standard error 0.2 eV. The D-value decreases with dose in similar fashion to that previously described but with fitting parameter A differing by approaching a factor of 2 compared to the raw samples, a matter that will be discussed in the discussion section. The situation is that larger mean D values are obtained at the lower dose point values.
compared to the raw samples, indicative of reduced sensitivity towards change from graphite at such doses. As with TL yields the indication is that the raw SWCNT formulations are seen to be more dose sensitive than the pure or super-pure as will be seen below.

Figure 72: D-value vs dose for pure sample B1, prepared from 0.05 g CNTs, 100 ml DI-water and 0.5 g Tx-100. Fig. 74 Measured D values associated with given doses and sp² and sp³ hybridisation for the pure sample B1.

Table 18 shows the quantitative data for pure sample B1 with dose-dependent D-values and change of hybridisation. The D-values for the sample at zero and at 5.85 Gy were 21.2 eV and 16.8 eV respectively.
Table 18: Quantitative results for pure sample B1 for different doses

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of sp² hybridisation</th>
<th>% of sp³ hybridisation</th>
<th>D-value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>85.2</td>
<td>14.8</td>
<td>21.2</td>
</tr>
<tr>
<td>0.21</td>
<td>81.8</td>
<td>18.2</td>
<td>20.9</td>
</tr>
<tr>
<td>0.63</td>
<td>77.3</td>
<td>22.7</td>
<td>20.5</td>
</tr>
<tr>
<td>1.05</td>
<td>71.6</td>
<td>28.4</td>
<td>20.0</td>
</tr>
<tr>
<td>3.50</td>
<td>48.9</td>
<td>51.1</td>
<td>18.0</td>
</tr>
<tr>
<td>5.85</td>
<td>35.2</td>
<td>64.8</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Fig. 75 shows the D-value vs dose for pure sample B2, the preparation process of this being identical to B1 having being cut from the same original buckypaper sample. The resulting equation fitting parameters were: \([A = 5.6 \text{ eV}, b = 0.20, c = 15.2 \text{ eV}]\). As before, each data point is the average of three measurements and the standard error is 0.2 eV for all samples. While the familiar shape of B1 is re-obtained, the fitting points to a lesser sensitivity at low dose, with a value \(A\) of 1.61 eV cf 6.28 eV for sample B1. What is apparent is that small changes in the D-value at low doses appear to be associated with a large swing in dose sensitivity, a behaviour that is almost certainly associated with sample inhomogeneity.
Figure 74: D-value vs dose for pure sample B2, prepared using 0.05 g of CNTs, 100 ml DI-water and 0.5 g of Tx-100. Fig. 76 measured D values associated with given doses projected to calculate the sp$^2$ and sp$^3$ hybridisation for the pure sample B2.

![Graph](image)

Figure 75: The percentages of sp$^2$ associated with the D values for pure sample B2.

Table 19 shows the quantitative data for pure sample B2. The D-values at zero and at 5.85 Gy were 20.9 eV and 17.0 eV respectively.
Table 19: Quantitative results for pure sample B2 for different doses

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of sp² hybridisation</th>
<th>% of sp³ hybridisation</th>
<th>D-value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>81.8</td>
<td>18.2</td>
<td>20.9</td>
</tr>
<tr>
<td>0.21</td>
<td>77.3</td>
<td>22.7</td>
<td>20.5</td>
</tr>
<tr>
<td>0.63</td>
<td>73.9</td>
<td>26.1</td>
<td>20.2</td>
</tr>
<tr>
<td>1.05</td>
<td>69.3</td>
<td>30.7</td>
<td>19.8</td>
</tr>
<tr>
<td>3.50</td>
<td>50.0</td>
<td>50.0</td>
<td>18.1</td>
</tr>
<tr>
<td>5.85</td>
<td>37.5</td>
<td>62.5</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Fig. 77 shows the D-value vs dose for pure sample F, a sample of similar impurity to that of the B samples as in table 17. For its preparation the following quantities were used: 0.03 g of CNTs, 50 ml DI-water and 0.3 g Tx-100. The resulting equation fitting parameters were: \( A = 20.8 \text{ eV}, b = 0.03, c = 0.0 \text{ eV} \). Each data point is the average of three measurements and the standard error is 0.2 eV for all samples. The fitted curve shows a greater degree of linearity compared to pure samples B1 and B2, with the fitting of the curve restricted to just the first two terms of the exponential expansion. Fig. 78 displays the measured D values associated with given doses together with the sp² to sp³ hybridisation.
Figure 76: D-value vs dose for pure sample F, the D-value decreasing in an approximate linear fashion with dose.

Figure 77: The percentages of sp\(^2\) associated with the D values for pure sample F.

Table 20 shows the quantitative data for pure sample F. The change of hybridisation and D-values associated with the deposited doses are shown. The D-values for the sample at zero and at 5.85 Gy were 20.7 eV and 17.8 eV respectively.
Table 20: Quantitative results for pure sample F for different doses

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of sp(^2) hybridisation</th>
<th>% of sp(^3) hybridisation</th>
<th>D-value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>79.5</td>
<td>20.5</td>
<td>20.7</td>
</tr>
<tr>
<td>0.21</td>
<td>78.4</td>
<td>21.6</td>
<td>20.6</td>
</tr>
<tr>
<td>0.63</td>
<td>76.1</td>
<td>23.9</td>
<td>20.4</td>
</tr>
<tr>
<td>1.05</td>
<td>74.4</td>
<td>25.6</td>
<td>20.3</td>
</tr>
<tr>
<td>3.50</td>
<td>58.5</td>
<td>41.5</td>
<td>18.9</td>
</tr>
<tr>
<td>5.85</td>
<td>46.8</td>
<td>53.2</td>
<td>17.8</td>
</tr>
</tbody>
</table>

7.1.4.3 Super-pure single-wall carbon nanotubes samples

Fig. 79 shows the D-value vs dose for super-pure sample G1. Sample preparation was similar to that for pure sample F, using: 0.03 g of CNTs, 50 ml DI-water and 0.3 g of Tx-100. The resulting equation fitting parameters were: \([A = 18.4 \text{ eV}, b = 0.02, c = 2.04 \text{ eV}]\), again with each data point being the average of three measurements and standard error of 0.2 eV. The fitted curve for the G1 sample shows a greater degree of linearity compared to the raw samples and pure samples B1 and B2, with a similar trend to that observed for the pure sample F. Fig. 80 displays the measured D values associated with given doses together with the sp\(^2\) to sp\(^3\) hybridisation.
Figure 78: D-value vs dose for super-pure sample G1, the D-value decreasing in a closely linear fashion with dose.

Figure 79: The percentage sp$^2$ associated with the D values for super-pure sample G1.

Table 21 shows the quantitative data for super-pure sample G1. The D-values for the sample at zero and at 5.85 Gy were 20.5 eV and 18.9 eV respectively.
Table 21: Quantitative results for super-pure sample G1 for different doses

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of sp² hybridisation</th>
<th>% of sp³ hybridisation</th>
<th>D-value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>77.3</td>
<td>22.7</td>
<td>20.5</td>
</tr>
<tr>
<td>0.21</td>
<td>76.1</td>
<td>23.9</td>
<td>20.4</td>
</tr>
<tr>
<td>0.63</td>
<td>75.0</td>
<td>25.0</td>
<td>20.3</td>
</tr>
<tr>
<td>1.05</td>
<td>73.9</td>
<td>26.1</td>
<td>20.2</td>
</tr>
<tr>
<td>3.50</td>
<td>65.9</td>
<td>34.1</td>
<td>19.5</td>
</tr>
<tr>
<td>5.85</td>
<td>59.1</td>
<td>40.9</td>
<td>18.9</td>
</tr>
</tbody>
</table>

Fig. 81 shows the D-value vs dose for super-pure sample G2. For preparation of the super-pure sample G1 similar quantities to that for pure sample F were used, as follows: 0.03 g of CNTs, 50 ml DI-water and 0.3 g Tx-100. The resulting equation fitting parameters were: \([A = 4.1 \text{ eV}, b = 0.14, c = 16.3 \text{ eV}]\). Each data point presented is the average of three measurements and the standard error is 0.2 eV. The fitted curve for the G2 sample shows similar curvature to that of pure samples B1 and B2 and the raw samples. Fig. 82 displays the measured D values associated with given doses together with the sp² to sp³ hybridisation.

Figure 80: D-value vs dose for super-pure sample G2.
Figure 81: The percentage sp\(^2\) associated with the D values for super-pure sample G2.

Table 22 shows the quantitative data for super-pure sample G2. The D-values for the sample at zero and at 5.85 Gy were 20.3 eV and 18.1 eV respectively.

Table 9: Quantitative results for super-pure sample G2 for different doses

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of sp(^2) hybridisation</th>
<th>% of sp(^3) hybridisation</th>
<th>D-value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>74.7</td>
<td>25.3</td>
<td>20.3</td>
</tr>
<tr>
<td>0.21</td>
<td>73.6</td>
<td>26.4</td>
<td>20.2</td>
</tr>
<tr>
<td>0.63</td>
<td>70.5</td>
<td>29.5</td>
<td>19.9</td>
</tr>
<tr>
<td>1.05</td>
<td>68.2</td>
<td>31.8</td>
<td>19.7</td>
</tr>
<tr>
<td>3.50</td>
<td>56.8</td>
<td>43.2</td>
<td>18.7</td>
</tr>
<tr>
<td>5.85</td>
<td>50.0</td>
<td>50.0</td>
<td>18.1</td>
</tr>
</tbody>
</table>

### 7.1.5 Discussion:

By projecting the D-value in association with dose, a process exemplified in the graph of fig. 66 and graphs thereafter, one can observe a regularity of change in the percentages of sp\(^2\) and
sp\(^3\). In particular, the sp\(^2\) hybridisation, expressed as the ratio \(\text{sp}^2/\text{sp}^3\), reduces for increasing radiation dose, a behaviour that has been observed for all of the samples investigated herein, be they raw, pure or super-pure. Similar such behaviour in terms of the reduction of sp\(^2\) has previously been observed in the study of (Bardi et al., 2017b), for samples of SWCNT exposed to x-ray radiation, at doses of 20 cGy and 45 cGy, for a technique based on measurement of accumulated charge. The Bardi study investigated the change in the structure of the SWCNT in powder form, investigations focusing both on the change of structure and the effect on raw SWCNTs as a potential device used in active dosimetry, such as that of the ion chamber (Bardi et al., 2017b). Apparent from present analysis is that the reduction in sp\(^2\) varies from sample-type to sample-type (raw, pure and super pure) being attributable to the level of impurity, thickness and roughness of the surface, affected as these are by the process of sample preparation.

Figure 66 has depicted the relationship between the deposited dose and the change in the D-value (sp\(^2\)/sp\(^3\)) for raw sample A. Over the dose range from zero up to 5.85 Gy, the D-value shows exponential reduction with increasing deposited dose. The change of sp\(^2\) to sp\(^3\) has subsequently been evaluated using the plot of figure 67, illustrating the percentages of sp\(^2\) associated with particular D-values, also making use of the fact that graphite is 100% sp\(^2\) while diamond is 100% sp\(^3\). In accord with this, test has been made of whether any dose dependent D-value can be measured from the linear fit between the diamond and graphite, a matter that has been demonstrated not only for all of the raw samples, but also for all of the other sample types tested herein, as further summarised below. From the results for the raw samples it has further been shown that there is a standard exponential reduction in D-value with deposited dose. The change in D-value can be measured with deposited dose, indicative of the degree of sp\(^2\) to sp\(^3\) hybridisation. For the raw samples the D-values varied from 21.1 eV to 17.7 eV. At zero dose the carbon nanotube walls contain carbon bonding of some 84%
sp² and 16% sp³ hybridisation. Depositing 0.21 Gy of beta particle dose is seen to lead to a reduction of sp² from 84% to ~80% and enhancement of sp³ to 20%.

When comparing the raw sample dose-dependent D-value curves against those for the pure and super-pure samples, with increasing purity it can be seen that the curves trend towards a more linear dependency. This phenomenon, attributed to the impurities in the raw samples, accords with the EDX analysis (see 6.1.3.2), showing that the raw samples have greater amounts of iron in them than the pure and super-pure, at 17.2%, 11.7% and 7.6% respectively.

For graphite, the lowest energy required for carbon atom displacement, on the c-axis direction, was found by (Banhart et al., 1997) to be 15-20 eV. Another study suggests the threshold energy required for carbon atom displacement in graphite 15-17 eV (Krasheninnikov and Nordlund 2004). Yet another threshold value for carbon atom displacement for SWCNT was reported to be 16.9 eV (Cress et al., 2010b). Simmons reported the value to be 25 eV in neutron damaged graphite, cited in (Marsden 1996). Conversely, for diamond, another form of carbon, the displacement threshold has been reported to be 30-48 eV (Bourgoin and Massarani 1976) (Koike et al., 1992). Thus said, graphite is formed from two different chemical bonds on each plane, a van der Waals bonds that links the basal planes and covalent bonds that work within the planes; Banhart has subsequently pointed out that SWCNTs are the smallest graphite-based structure, their specific geometry allowing them to be unaffected by van der Waals forces (Banhart 1999). From these studies in graphite it has been estimated by the group of Banhart that the threshold energy required to displace a carbon atom in the walls of the SWCNTs is in the range 15-20 eV, estimated assuming the lack of van der Waals bonds between the graphite layers in the SWCNTs (see fig. 83). Such atomic displacement can be expected when the beta
particles emitted from the $^{90}\text{Sr}$ source (maximum energy 0.546 and 2.28 MeV respectively for $^{90}\text{Sr}$ and $^{90}\text{Y}$) interact with the SWCNT samples.

**Figure 82:** diagram illustrates the covalent and Van der Waals bonds in the graphite structure.

In regard to the results for the pure samples it can be seen that again there is an exponential reduction in the D-values with deposited dose, the D-values change varying progressively from 21.2 eV to 16.8. For these samples, as a function of dose deposited in the sample, sp$^2$ hybridisation is again observed to alter (with associated proportionate increase in sp$^3$). Thus for example, while at zero dose the carbon nanotubes walls contain 85.2% sp$^2$ (14.8% of sp$^3$), dose deposition of 0.21 Gy leads to reduction of sp$^2$ from 85.2% to ~ 81.8% and enhancement of sp$^3$ to ~ 20.9%.

As commented upon before, comparing the pure sample dose-dependent D-value curves against those for the raw samples, with increasing purity it can be seen that the curves trend towards a more linear dependency, the fitted curves now showing a high degree of linearity when comparing to for instance the samples B1 and B2. In the associated regard to the carbon concentration in the raw and pure samples, these were found to be 68.2 % and 72.1 % respectively.

In regard to the results of the super-pure samples, it can be seen that the super-pure samples can again be depicted in terms of an exponential reduction, limited in number of terms, D-values continuing to be associated with progressive change with increase in deposited dose.
The D-values for these samples have been observed to range from 20.3 to 18.1 eV. At zero dose (as that for an annealed sample) the D-value is some 20.3 eV, corresponding to 74.7% sp² and 25.3% sp³. The dose-dependent response of the super-pure samples is similar to that for the pure samples (the D-value decreasing with dose and for the fitted curve for the super-pure sample G2 this shows similar linearity with that to the pure samples B1 & B2. The more limited curvature than that seen for the raw samples can be neglected in a linear approximation, given consideration of the errors associated with the measurements.

Table 22: The fitting parameters were produced by the least square fitting for variables A, b and c

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>b</th>
<th>c</th>
<th>A + c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>3.5 eV</td>
<td>0.38</td>
<td>17.5 eV</td>
<td>21 eV</td>
</tr>
<tr>
<td>Raw</td>
<td>3.5 eV</td>
<td>0.59</td>
<td>17.6 eV</td>
<td>21.1 eV</td>
</tr>
<tr>
<td>Raw</td>
<td>3.1 eV</td>
<td>0.53</td>
<td>18.1 eV</td>
<td>21.2 eV</td>
</tr>
<tr>
<td>Pure</td>
<td>6.3 eV</td>
<td>0.2</td>
<td>14.9 eV</td>
<td>21.2 eV</td>
</tr>
<tr>
<td>Pure</td>
<td>5.6 eV</td>
<td>0.2</td>
<td>15.2 eV</td>
<td>20.8 eV</td>
</tr>
<tr>
<td>Pure</td>
<td>20.8 eV</td>
<td>0.03</td>
<td>0 eV</td>
<td>20.8 eV</td>
</tr>
<tr>
<td>Super-pure</td>
<td>18.4 eV</td>
<td>0.02</td>
<td>2.04 eV</td>
<td>20.44 eV</td>
</tr>
<tr>
<td>Super-pure</td>
<td>4.1 eV</td>
<td>0.14</td>
<td>16.3 eV</td>
<td>20.4 eV</td>
</tr>
</tbody>
</table>

To sum up, the XPS study discussed herein show results with a clear relationship between deposited dose and enhancement of sp³ hybridisation. The D-values decrease (hence sp³ hybridisation increase) with dose deposited in the samples. It is further clear from the above discussion and also with reference to the summary results of Table 22, showing the fitting parameter values for the various samples A (raw) to G (super-pure), that relation (8) provides for a threshold energy, the sum of each of the energy values leading to a mean value of (20.9 ± 0.3) eV. This can be related to the estimate of the group of Banhart (1997; 1999) for the threshold energy in the range of 15-20 eV that is required to displace a carbon atom in the walls of the SWCNTs. These results suggest the use of XPS to provide for a new technique for radiation dosimetry. However, as it is a surface analysis technique, this would seem to
limit the application to relatively low penetration radiation, potentially including alpha (for ultra-thin CNTs) and beta particles and low-energy photons. Thus said, the limitation points to considerable potential for the use of this novel soft tissue equivalent technique in estimating skin dose in personal dosimetry (noting that the previous work of Bardi (2017) has shown measurable effects at mGy levels) and when electrons or ions are used to treat superficial tumours.
Chapter 8

8 Conclusion

In its practice, radiotherapy, one of the major methods of cancer treatment, targets the cancerous cells with deposition of high/low-energy ionization radiation whilst seeking to minimize dose to the surrounding healthy tissue. Numerous methods and techniques have been introduced to control the dose distribution and minimize the dose to the surrounding healthy tissue, including IMRT (Intensity Modulated Radiation Therapy), IGRT (Image Guided Radiation Therapy), and heavy ion radiation. Generally, all radiotherapy treatment techniques are associated with and dependent on the performance of the radiation dosimetry system. In other words, dose delivery requires the support of a precise and accurate means of radiation dosimetry. For example, the small radiation beam produced by the IMRT technique requires a dosimetry system that is small in size (submillimetre) and of large dynamic range in order to verify the precision and accuracy of the delivered dose to the target. There has been much in the way of research to develop radiation dosimetry systems that meets Bragg-Gray cavity theory requirements, while less effort has been paid for example in providing for a bone-tissue equivalent dosimetric medium that satisfies the theory. This research have sought to provide for both soft and calciferous tissues, developing novel passive dosimetry materials that meet the challenge of providing soft tissue and bone equivalent materials. The novelty within current research lies in studies on proton dosimetry and neutron dosimetry (using doped silica materials for TL investigations) and electron dosimetry (using carbon nanotubes for TL and XPS-based investigations). Optical fibres with a diameter of 126 µm have been used to determine the dose for proton and neutrons at therapeutic energies, while SWCNTs (single-wall carbon nanotubes) in the form of buckypaper (with thickness ranging from ~ 10- to ~ 100 µm) have been developed along with a new technique, that of XPS, for
dosimetry. It must be noted that this method has not been previously used and the study herein has therefore sought to characterise the various aspects needed in development of the methodology.

With regards to protons, two situations were examined in the use of commercially available Ge-doped silica fibres. The first situation was a modulated proton beam, wherein the depth-dose profile was measured for a 62 MeV proton beam at high spatial resolution (0.1mm). Such resolution for point dose measurement is unsurpassed, as recorded in the various sources of literature, underlining the potential importance of the use of this proposed method. For an unmodulated beam, a similar methodology to that for the modulated beam was applied and showed similar capability for this material in providing for the high spatial resolution demands of a modern radiation therapy beam. This application could also be adopted to help determine the depth-dose profile for other types of radiation therapy beams. Moreover, for heavy charged-particles previous literature has drawn attention to the commonly shared issue of there being a quenching effect that results from the increasing ionization density of the radiation field in the Bragg peak region. Judging from the obtained results for the silica fibres it has been evident that single exposures to a continuous collection of fibres aligned in a row can provide data profiles that accord well with expectation, saving a considerable amount of time when compared to point-by-point measurements of a parallel plate ionization chamber. In addition, the irradiated fibres with variations of up to 10% provide analogous performance to well established methods such as that of the LiF:Mg, Ti (TLD-100) phosphor-based medium. To sum up, one can conclude that the now established optical fibre method gives access to very high spatial resolution measurements, also offering high dynamic range, and is highly competitive to gold-standard methods such as the parallel plate ionization chambers.
Over and above rapid changes in dose-rate as above, previous Surrey scholars have also emphasized the significance of small size detectors with regard to challenging radiation field dimensions, this also being realised through investigations illustrating the effectiveness of glass (silica) bead dosimeters for applications in radiation dosimetry. Extending beyond this, a similar study to that carried out using protons was adopted to explore the depth-dose distributions for an Americium-Beryllium (²⁴¹Am-Be) neutron source placed in a water tank. The silica beads used have a diameter of 1 mm, offering the highest spatial resolution neutron detection method to date. The results achieved through use of such high-density spatially-resolved detection of neutrons point to general agreement in shape with that obtained using Monte Carlo simulation. However, going beyond this, the exceptional spatial resolution has also discerned fine resolution spikes in intensity that have previously not been documented in the literature, a matter that clearly invites further investigation.

The afore-mentioned work concentrated on silica-based media (optical fibres and glass beads) modeling effective atomic numbers closely equivalent to human tissue, in particular calcified tissues. The following discussion summarizes findings on the effects of electrons (beta particles) on the soft tissue equivalent material provided by single-wall carbon nanotubes (SWCNTs) in the form of free-standing buckypaper (with thicknesses down to that of human cells ~10 µm). Different purity samples of single-wall carbon nanotubes, raw, pure and super pure were exposed to a strontium-90 source, allowing delivery of various doses to the samples, as follows: 0.21, 0.63, 1.05, 3.5 and 5.85 Gy. The first method explored was the conventional thermoluminescence technique, the SWCNT buckypaper showing a TL response that is proportional to the deposited doses. This line of investigation then progressed to that of investigation of the effect of radiation (in this case beta particles) on the structure of
SWCNTs. The X-ray photoelectron spectroscopy technique (XPS) was used to study the bonding orbitals in the lattice between the atoms of the carbon nanotubes.

In regard to the above, the XPS technique was applied to the various samples before and post-irradiation, it becoming evident that this approach provides an alternative technique to that of TL, representing a novel dosimetric method, with the change in carbon orbital bonding from sp$^2$ to sp$^3$ (referred to as hybridization) investigated by the XPS. The change of the hybridization in the orbitals was found to increase exponentially with dose, whereby sp$^2$ decreases and sp$^3$ increases. Further apparent has been that reduction in sp$^2$ varies from sample-type to sample-type, being attributable to the level of impurity (raw, pure and super-pure), thickness and roughness of the surface, all being factors that affect the sample as these are introduced in the process of preparation. The XPS study has shown a clear relationship to exist between the projected dose and enhancement of sp$^3$ orbital hybridisation. The findings concern a surface analysis technique, the investigations currently being limited to low penetration radiations, beta particles specifically, although it is thought to also be applicable to alpha particles, heavy ions and low-energy photons. Thus said, the limitation indicates substantial potential for the use of this innovative soft tissue equivalent technique in providing accurate estimates for skin dose in personal dosimetry and when electrons/ions are used to treat superficial tumours.

### 8.1 Future Work

The work performed in this thesis has the potential to be enhanced through further study of the following issues:

1. The buckypaper samples used in present study were developed at the University of Surrey using different impurities of carbon nanotubes in the form of powder, the
methods of preparation being altered to obtain different thicknesses for different levels of impurity (raw, pure and super-pure CNTs). The methods of preparation resulted in non-homogeneous samples and it might be expected that having homogeneous samples would improve the quality of results. While this might be solved by following a number of techniques that have been suggested in the literature, the purchase of commercially available samples could be more effective, not least saving money and time. Additionally, the purchase of samples from reputable producers and suppliers is surely important in allowing other researchers to obtain the same materials, semiconducting carbon nanotubes and metallic like SWCNTs being certainly available in the market, allowing conduct of similar studies and examination of the performance of different impurities. The thickness of the buckypaper samples needs to be considered when purchasing these semiconductors or metallic like samples. It might be useful to obtain samples with thickness in the micrometer range.

2. In highly preliminary work, carried out by the present investigator, a shift from sp² to sp³ in orbital hybridization was witnessed in study of car-engine polymer coated wires. The wires were examined pre and post irradiation through use of the XPS technique. Thus, further investigations are needed to verify the change in hybridizations of the orbitals in such materials.

3. During a study of the neutron depth-dose distribution using glass beads, samples of SWCNTs buckypaper were also irradiated and a TL signal was observed. Detailed investigations should now be performed, also examining the structural effects on SWCNTs resulting from neutron irradiation. It may be noted that the effect of neutrons on graphite in power reactor systems suggest that such investigation using the XPS dosimetry technique could be important. Here it is worth mentioning that the degradation of a number of graphite properties has been noted to change
exponentially, being in line with that observed in regard to the shift of $sp^2$ to $sp^3$ in this research.

4. Research is currently in progress to understand radiation damage on carbon nanotubes using Raman microspectrometry technique, a facility that is widely available. While it is not suggested that the technique is preferable to study of $sp^2$ to $sp^3$ hybridization, however it could give other structural information which could enhance the finding of the XPS technique and help explain the cause of these shifts in the orbital hybridization.

In the above, the research has somewhat widened the possible applications, the observed exponential change in SWCNTs in regard to bonding also having been described in the degradation of graphite properties that result from neutrons emitted by nuclear reactors. It is believed that this points to potentially exciting prospects for XPS dosimetry study of graphite moderators in power reactor systems. Also of pertinence is XPS dosimetry study of car-engine polymer coated wires that are cross-linked by high dose electron irradiation (~ a few hundred kGy) in order to withstand the elevated temperatures that such wiring will be exposed to over periods of many years. In both of these industrial applications, the medium under irradiation would become its own dosimeter, in the case of the polymer coatings leading to inherent self-validation of dose, an ultimate target in quality assurance terms. Finally, one other extension to present studies would be examination of spectral changes in use of Raman microspectrometry, and with this possibility of using a technique that is currently more widely available than access to XPS systems. In the wider terms, such investigations might also be expected to have important biomedical consequences, being matters that have yet to be understood.
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10 Appendix
Developments in production of silica-based thermoluminescence dosimeters

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HIGHLIGHTS

- Review of developments in doped silica dosimetry.
- Overview of fabrication and irradiation dependent defects.
- Application to proton radiotherapy dosimetry.
- Applications in environmental radioactivity.

ABSTRACT

This work addresses purpose-made thermoluminescence dosimeters (TLD) based on doped silica fibres and sol–gel nanoparticles, produced via Modified Chemical Vapour Deposition (MCVD) and wet chemistry techniques respectively. These seek to improve upon the versatility offered by conventional phosphor-based TLD forms such as that of doped LiF. Fabrication and irradiation-dependent factors are seen to produce defects of differing origin, influencing the luminescence of the media. In coming to a close, we illustrate the utility of Ge-doped silica media for ionizing radiation dosimetry, first showing results from gamma-irradiated Ag-decorated nanoparticles, in the particular instance pointing to an extended dynamic range of dose. For the fibres, at radiotherapy dose levels, we show high spatial resolution (0.1 mm) depth-dose results for proton irradiations. For novel microstructured fibres (photonic crystal fibres, PCFs) we show first results from a study of undisturbed and technologically modified naturally occurring radioactivity environments, measuring doses of some 10 s of μGy over a period of several months.

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1. Introduction

Over the past three years we have been exploring the association between design and performance of silica-based media, our interest being in the utility of the latter in sensing ionizing radiation and in radiation dosimetry. Our efforts stem from earlier adventitious use of commercially available Ge-doped single mode telecommunication fibres (SMF) in such applications, the design of these being entirely unrelated to the needs to which the fibres were put. The SMFs, as well as other telecommunication fibres such as multi-mode fibres (MMF) and variants of these including Bragg gratings, are fabricated from low-defect silica, as an example, very pure SiO\textsubscript{2} in the form of Suprasil F300, a product of Heraeus (Hanau, Germany). Doped fibre fabrication starts from a

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hollow capillary (of a few cm diameter), doped using the Modified Chemical Vapour Deposition (MCVD) process. This process requires the introduction of gases (typically germanium tetra-chloride, GeCl₄, and silicon tetrachloride, SiCl₄) into a rotating hollow silica capillary, at the same time applying highly elevated temperatures, typically between 1800- and 2100 °C, to allow a deformable material and the deposition on the inner walls of SiO₂ and Ge₂O₃. The preform resulting from this MCVD process can then be pulled into fine diameter (~0.1 mm) cylindrical fibres, a form typically used in telecommunications, again using elevated temperatures to soften the silica. The pulling requires use of a rig typically referred to as a pulling tower. For telecommunications the extrinsic dopant creates a change in refractive index between the boundary of the doped silica core and the silica cladding, light within a particular band of wavelengths suffering total internal refraction, transporting the light forward with very low losses from as low as 0.2 dB km⁻¹ to perhaps ~few dB km⁻¹.

The presence of defects extrinsically introduced into such silica-based insulator media provides for the trapping of electrons that have been excited by incident radiation, with these then being stored as a luminescence signal pending stimulated de-excitation. Storage of the trapped electrons in such media is typically good, providing integration of the irradiation-mediated signal, strongly preserved over a period many orders of magnitude greater than the duration of the exposure. The situation is imperfect, a fraction of the trapped electrons spontaneously relaxing, due to sources of ambient energy, a loss referred to as fading. The fractional loss of TL signal depends on the depth of traps, deep traps (~few eV) suffering markedly less fading than more superficial traps. Practical systems of readout through stimulated de-trapping can either function through the application of heat, producing thermo-luminescence (TL), or exposure to a controlled source of light, producing optically stimulated luminescence, the emission spectrum that reflects the trapping levels being picked up by a photomultiplier tube. Such systems provide a passive form of detection, contrast with active devices such as diodes or ionisation chambers.

Present interest is in TL, a less favourable practical feature of such systems is the lack of on-line monitoring capability. For a well-behaved TL medium, one that can be used for radiation dosimetry, it is desirable for the system to respond sensitively to the radiation levels of interest and to provide TL yield linear with radiation dose. The range over which this occurs is referred to as the dynamic range. A highly sensitive medium points to lower limits of detection, the tendency being for the available defects to become occupied at relatively low doses. Indeed, we are currently pursuing doses down to a small fraction of a mGy as will be shown later. Conversely, the benefit of a less sensitive dosimeter for a particular source of radiation is that it can be used beyond the upper limit of linearity of the more sensitive dosimeters. As such, the question as to whether a dosimeter is considered good or poor is ultimately linked to the level of dose and range of dose that one wishes to detect, the arbiter of utility being whether it can be used as a monitor of environmental radioactivity, accumulating annual dosages of as low as a few mGy, in dosimetry of synchrotron radiation, or exposure to a controlled source of light, producing optically stimulated luminescence, the emission spectrum that reflects the trapping levels being picked up by a photomultiplier tube. Such systems provide a passive form of detection, contrast with active devices such as diodes or ionisation chambers.

In regard to (vi), with fibres popularly cut to 5 mm lengths for ease of handling, to-date the fibres have been read-out with their long dimension in contact with the planchet (the heating plate of the TL reader), not least allowing good thermal contact between the heating plate and TL medium. With TL light transporting preferentially along the fibre, normal to the photomultiplier tube, this sub-optimal readout situation has nevertheless been shown to offer excellent capability for radiotherapy applications (with doses from a fraction of a Gy to 10 s of Gy and beyond). A further issue in design of silica fibres is that the MCVD and fibre pulling facilities are expensive to establish and operate. Thus said, access to such facilities provides for novel microstructured assemblies that offer particularly high levels of sensitivity, a matter which we are presently testing at low (environmental) levels of dose, as will be discussed towards the end of this article.

In what is to follow we review the MCVD-based fabrication method and a wet-chemistry sol–gel nanoparticle approach that offers lower costs of fabrication, summarizing what we know from the characterization of defects and the radiation performance parameters. We will then provide example situations, our choices being limited by the length restrictions placed upon the invited article.

2. Silica production routes

Understanding the origin of luminescence from the various silica fibres involves study of intrinsic defects in the starting material, as well as those that result from fabrication, eg strain-related defects and extrinsic doping, and those that arise from exposure to ionizing radiation, all existing in differing concentrations and charge states. As intimated, commercial optical telecommunication fibers can lead to a poorly posed situation, the fabrication parameters having been set up to provide for optimum telecommunications. As such, the primary intent of the present collaboration has been to work with preforms and fibres based on use of the MCVD process, in particular those that have been tailored towards radiation detection, contrasting this route towards production with the surface decorated nanoparticle sol–gel approach. The sol–gel route offers a very much cheaper processing technique for production of doped glass developed for TL purposes (Rivera et al., 2007a; Siti Shafiqah et al., 2015; Wang et al., 2012) but as with the MCVD product it provides a solution that is not entirely without issues, not least in seeking to obtain closely similar quality product from each production batch. The variant of
the sol gel technique of interest herein involves producing surface-decorated/surface-coated silica nanoparticles, the surface decoration/coating creating luminescence centres. Herein we report on production of Ag-doped silica nanoparticles. Our analytical approaches in investigating the utility of the two forms of doped silica media involve:

1. elemental composition and morphological studies, to-date the sol–gel media being limited to use of SEM-EDX and x-ray diffraction (XRD);
2. defects characterization via optical properties (UV–vis, Raman spectroscopy, photooluminescence spectrometry, RIP and X-ray photo spectroscopy, XPS), to-date limited to the optical fibers;
3. dosimetric performance, for the MCVD fibres including the challenging situations of exposure to alpha particles and neutrons in aqueous environments.

Given article length restrictions and noting that previous publications by this group have detailed results from optical and ionizing radiation spectroscopies, we choose here to limit materials analysis results to those arising from use of XRD for the sol gel media. SiO2, be it crystalline (e.g. quartz, coesite, moganite) or amorphous (e.g. opal, hyalite, and silica glass, the latter being the main focus of our interest), is formed of a 3D network of four oxygen atoms surrounding each Si ion. The amorphous oxide lattice closely matches siliconin size, the tetrahedral structure of introducing a new luminescence band, impurity atoms might one electron can stabilize itself on one of the silicon atoms (Beall Fowler and Edwards, 1997). ESR studies in silica glass have shown the same E′ centre structure (Griscom, 1979). The Si–Si centre is capable of forming a hole–trap (Tsai et al., 1988). At annealing temperatures the E′ centre can transform into a Si–Si centre, while at even greater temperature the Si–Si centres tend to transform into excess silicon atoms in SiO2. These excess silicon atoms will then no longer produce luminescence (Rebohle et al., 1998).

In regard to the self-trapped exciton, when an electron is excited in a lattice it leaves a hole in the valence band. This electron will experience a Coulombic interaction with the hole, screened by ions and other electrons. The electron–hole pair, termed an exciton, can propagate through the crystal. In SiO2, the electron–hole pair is strongly bound due to the low dielectric constant of the base compound. The presence of the self-trapped exciton in silica leads to energy levels inside of the normal bandgap. Tsai et al. (1988) have estimated the exciton binding energy in SiO2 to be about 1.3 eV. Further, the existence of a photoluminescence (PL) band at 440 nm in SiO2 supports the suggestion that excitons are trapped in the SiO2 matrix, a phenomenon absent in an ideal crystal. It is now accepted that the mechanism for this defect in silica is motion of oxygen atoms in the crystal. The motion, first proposed by (Fisher et al., 1990) is an oxygen atom rotation about another Si–O bond of a neighboring silicon atom. This motion causes a lattice distortion that significantly changes the local energy level in the crystal.

In regard to extrinsic defects or impurity centres, when impurities are introduced into the SiO2 substrate it involves a model in which the impurity centres become either substitutional atoms, interstitial atoms or an impurity–intrinsic complex, with any of these being present inside the material. Apart from the possibility of introducing a new luminescence band, impurity atoms might also change the number of electron or hole traps or else provide much deeper traps in the media. One of the main desirable properties involving Ge impurities is its photosensitivity. Much attention has been paid to the defect produced by the

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**Fig. 1.** (a) silica molecule; (b) 6-membered ring lattice of silica molecules [adapted from: http://www.iue.tuwien.ac.at/phd/filipovic/node26.html].
photosensitivity, known as the germanium oxygen deficient centre (GOCD). This defect is commonly considered to be responsible for the changes in the refractive index in germanosilicate glass (Dianov et al., 1996). Concerning the absorption optical activity of these germanium related defects, it has been observed to have connection with the band peaks at 240 nm and 245 nm, referred to as the GOCD and NOV (neutral oxygen vacancy) respectively. These two defects have sometimes been assigned to the wrong bond, such as Ge–Ge, Si–Ge, rather than the usual Si–O–Ge bond in Ge-doped-silica media. It is found that these defects can be bleached with UV irradiation, producing defects such as GeE′, GeE′′, GeE, Ge (1) and Ge (2). GeE′, GeE′′, GeE, Ge (1) and Ge (2) are the most common Ge related paramagnetic defects that can be detected by electron paramagnetic resonance (EPR) in irradiated Ge-doped silica media. The GeE′ is representative of (≡Ge∗), associated with an absorption band at 6.2–6.4 eV. The Ge (1) defect consists of an electron trapped at the site of a substitutional 4-fold coordinated Ge precursor (GeO4)2− (Chioldini et al., 1999; Neustueve, 1994; Pacchioni and Mazzeo, 2000), attributed to the absorption band at 4.4–4.6 eV. The Ge (2) defect is assigned as ionized twofold coordinated Ge (≡Ge∗∗). Based on EPR analysis, the presence of GeE′, Ge (1) and Ge (2) are found to be in the region g = 1.9937, 1.9933 and 1.9866 respectively.

The photosensitivity of Ge-doped silica material is found to be correlated with a defect observed in the photoluminescence spectrum, known as the Ge Lone Pair Centre (GLPC) with microscopic structure that has been illustrated to be similar to the Ge (2) defect. This defect can be observed in two band peaks in the photoluminescence spectrum, at 3.2 eV and 4.3 eV, with the absorption band referred to as transitions from a point defect ground singlet state (S0) to the first single state (S1) (Hosono et al., 1992; Skuja, 1992).

2.1. Ge-doped optical fiber produced via MCVD technique

The fibers used by us in TL studies have employed the MCVD technique, produced in a high temperature environment using GeCl4 and SiCl4 as the precursor (Jacqueline et al., 2004; Liu et al., 1997; Mat-Sharif et al., 2013). The TL response of commercial SiO2 doped optical fiber has been investigated for photons (see for instance, Abdul Rahman et al., 2011; Youssef et al., 2001), electrons (e.g. Abdul Rahman et al., 2011; Hashim et al., 2009) and alphas (e.g. Ramli et al., 2009) in each case showing considerable potential in dosimetric applications. Abdulla et al. (2001a, 2001b) carried out a study on commercially available Ge-doped optical fiber using a gamma source, the response being found to be linear over the range of doses 0.02–0.24 Gy (Yaakob et al., 2011), tying in with the fact that Ge in the core allows increase in the value of the refractive index due to the photosensitivity.

Developments beyond the commercially available telecommunication fibre, also obtained using the MCVD technique, have included fabrication of hollow cylindrical fibres, collapsed fibres, photonic crystal fibres and flat fibres, with various Ge dopant concentrations extrinsically introduced and with various dimensions. As an instance, Ghomeishi et al. (2015) have investigated three types of Ge-doped optical fibres: conventional cylindrical fibre, capillary fibre, and flat fibre, all fabricated using the same optical fibre preform. For electron and photon irradiated fibres at doses from 0.5 to 8 Gy, the results show for capillary fibre collapsed into a flat shape that the TL yield is increased by a factor of 5.5, also some 3.2 times that of the cylindrical fibre. This suggests a strain-generated means of production of suitably sensitive TLD for in-vivo dosimeter applications, with changes in the form of glow curve also being noted. Begum et al. (2015) have also been among those who have shown that the sensitivity of FF constructs can be made to be competitive with phosphor-based TLD, in the particular case that of TLD-100 and TLD-700 (doped LiF). Further investigations have concentrated on novel microstructured fibres, one example being the photonic crystal fibre (PCF), produced by what is referred to as a stack and draw method (multiple doped fibres stacked together, as for example in a hexagonal array and then pulled into a fine fibre form), the TL arising from the dopant (Ge and B as an example) and induced strains (Dermosesian et al., 2015). Here, an interesting question concerns whether methods might be developed that could apportion the fractional TL yield due to the strain-related defects and extrinsic dopant(s). Glow curve analysis would seem to hold the key to this. The report of Dermosesian et al. shows that PCFs can markedly improve upon the sensitivity of an SMF, in one instance by a factor of some 30 ×.

2.2. The sol–gel technique

Chemical precursors are applied in this low temperature technique, providing a means of producing ceramics and glasses with purity and homogeneity greater than that achievable using the conventional high temperature MCVD technique. The method has been used to produce a wide range of compositions, mostly oxides, in various forms including powders (Rivera et al., 2007b, 2007c), fillers (Wen and Mark, 1994), coatings (Kurz et al., 2006; Natsume and Sakata, 2000) and thin films (Kajitvichyanukul et al., 2005; Marikkannan et al., 2015). The technique starts from mixtures of a chemical solution, the precursors acting as the source of elements to be incorporated into the final product. The most common precursor used for silica glass is tetraethylorthosilicate, Si(OC2H5)4, commonly referred to as TEOS. The main chemicals in the mixture are then made to undergo chemical processes with the intent of forming a colloidal suspension known as sol. After going through a sequence of chemical reactions the sol stiffens to form a gel, subsequently heated and dried to form solid (sometimes as powders). In fabrication, Dabbaghian et al. (2010) found ethanol co-solvent to have the most significant effect on particle size and size distribution of the synthesized silica nanoparticles. Park et al. (2002) reported that smaller sized silica particles can be obtained by employing a small ratio of ethanol in the mixture. The synthesis of mono-dispersed silica particles have been explained in detail by Bogush et al. (1988). To-date, most TLDs in nanoparticle form have been made of ceramics such as ZrO2 and ZnS. Purpose-made for TL studies, these have been demonstrated to have good performance under UV light (Azorín et al., 2005). Fewer studies have reported on the TL response of silica nanoparticles, Carvalho et al. (2010) reporting on the TL response to gamma rays of natural quartz at nm particle size and Mendoza-Anaya et al. (2003) discussing the TL performance of pure silica nanoparticles, comparing these with Fe and Cu-doped material. Pandey et al. (2004) investigated TL from pure silica nanoparticles supported by results from photoluminescence spectroscopy for defect characterization.

2.2.1. Ag-doped silica nanoparticles

In what is to follow we abbreviate nanoparticles to Np and focus on Ag as the dopant of interest. Elsewhere, Cds and ZnS have been doped with Ag (Tiwari et al., 2014), the TL intensity increasing with increase in UV exposure time, indicative of TLD potential. The use of Ag nanoparticles in ZnO2 has resulted in modification of the kinetic parameters, inducing a shift of the TL temperature towards higher values (Villa-Sanchéz et al., 2007), being of particular importance in ensuring a low fading rate of the stored TL signal.

One concern in introducing dopants into SiO2 in the form of molten glass is the solubility. While in principle any element can
mix with the SiO2 precursor during the solution stage. The doping of Ag in SiO2 is advantageous because SiO2 reduces the tendency towards Ag Np agglomeration, important in achieving mono-dispersal of the AgNp. There is already a good deal of experience in working with Ag nanoparticles. As an example, coating of nanoparticles of this metal with a SiO2 shell has been studied in attempts to enhance colloidal and chemical stability (Niitsoo and Couzis, 2011). SiO2 coatings have also been successfully produced in forming a controlled dielectric environment around the AgNp, improving precision in surface plasmon resonance (SPR) sensing. Ag-doped SiO2 has also been applied in surface enhanced Raman scattering (SERS), with Ag as one of the plasmonic materials, light excitation enhancing the local electromagnetic field (Feng Xian Liu et al., 2001; Long et al., 2012). In Fig. 2, the Cu Kα XRD pattern shows a broad distribution peaking at $2\theta = 23^\circ$, indicating successful production of amorphous silica and agreeing with others (Gorji et al., 2012; Tabatabaei et al., 2006).

The results of Fig. 3 reveal crystalline peaks for the Ag-doped medium, at $2\theta = 38.2, 44.4, 64.7$ and $77.5^\circ$, confirming the presence of Ag nanoparticles in agreement with others (Hilonga et al., 2012; Mie et al., 2014; Torres et al., 2007) (Table 1). In Fig. 4, it is apparent that particle size manifestly influences the TL properties of the silica nanoparticles, smaller particles, with proportionately greater surface area, exhibiting the greater TL yield compared to that of larger samples (Siti Shaqiqah et al., 2015). As such, there are a proportionately greater number of light-emitting ions on the surface. The TL response of the nanoparticles increases with dose, pointing to the possibility of using silica nanoparticle powder as a dosimetric base-material. Mendoza-Anaya et al. (2003) report silica gel glow peaks to achieve an intensity maximum at much lower temperature compared to present results, indicative of a potential for enhanced TL performance in using present nanoparticle samples.

With Ag as the extrinsic impurity, effects are revealed in Fig. 5 that contrast with the use of Ge, one similarity being that with both Ag- and Ge-dopants saturation appears at much greater dose, beyond 500 Gy, compared to that of pure silica samples. For the latter, saturation starts at around 300 Gy. For present samples the AgNps reduce the TL signal, with response less than that of the pure silica samples. Here the Ag multilayer coating the silica surface acts not only as a promoter of TL yield on the silica nanoparticles surface but also as an attenuator, absorbing and scattering a fraction of the incident radiation. Additionally, the layer acts as an inhibitor, reducing the efficiency for transport of TL from the silica nanoparticle surface. Thus said, a particularly attractive feature of the Ag is the extended dynamic range, providing greater versatility of the Ag-doped medium in radiation technology applications at elevated doses, as are found in radiation processing.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E5</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>E10</td>
<td>80 ± 18</td>
</tr>
<tr>
<td>E20</td>
<td>140 ± 17</td>
</tr>
<tr>
<td>E30</td>
<td>550 ± 9</td>
</tr>
</tbody>
</table>

### 3. Examples of fibre TL applications

Here we choose two situations, the first being that of modulated and unmodulated proton beams, illustrating the considerable...
spatial resolution (0.1 mm) capability of fibres in making depth-dose measurements, in this case of a 62 MeV proton beam. Use was made of commercial Ge-doped silica fibres, purchased from CorActive (Canada), the fibres having a core diameter of 50 μm and a cladding diameter of 125–127 μm. In order to use the fibres, the coating was first carefully removed through use of a fibre stripper (Miller, USA). The fibre was then cleaned to remove any residual polymer. The product was then cut into small fibre lengths of approximately 0.3 ± 0.1 cm, use being made of a scalpel.

The measurements (Fig. 6) were made in a thin window (0.1 mm mica) water phantom, the irradiations being carried out using the UK National Health Service Clatterbridge proton therapy facility. The results have been compared against gold standard parallel plate ionization chamber measurements. In measuring the Bragg peak, the commonly observed issue of a quenching effect is evident, with a decreased response with increasing ionization density of the radiation field. This dose underestimation in the Bragg peak of heavy charged-particles (Rah et al. 2012), also referred to as the quenching effect (Azangwe et al. 2014), has been reported most for chemical dosimeters such as film, polyacrylamide gels (PAG), Fricke gels, PRESAGE®, and alanine (Doran et al. 2015; Baldock et al. 2010 and Gustavsson et al. 2004). This phenomenon is not yet fully understood; high-dose saturation, ion-recombination and track structure theory are among the possible explanations, as discussed by Gustavsson et al. (2004); Jirasek and Duzenli (2002); Katz (1978); Zhao et al. (2012) and Gorjia et al. (2012). More detailed investigations are ongoing, the present work simply being to illustrate the utility of the fibres. From this preliminary study it is evident that:

- Data for the profile can be obtained in a single exposure, saving considerable beam time, a matter contrary to the experience in making use of a parallel plate ionization chamber for point-by-point measurements;
- Very high resolution range verification is to be had;
- The irradiated fibres show variations about the mean of up to ±10%, an outcome that is highly competitive with results obtainable using the well-established LiF: Mg, Ti (TLD-100) phosphor-based medium.

The graphed results of Fig. 7 relate to the second set of situations, showing mass-normalised data from irradiations of fibres of various form and also of phosphor-based TLDs, obtained using a tube x-ray facility (model ERESCO 200 MF4-RW) located at the Physics Department of the University of Malaya. For present work the tube x-ray facility was operated at 80 kVp nominal tube potential, with doses to the samples ranging from 0.5 mGy to 10 mGy, verified through use of a calibrated ionisation chamber. The fibre results are for doped PCFs (Ge and B doped), PCF_Ge and PCF_B, the subscript c indicating that under the action of a vacuum, the fibres have been collapsed down from hollow bores into a solid assembly (see for instance, Ghomeishi et al., 2015; Dermosesian et al., 2015), inducing strain-related defects and thus additional TL sensitivity. The inset shows the sensitivity of the PCFs to greatly exceed that of TLD-100 (a doped LiF medium) while the main figure illustrates the sensitivity of TLD-200 (CaF2:Dy) phosphor, a material notable for its ability to sense environmental levels. Under the well controlled situation of x-ray irradiations, the sensitivity of TLD-200 is seen to out perform the present capability of our PCF media. It is to be noted that at calibrated doses the individual TLDs have been selected to provide uniform response to within ±5% of the mean TL yield.

We have subsequently tested the various media under field conditions, locating the media in glass containment in soil at a site that is known to be marginally affected by technologically enhanced levels of naturally occurring radioactive material (TENORM). The dosimeters were buried in soil at 20 cm depth, as shown in Table 2 and left there for periods from two to four
months. Mean above-ground dose-rates in air at 1 m of some 11 nGy/h correspond to a dose of \(\sim 32\, \mu\text{Gy}\) over a four month period (Tikpangi Kolo et al., 2015). Samples of each type of TLD were collected two and four months after burial (with R1 representing the first sample collection and R2 the second sample collection).

The results, in histogram form (Fig. 8), are accompanied by glow curves for the various TL media (Fig. 9), soils analysis at the five specific locations including high-resolution gamma-spectrometry using a shielded high-purity Ge (HPGe) detector. The choice of locations were guided by the gamma-spectrometry analysis and hand-held survey meter findings, obtained regularly over a two-year period, identifying potential elevations (of a factor of up to 2) of NORM over undisturbed soil values (sampling location L1, L2, L3 offering particular examples). For the second sample collection (R2), the TLD results are typically greater than those from first sample collection (R1). The PCF\(_{\text{Ge}}\) samples offer greater TL yield compared to the PCF\(_{\text{GeB}}\), the converse of that found in using 80 kVp X-ray irradiations, a matter linked to the differing energy response of the two fibre types for the two very different spectral distributions (80 kVp x-rays and NORM). In line with the broad indication offered by the x-ray tube irradiations, TLD-100 offers a lesser response compared to the PCFs, as expected, while the TLD-200 falls short of the indicative relative sensitivity recorded for the other media in use of 80 kVp calibrations. As expected, the PCF dosimeters provide sensitive measurement, unaffected by moisture, while the degraded in-field performance of the TLD-200 phosphor accords with evidence of moisture intrusion.

In Fig. 9, the glow curves for R2 for both PCFs are seen to be of manifestly greater intensity than R1 data. As further observed in the histogram of TL yields of for example the L1 sampling location, PCF\(_{\text{Ge}}\) offers the greater TL yield compared to PCF\(_{\text{GeB}}\). For R2 data, the peak maximum is observed to occur between 255 to 260 °C for both PCFs. The glow curves for the PCFs show the beginning of a high temperature shoulder indicative of strain-related defects.

4. Conclusions

The collaboration whose work is represented herein have made progress towards understanding a number of the major issues guiding development of silica based media for TLD. We have discussed fabrication issues and how these can influence defect types and concentrations. We have subsequently illustrated the discussion by providing examples from our most recent TLD results, pointing to the potentials of such media.

Acknowledgement

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Bhushan, B., 2007l. The effect of size scaling on the fundamentals and appli-
Bhushan, B., 2007m. The effect of size scaling on the fundamentals and appli-
Latest developments in silica-based thermoluminescence spectrometry and dosimetry

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HIGHLIGHTS

- We provide a status report for our work on silica-doped media for TL dosimetry.
- The construction and performance of a TL emission spectra facility is described.
- Oxygen-rich/oxygen deficient Ge-doped SiO2 defects/lattice relaxation phenomena are related to TL spectra.
- Ge-doped SiO2 are used to obtain high spatial-resolution Am–Be neutron source measurements.

ABSTRACT

Using irradiated doped-silica preforms from which fibres for thermoluminescence dosimetry applications can be fabricated we have carried out a range of luminescence studies, the TL yield of the fibre systems offering many advantages over conventional passive dosimetry types. In this paper we investigate such media, showing emission spectra for irradiated preforms and the TL response of glass fibres and beads following irradiation to an 241Am–Be neutron source located in a tank of water, the glass fibres and beads offering the advantage of being able to be placed directly into liquid. The outcomes from these and other lines of research are intended to inform development of doped silica radiation dosimeters of versatile utility, extending from environmental evaluations through to clinical and industrial applications.

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1. Introduction

Over the past three years the consortium effort that this work represents has focused on developing small diameter (0.1 mm through to ~1 mm) GeO2 doped SiO2 glass fibres for luminescence dosimetry. For the same reasons, we have also investigated commercial jewellery beads of various diameters (1–3 mm), with the additional benefit of reduced cost and robust utility. Both media are silica based, with compositional studies being carried out to locate and quantify dopants within the silica; see for instance the elemental analysis studies of beads, conducted by Jafari et al. (2014a). The intention has been to produce high spatial resolution thermoluminescence dosimeters (TL) for sensitive radiation detection.

For the preforms from which the fibres are produced, using a custom-built spectrometer we show first results for emission wavelengths, revealing the predominant wavelengths to be towards the blue end of the visible spectrum. In respect of TL yield, we are seeking to define optimal concentrations of GeO2 in SiO2 fibres, to-date the dopant concentration being incremented from

[References and further details]

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that of standard telecommunication fibres (∼4 mol%) up to some 12 mol%. At low dopant concentrations and minimal shape deformity the short-range SiO₂ network suffers minimal strain. Conversely, the interface between the pure SiO₂ cladding and the GeO₂ doped silica network becoming increasingly strained with increase in extrinsic doping and shape deformation. As reported elsewhere (Abdul Sani et al., 2015a, 2015b), elevations of Ge dopant beyond 4 mol % tend to reduce TL yield, a result of concentration quenching, sometimes also referred to as self-absorption. The predominant focus of present work is on investigation of the preforms from which the fibres have been formed.

Using a standard TL reader, measurements of TL from an irradiated sample typically concern the emitted total light intensity, the emission resulting from insulating/semiconductor material containing defects, intrinsic and extrinsic. With present interest being on Ge-doped silica preforms, attempts are made to measure changes in emission resulting from changes in defect concentrations. Our starting point in studying the TL glow curve is use of the standard energy level description for defects in such media (Fig.1). Although described for crystalline media, the model is also applicable to the short-range order of amorphous media, including the silica studied herein (Bradley et al., 2014). The band model of Fig. 1 is typically represented by ₓ, the activation/conduction energy, also referred to as the conduction energy, pointing to the least energy needed to drive de-trapping, ₓ, the valence band energy and ᵧ the Fermi energy.

2. Energy band diagram

Optical activity concerns the absorption and luminescence process. In the glass-matrix lattice, the extrinsically introduced Ge atoms occupy interstitial or substitutional positions, the modification in bond energy allowing the donor electrons to move freely from ion to ion. At ∼9 eV, the energy difference between the valence and conduction band of silica is wide, as shown in Fig. 2. When light energy is absorbed and if the absorbed energy is sufficiently great, then electrons may be raised from ground energy to the conduction band, giving rise to a current. At intermediate energies, the electrons can be trapped by impurity atoms (Ge in the present case) or lattice irregularities in the silica glass that create localized electron states. These electron states normally have very narrow energy level and are sometimes capable of trapping electrons for long durations (from seconds to years). The release of this energy in the form of photons are categorized in terms of typical time scales, as in fluorescence (∼10⁻³ s) and phosphorescence (10² s). Our main interest is in the photons emitted by the phosphorescence process, utilized in many applications. The localized energy states created by impurity atoms have been the focus of many studies, detailed by among others, Randall (1945), Skuja (1992, 1998), Imai and Hirashim (1994) and Amossov and Rybaltovsky (1994), the outcome of these providing for a broad summary of the energy levels for Ge-doped silica glass (Fig. 2) and the signature absorption and luminescence bands or colour centres (Table 1).

3. Energy level of GeO₂–SiO₂ glass

In the extrinsic doping of an insulator or semiconductor the point defects are produced as a mixture of vacancies (between neighbouring atoms) and interstitials (with other atoms placed between neighbouring lattice atoms). These will distort the structure plane, altering compactness and local charge and strain. The point defects produce colour centres as a result of the modification of electronic neutrality, line defects are from dislocations and of electronic neutrality, line defects are from dislocations

![Image](image_url)

**Table 1**

<table>
<thead>
<tr>
<th>Defect acronym(s)</th>
<th>Suggested-structural model(s)</th>
<th>Position-of optical absorption band peaks (eV)</th>
<th>Peaks of PL bands (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si ODC(II), Ge ODC (II)</td>
<td>Oxygen vacancy</td>
<td>6.8–7.0</td>
<td>4.2–4.3</td>
</tr>
<tr>
<td>Bₓ(Si)</td>
<td>Oxygen divacancy</td>
<td>4.95–5.05</td>
<td>4.3–4.4</td>
</tr>
<tr>
<td>Bₓ(Ge)</td>
<td>Oxygen divacancy</td>
<td>5.1–5.4</td>
<td>4.3–4.4</td>
</tr>
<tr>
<td>Siₓ²⁺, Geₓ²⁺</td>
<td>dicoordinated Si/Ge</td>
<td>3.15</td>
<td>2.7–2.8</td>
</tr>
<tr>
<td>Non-bridging-oxygen hole centre (NBOHC)</td>
<td>dicoordinated Ge</td>
<td>3.7</td>
<td>3.0–3.2</td>
</tr>
</tbody>
</table>

* Skuja has commented on the continuing controversy over the basic structure of ODCs (oxygen deficient centres), with different naming conventions for ODCs as a result of this, including ‘non-relaxed oxygen vacancy’, ‘defect of type oxygen vacancy’, ‘divacancy’, ‘B2-centre’ and ‘silicon lone-pair centre’ (SLPC) for ODC(II). PL indicates photoluminescence.
and area defects arise from for instance grain boundaries. These are reflected in the standard energy level description of the host material, as in the doping of silica by GeO₂ (Fig. 2). Investigations of such doped media are summarized in Table 1, the method of investigation being identified therein. In present discussion we will focus on study of the glow curves and emission spectrum, examining in particular oxygen rich and oxygen deficient GeO₂ doped silica preforms.

4. Samples preparation

The approach of the present group has been to develop oxygen rich (sample P1) and oxygen deficient (sample P2) preform samples, their preparation and optical spectroscopy characterisations being described in detail by Tamchek et al. (2013) and Siti Shafiqah et al. (2015).

5. Experimental set-up for conventional glow curves

Glow curves were obtained using a Harshaw Model 3500 Manual TLD reader located in the University Malaya Radiation Laboratory. The samples were pre-heated to 80 °C to remove the thermally unstable luminescence component of the glow curve and then subsequently heated to 400 °C at a rate of 10 °C/s. The glow curves were then analyzed and deconvolved, starting with a Voigt profile from which it has been shown in the present case that the Gaussian function can approximate the component peaks, also allowing the peak central temperature and FWHM to be approximated, this being a limited approach discussed by among others Alawiah et al. (2015). In this present case, the much smaller Lorentzian contribution to the Voigt profile has been neglected. The information was fitted to the TL model proposed by Randall and Wilkins, ergo obtaining the activation energy, $E_c$ of the glow curves (Fig. 1). One feature of the Randall and Wilkins first-order kinetic model is that the peak positions stay fixed, while the height of the peaks are directly proportional to the dose. An in-house experimental set-up has been produced for thermoluminescence emission spectra analysis, as described below.

5.1. Experimental set-up for thermoluminescence emission spectra

Fig. 3 shows the experimental setup used in measuring the emission spectra of heated samples. The whole system consists of three main components: the heater chamber; the spectrograph (wavelength/energy dispersive) and a high sensitivity CCD array. This system has been designed to measure very low light intensities, the sample being heated over a pre-determined interval. Collection of the emission spectra from the sample was by means of a large diameter (24 mm) collimation lens of focal length.
35.4 mm, the collected light being transferred by a Czerny–Turner spectrograph (monochromator) using a 600 μm core diameter optical fibre. Following dispersion of the spectra using a grating groove of 150 g/mm that is capable of producing a spectral bandwidth of 400 nm and spectral resolution of 0.4 nm, the spectral information is acquired through use of a high sensitivity cooled charge coupled detector (CCD) (Andor Technology, Model iDUS DU401). The CCD has a pixel array of 1024 × 128 at pixel size 26 × 26 μm with a quantum efficiency of more than 95% in the visible region (550 nm). When the CCD is cooled to −80 °C, the total dark current is about 0.001 electrons/pixel/s; the system light sensitivity has been observed to be comparable with a conventional photomultiplier tube. To reduce heat loss from the heater ceramic, the heater chamber has been shielded by a double layer copper cylinder insulated with glass wood, the heat capacity of the former being 900 W with considerable heat conductivity of 100 W/(m K), allowing maximum heat transfer to the sample. In the particular arrangement, to provide for accurate temperature measurement of the sample, use has been made of an external type K temperature probe attached to the top of the sample. The temperature of the sample and the CCD are recorded and controlled by a PC running custom-made automation software using LabView (National Instruments).

The samples (control and irradiated) are placed in turn on the heater and the heater chamber, the latter being purged with N2 gas to remove water vapour and to inhibit oxidation of the sample. The choice has been made to heat the sample at the rate of 1.5 °C/s, the emission spectra being recorded for about 250 s. The CCD is used in the Photon Counting mode, accumulating the data at 5 × the shutter duration of 150 ms. As such, the time taken for a single acquisition, also allowing the sample temperature to stabilize, is about 1 s/°C. The emission spectra have been corrected for background emission, ceramic heater blackbody radiation and CCD.

**Table 2**
Some frequently reported luminescence bands found in quartz and silica. Indications of possible defect models are given.

<table>
<thead>
<tr>
<th>Band (nm)</th>
<th>eV</th>
<th>Method†</th>
<th>Possible models for origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>4.77</td>
<td>CL</td>
<td>Oxygen vacancy</td>
</tr>
<tr>
<td>290</td>
<td>4.28</td>
<td>PL,CL</td>
<td>Oxygen vacancy</td>
</tr>
<tr>
<td>300</td>
<td>3.25</td>
<td>RL,CL</td>
<td>Aluminium impurity, an impurity imported during growth of quartz</td>
</tr>
<tr>
<td>390</td>
<td>3.17</td>
<td>RL</td>
<td>E5</td>
</tr>
<tr>
<td>400</td>
<td>3.1</td>
<td>PL</td>
<td>O2 intrinsic defects and Ge impurity</td>
</tr>
<tr>
<td>450–480</td>
<td>2.5–2.8</td>
<td>RL,CL</td>
<td>Recombination of self-trapped excited state (S2)</td>
</tr>
<tr>
<td>580</td>
<td>2.15</td>
<td>CL</td>
<td>Oxygen vacancy</td>
</tr>
<tr>
<td>640</td>
<td>1.9</td>
<td>IB1,CL</td>
<td>Oxygen vacancy and Na impurity</td>
</tr>
</tbody>
</table>

† CL, PL, RL are cathodo-, photo- and radioluminescence and IB1 is ion beam implantation.

**Table 3**
Calculated value of N_{def}, α and W from absorption measurement (from Siti Shaﬁqah et al., 2015).

<table>
<thead>
<tr>
<th>Preform</th>
<th>Peak (eV)</th>
<th>Absorbance, α (cm⁻¹)</th>
<th>Full-wave-half maximum, W (eV)</th>
<th>Defect concentration, N_{def} (1 × 10¹⁵ cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>6.9</td>
<td>1.101</td>
<td>0.471</td>
<td>3.83</td>
</tr>
<tr>
<td>P2</td>
<td>5.1</td>
<td>3.492</td>
<td>0.565</td>
<td>14.63</td>
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<tr>
<td></td>
<td>6.8</td>
<td>2.174</td>
<td>0.844</td>
<td>13.61</td>
</tr>
</tbody>
</table>

**Fig. 7.** Emission spectrum Contour plot of P1. A relative heat (TL intensity) bar is shown to the right.

**Fig. 8.** Emission spectrum contour plot of P2.
Fig. 9. (a) 1 mm spatial resolution depth dose distribution obtained from an Am–Be neutron source in a water tank using 1 mm thick silica glass beads. (b) Visualization of the lower part of the mathematical model for use in the Monte Carlo simulation. The dosimeters (red) are threaded onto nylon-66 thread (pink). The $^{241}$Am/Be source has a Be–Am filling material (green) and a double skinned stainless steel casing (yellow). Water (blue) surrounds the source and dosimeter irradiation apparatus. (c) Neutron source spectrum obtained from High Tech Sources $^{241}$Am/Be data sheet (HTS data sheets, 2006) used as source distribution in MCNPX simulation. (d) Three independent runs of the MCNP Monte Carlo simulation, with the separate runs showing sharp peaks in the measured data to be re-obtained at the same approximate positions allowing for small uncertainty in the position of the first measurement point. Further investigations of this are underway but it is noted that the particular MCNP code used in simulating the experiment did not include diffractional phenomena or account of the 59.54 keV gamma rays emitted from the $^{241}$Am source, the latter providing for some of the fractional discrepancy in intensity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
quantum efficiency.

5.2. Peak temp (°C)

Figs. 4 and 5 show the glow curve results for samples P1 and P2 respectively. For P1, the deconvolved results show there to be two peaks, the lower peak (peak 1) achieving a maximum yield at 323.8 °C, commensurate in using the Arrhenius equation with an activation energy ($E_a$) of 0.4567 eV, while the upper peak (peak 2) achieves a maximum yield at 328.5 °C, commensurate with an $E_a$ of 0.5035 eV. For P2, the single peak achieves a maximum yield at 315.6 °C, commensurate with an $E_a$ of 0.5377 eV.

6. Spectral analysis

Use has made of the custom-built spectrograph previously described in analyzing the preform samples P1 and P2, the results being shown in Fig. 6. It is found that the intensity of P2 is some several times that of P1. Fuller interpretation can be had in making calculation of the defects concentration (Table 3), use being made of the Smakula formula (Smakula, 1930; Afanasyev-Charkin et al., 1999), as follows:

$$N_i = \frac{n}{(n^2+2)^{\alpha m}} \propto m U$$

where, $N_i$ is number of defects, $f$ is the oscillator strength of the optical transition, $\eta$ is the refractive index of the sample, $\alpha$ is the height of absorption coefficient of the peak and $U$ is the band width (FWHM).

The TL yields were found to be in linear proportion with defect concentrations. This leads to the prediction of a three to fourfold increase in TL signal. Also apparent is that the TL emission is some 4–4.5 eV (Fig. 6), pointing to light of wavelength 290 nm, according with the deep trapping levels shown in Tables 1 and 2 and Fig. 2 (Khanlary et al., 1993).

The TL emission spectrum for sample P1 is shown in Fig. 7 as a contour plot of temperature, energy and TL intensity. The main dosimetric peak has an emission maximum between 3.9 and 4.5 eV; there is additional evidence of the presence of more than one band at energies above 6 eV. From the plot, the peak maximum at 3.90 eV corresponds to a sample temperature of 187.7 °C. Another two peaks of lesser intensity are observed at energies of 4.37 and 4.60 eV. Starting at 4.20 eV, with temperatures greater than the peak at 187.7 °C up to a maximum of 400 °C, the TL emission is continuous. Defect analysis by Skuja (1998) has identified these emission energies to be related to the oxygen vacancy and divacancy, belonging to Si ODC (II), Ge ODC (II), B$_2$(Si) and B$_2$(Ge).

The counterpart TL emission spectrum for sample P2 is shown in Fig. 8, the emission spectrum running from 4.2 to 5.2 eV, with an additional high energy band at 6 eV. The peak maximum was found at 4.94 eV, the intensity also being much greater than that of sample P1. Most importantly, this peak starts to emit at higher temperature, at 368 °C, similar to that found during conventional glow curve measurement. Using the defect analysis of Table 1, it is apparent that this emission energy is related to oxygen divacancy, belonging to B$_2$(Si) and B$_2$(Ge).

7. Example case of silica beads irradiated by an Am–Be neutron source

With underpinning information such as above, we continue to develop doped silica media for versatile luminescence dosimetry, now seeking to include study of neutron detection capability. Adopting 1 mm diameter hollow silica beads of a form previously used for photon TL dosimetry (Jafari et al. 2014a, 2014b, 2014c), we have recently obtained preliminary depth-dose distributions from an Am–Be neutron source contained in a water tank (Fig. 9), more detailed investigations being in progress. With the beads threaded onto a thin nylon filament, the string of beads have been suspended directly above the neutron source. The source has an activity of 17.6 GBq, providing a neutron emission rate of 62.6 n/s MBq. The bead proximal to the source was some 0.6 cm from the source surface, the remaining 168 equi-spaced beads covering distances up to ~20 cm away from the source. The arrangement was exposed to the source for a period of 10 days. Individual sensitivity corrections have been applied to the beads from a photon irradiation to a standard dose (details of the calibration have been explained in a previous publication). Fig. 9 demonstrates the utility of obtaining dense, spatially resolved detection of the neutrons at unsurpassed spacing, general agreement in shape being obtained with the Monte Carlo simulations of Yury Zevallos-Chávez and Bugno Zamboni (2005). An intriguing feature of the measurements, the possible basis of which has yet to be explored, concerns a number of variations in the otherwise smooth downward trend in the data, the most prominent example of which is that around a source to detector separation of 5 cm. Our own use of Monte Carlo simulation have revealed sharp peaks, re-obtained at the same approximate positions as those in the measured data, also agreeing between three independent runs (Fig. 9(d)). With further investigations of this underway, it is noted that the particular MCNP code used in simulating the experiment has not included diffractional phenomena or account of the 59.54 keV gamma rays emitted from the $^{241}$Am source during alpha emission, the latter accounting in part for differences in intensity.

8. Conclusions

Based on oxygen rich and oxygen deficient Ge-doped preforms we have presented a detailed overview of the physics underpinning our studies of the luminescence of irradiated doped silica media. This has entailed discussion of the band gap model and defects that give rise to the TL phenomenon. We observe correspondence between the model system for doped silica obtained from literature and our own measurements of the emission spectrum and glow curves from the silica preforms. We have proceeded to demonstrate the versatility of such media, making TL measurements from a neutron source held within a water tank, the focus being on the unsurpassed spatial resolutions obtainable using these dosimeters.

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The authors are grateful for the University of Malaya – Ministry of Higher Education of Malaysia, UM – MOHE High Impact Research Grant UM.C/625/1/HIR/33. Fig. 1 is reprinted from Published ‘Theory of thermoluminescence’, Radiation Measurements, doi:10.1016/j.radmeas.2007.01.003, with permission from Elsevier. Table 3 is reprinted from publication ‘enhanced TL response Enhanced TL response due to radiation induced defects in Ge-doped silica preforms’, Radiat. Phys. Chem., doi:http://dx.doi.org/10.1016/j.radphyschem.2015.02.015, with permission from Elsevier.

References

Characterisation of an isotopic neutron source: A comparison of conventional neutron detectors and micro-silica glass bead thermoluminescent detectors

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\textbf{ABSTRACT}

As a result of their thermoluminescent response, low cost commercial glass beads have been demonstrated to offer potential use as radiation dosimeters, providing capability in sensing different types of ionising radiation. With a linear response over a large range of dose and spatial resolution that allows measurements down to the order of 1 mm, their performance renders them of interest in situations in which sensitivity, dynamic range, and fine spatial resolution are called for. In the present work, the suitability of glass beads for characterisation of an Americium-Beryllium (\textsuperscript{241}AmBe) neutron source has been assessed. Direct comparison has been made using conventional \textsuperscript{3}He and boron tri-fluoride neutron detectors as well as Monte Carlo simulation. Good agreement is obtained between the glass beads and gas detectors in terms of general reduction of count rate with distance. Furthermore, the glass beads demonstrate exceptional spatial resolution, leading to the observation of fine detail in the plot of dose versus distance from source. Fine resolution peaks arising in the measured plots, also present in simulations, are interesting features which based on our best knowledge have previously not been reported. The features are reproduced in both experiment and simulation but we do not have a firm reason for their origin. Of greater clarity is that the glass beads have considerable potential for use in high spatial resolution neutron field characterisation, subject to the availability of a suitable automated TLD reader.

1. Introduction

Mapping mixed radiation fields with conventional gas based neutron detectors to achieve mm spatial resolution is a challenge. However, detailed knowledge of different radiation intensities as a function of position surrounding neutron sources is required to use these sources as a characterisation tool (for example in detector testing or neutron activation studies). Hence, in this work, we report the potential to use the thermoluminescent response of 1.1 mm diameter micro-silica glass beads to map the radiation field caused by an AmBe neutron source submerged in a water tank.

The convolution of neutron emission energies with the moderation due to the presence of the water and reduction in intensity per area with increasing distance is known to cause peaks in the distribution of the neutron capture cross section (Lorch, 1973; Coehlo et al., 1989; Thompson and Taylor, 1965; Anderson and Neff, 1972); indeed, this was seen in prior studies (Taggart, 2007; Nicolaou, 1983; Matthews, 1979) of the neutron tank, albeit at far poorer spatial resolution than the present study. The dosimeter size of \textasciitilde{1} mm (Jafari et al., 2014b, 2014a) of the neutron tank, albeit at far poorer spatial resolution than the present study. The dosimeter size of \textasciitilde{1} mm (Jafari et al., 2014b, 2014a) enables a far finer \(\Delta E^{(neutron)}\) sensitivity than that provided by alternative techniques. The energy response of the glass beads has previously been reported in (Jafari et al., 2014c), whilst that of conventional gas detectors are well-documented.

Work thus far has concerned the effectiveness of glass bead dosimeters for use with the latest radiotherapy developments (Teoh et al., 2011; Chang and Timmerman, 2007) and specifically that the dimensions of the dosimeter should be small with respect to the radiation field dimensions (Jafari et al., 2014a; Bjarnard et al., 1990;...
Higgins et al., 1995; Fracescon et al., 1998; Sauer and Wilbert, 2007; Aspradakis et al., 2010) whereas the focus of the most recent studies have been the introduction of a mixed radiation field as described in Bradley et al. (2016) and here. The relevance of this point is that the response of the glass bead cannot be solely due to neutron interactions (capture, scattering, or gamma production) and that a significant gamma factor will contribute to the thermoluminescent yield whereas the $\gamma$ efficiency is very low for the comparative gas detectors (Kouzes et al., 2009; Reilly et al., 1991).

2. Experimental setup

All experiments were performed using a single 11 GBq AmBe source (Ziegler, 2007) at the University of Surrey as depicted in Fig. 1 where the beads were wholly submerged within the shielding water tank and the vertical gas-detectors (both $^3$He and boron trifluoride) were housed within an air-tube. Note that the tube was raised with the detector, thereby providing protection for the high-voltage supply rather than to preferentially select fast neutrons by displacement of the moderating water. The gas detectors were powered using an Ortec 710 PSU, with the $^3$He tube held at 1200 V and the BF3 detector at 1800 V. The respective detector outputs were fed into an Ortec 142A preamplifier and an Ortec 672 spectroscopy amplifier with a shaping time of 3 $\mu$s for each tube. Online monitoring was provided by the Ortec Maestro (Ortec, 2016) program connected to an Ortec Easy-MCA whereas offline analysis was performed with an in-house code built using the Root (Brun and Rademakers, 1997) framework.

2.1. Surface scan

Initial measurements investigated the response of the gas detectors scanning across the surface of the neutron tank. As can be seen in Fig. 2, although both detector systems show the same response curve peaking about the source location, the greater neutron interaction probability granted by the $^3$He tube allows for a more statistically reliable neutron count. Furthermore, the spatial resolution of these detectors is comparatively poor, with the active volume 76 cm$^3$ for the $^3$He and 152 cm$^3$ for the BF3 tube. This corresponds to a spatial “bite” of $\sim$2 cm in the horizontal surface plane. In addition to the bare detector measurements, a repeated data set was recorded with a cadmium sheath to remove the contribution of thermal neutrons. However, in the case of the BF3 detector this made analysis of the data statistically unsound, and so cadmium-sheathed BF3 results are not presented.

2.2. Depth measurement

Due to the limited resolution of the BF3 tube only the $^3$He detector was used for depth comparison measurements. The relatively large active area of the gas detector results in a substantial “energy bite” being observed for each data point, an example of the poor spatial resolution of conventional neutron detectors. However, spectroscopy is available in this instance with measurements also benefitting from a greatly reduced gamma interaction component. Likewise with the surface measurements, a cadmium-sheathed set of measurements were also taken, whereby the high thermal-neutron capture cross section allows for preferential investigation of fast neutron flux with respect to distance from the source.

2.3. Glass beads

Prior to irradiation the sample beads (shown in Fig. 3) had been prepared as described in Jafari et al. (2014b). The beads were annealed to provide a clean dosimeter, removing any historical record of irradiation from the individual sample. The preferred annealing technique applied a temperature of 400 °C for 1 h with a ramp rate of 10 °C per minute and a cool down rate of 1 °C per minute. The samples were then maintained at a constant temperature of 80 °C for 16 h. The measurements performed in Jafari et al. (2014b) confirm that the annealing procedure has no effect on the radiation response of the glass beads.

Three separate strings of glass beads were suspended directly above the source as per Fig. 1 with a small gap of $\sim$3 mm between the bottom bead and the source itself. Each string comprised 370 individual hollow...
~1.1 mm diameter beads (examples of which can be seen in Fig. 3) threaded onto a nylon filament for a length of approximately 410 mm. The samples were irradiated by the 11 GBq AmBe source for a duration of 14 days, equating to a neutron fluence of approximately 9.5 k neutrons/s/cm² for the beads in closest proximity down to ~1.2 neutrons/s/cm² at the full length of the bead string.

Post-irradiation, bead sets were measured using a Toledo 654 TLD reader at the University of Surrey with the technique described in Jafari et al. (2014b). The beads were stored in a dark environment and allowed to stabilise prior to measurement in order that the rapid fading component of TL materials should not be taken into account (Jafari et al., 2014c).

2.3.1. Calibration

It has been shown in previous publications that the uncertainty in the response of individual beads is substantially better than that of other common TLD materials (Jafari et al., 2014b). The glass beads exhibit an ~8% variation, and this is applied to the results presented here, which compares favourably to the ~15% variability in LiF TLDs (Jafari et al., 2015). It should be noted that although there is presently no absolute reference until the calibration is performed (see Conclusions and Further Work) the variation of the data shown in Fig. 5 agrees within uncertainty, and therefore, with the obvious exception of peaks, we expect similar yields from the individual beads.

2.4. Monte carlo simulation

The mixed radiation field of the AmBe source coupled with the dual neutron-gamma response of the dosimeter necessitates some attempt to deconvolve the respective components. A simulation was developed using the general Monte Carlo N-Particle transport code, MCNPX (Hendricks et al., 2008) modelling the passage of neutrons through the pure water shield. It was previously discussed in Bradley et al. (2016) and is based on a preliminary mathematical model representing the physical neutron tank used to expose the beads. Several assumptions were made about the AmBe source including a neutron energy spectrum from Amersham source calibration data and an internal source construction based on an americium-beryllium layered structure. Further work is planned to optimise the mathematical model used in the Monte Carlo simulations.

3. Results and discussion

The surface scanning measurements presented in Fig. 2 show relatively minor variation of neutron yield over the surface of the tank, some >20 cm being required to show a two-fold reduction in count rate, which classical trigonometry tells us is not an unreasonable result. Conversely, the vertical depth measurements (which can be seen for both the 3He tube and the glass beads in Fig. 4) shows the combined effect of the geometric range of data and the reduction in neutron moderation, a substantial fall-off in count rate observed within a few cm from the AmBe source. Furthermore, the 3He detector measurements were also taken with a ~1 mm-thick cadmium sheath and show the expected drop in count rate due to the resonances in the neutron capture cross section as the energy range passes from the fast region and neutrons become thermalised.

The overlaid vertical measurements shown in Fig. 4 exhibit the same general trend of reduced count rate with increasing distance to the source for each of the experimental data sets as well as the simulation. However, the greater resolution of the glass bead allows for far finer structure to be observed. In effect the gas detectors are integrating the energy regions encountered by many glass beads simultaneously. This is to be expected, and indeed confirms the superior performance of the glass beads in terms of spatial resolution.

In addition to the clear energy sensitivity, by more closely examining the glass bead data of Fig. 4, as well as that of the additional string measurements displayed in Fig. 5, further observations may be made. There appears to be a lower level plateau region exhibited by the glass bead dosimeter that is not apparent when using the gas detectors. This would suggest a lower energy limit, below which the glass beads would be insensitive, coinciding with a distance approximately 23 cm from the source. The measurements performed previously, and reported in Jafari et al. (2014c) have discussed the energy and dose limitations of the glass bead dosimeters.

The most notable feature of the glass bead spectra however, is that of the quasi-regular spikes in the thermoluminescence intensity which notably are reproduced in the simulation. While there is some similarity between the thermoluminescence intensity spikes of the dosimetric data sets this is not sufficient to conclude the origin of the feature to be simply that of the peaks of the AmBe neutron energy spectrum (Lorch, 1973; Coelho et al., 1989; Thompson and Taylor, 1965; Anderson and Neff, 1972). Therefore, one must conclude that some other phenomena be involved (Lorch, 1969; Wright, 1994), or possibly the result of a neutron-induced charged-particle reaction, say, (n,α) or (n,p). At this point it may be worth considering the dominant interactions at play with the glass beads. The main constituents of the elemental composition are silicon, oxygen, and sodium (at 33.62%, 42.18%, and 10.55% by weight respectively) (Jafari et al., 2014c). For each element comprising the glass beads the dominant neutron interaction is elastic scattering Kim et al., 2013; this is true across the whole energy range that has been investigated, and may in fact support the theory that low-probability, but high Q-value, neutron reactions are the cause.

Prior to installation of the AmBe source used in this investigation (Ziegler, 2007) a similar measurement was performed with a slightly different configuration (Bradley et al., 2016) and was identical to that studied by Taggart (2007); Nicolaou (1983); Matthews (1979) with two AmBe sources ~20 cm apart. Therefore, in these previous studies, it is important to consider that there will be independent contributions from each separate source. The spikes were less likely to be observed either due to lower spatial resolution (Taggart, 2007; Nicolaou, 1983; Matthews, 1979) or the possibility of the effect of combining contributions from two sources in the water tank (Bradley et al., 2016).

4. Conclusions and further work

Determining the suitability of these commercial glass beads for a variety of dosimetric applications is an ongoing task. However, in the short term they have clearly demonstrated the ability to provide a dosimetric information with respect to the neutron tank. The immediate needs of this work come in four-fold:

1. Secondary calibration via AmBe “halo”.
2. Improved sophistication of Monte Carlo simulation.
3. Evaluation of the relative n/y bead sensitivity by repeated measurements with additional lead shielding.
4. Evaluation of the relative fast/thermal neutron sensitivity through cadmium shielding.

Where the “halo” configuration refers to a circular support to maintain a fixed source-bead distance, thereby ensuring that all beads receive an equal mixed radiation field dose. The potential source of the “quasi-regular” spikes could be uncovered through the above experiments. In particular, if the cause of the spikes is indeed neutron-induced charged-particle reactions we would expect to see a shift in position in future simulations; likewise, with the “halo” configuration spikes should be present if a reaction is the origin.

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References


Carbon nanotubes buckypaper radiation studies for medical physics applications

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HIGHLIGHTS

- Carbon nanotubes explored as a dosimeter for ionising radiation.
- The potential for application at therapy doses investigated.
- Predominant TL yield found between 180 and 250 °C.

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ABSTRACT

Graphite ion chambers and semiconductor diode detectors have been used to make measurements in phantoms but these active devices represent a clear disadvantage when considered for in vivo dosimetry. In such circumstance, dosimeters with atomic number similar to human tissue are needed. Carbon nanotubes have properties that potentially meet the demand, requiring low voltage in active devices and an atomic number similar to adipose tissue. In this study, single-wall carbon nanotubes (SWCNTs) buckypaper has been used to measure the beta particle dose deposited from a strontium-90 source, the medium displaying thermoluminescence at potentially useful sensitivity. As an example, the samples show a clear response for a dose of 2 Gy. This finding suggests that carbon nanotubes can be used as a passive dosimeter specifically for the high levels of radiation exposures used in radiation therapy. Furthermore, the finding points towards further potential applications such as for space radiation measurements, not least because the medium satisfies a demand for light but strong materials of minimal capacitance.

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1. Introduction

Since CNTs were first reported upon by Iijima on early 1990s (Iijima, 1991), the properties of carbon nanotubes have been the subject of intensive investigation and have been considered for many potential applications, such as chemical sensors (Kong et al., 2000; Moradi et al., 2013; Penza et al., 2010; Wongchoosuk et al., 2010; Zhao et al., 2005), biosensors (Timur et al., 2007; Balasubramanian and Burghard, 2006; Koehne et al., 2004; Li et al., 2003; Wang, 2005) field-emission displays (Talin et al., 2001; Saito, 2010; Lee et al., 2001; Kuznetzov et al., 2010; Choi et al., 1999), memory storage (Lu, Dai, 2006, Ganguly et al., 2005) and hydrogen storage (Yang et al., 2010; Ranjarbar et al., 2010; Liu et al., 2010). In particular, the structural arrangement of the atoms forming the carbon nanotubes give interesting physical and chemical properties such as electric and thermo conductivity. Carbon nanotubes, CNTs, can be described as a beehive sheet fabricated to form a cylinder, the two ends of the cylinder being open or closed with a semicircle lid. This cylinder-like form can be shielded by other cylinders with open ends to form a multi-wall carbon nanotubes structure, MWNTs. Fig. 1 displays single and multi-wall carbon nanotubes with open ends. The dimensions of the
structure are of the range of nanometres, the diameters ranging from a few nm up to 30 nm and the length of the tubes going up to ~1 μm (Iijima, 1991). These dimensions can vary depending on the method of growth and the procedure parameters (Nilhei et al., 2003).

In this study, carbon nanotube buckypaper was made at the University of Surrey, with irradiation by strontium-90, a source of beta rays. The thermoluminescence (TL) signal was obtained as the primary indicator of dose absorption.

Although the present work focuses entirely on TL studies, continuation of the work will clearly involve developing a fuller understanding of the basis of the TL signal, whether it be due to inherent defects as is possible in what is otherwise described as pristine material or due to the presence of impurities. Raman Spectroscopy is expected to provide one of the best methods in seeking to understand the basis of the TL signal from the carbon structure. Here, the ratio of the intensities in the Raman spectra D/ G bands can provide a measure of the defects that are present, with the G band being a result of in-plane vibrations of SP² bonded carbon atoms and the D band to out of plane vibrations that are attributable to the presence of structural defects. A greater intensity D band is indicative of disruption of SP² bonds of the carbon, an example being that of graphene oxide (GO), with GO having oxidative functional groups. More intense D bands would point to broken SP² bonds, indicative of an increase in SP³ bonds. More generally, a D band intensity greater than that in the pristine media could be due to a mixture of inherent defects and impurities, an increased D/G ratio showing there to be increased SP³ bonds.

1.1. Buckypaper samples

To enable the carbon nanotubes to be used as a passive radiation dosimeter they first need to be produced in such a way that they can be handled and used safely. For this, buckypaper can be made from the starting carbon nanotubes powder. Examples of buckypaper are illustrated in Fig. 2. The dimensions of the buckypaper can be controlled, dependent on the application and the interest prompting dose measurements. Typically the thickness of the buckypaper can be varied from few micrometres up to 0.5 mm.

Different qualities of single-wall carbon nanotubes, SWCNTs, were purchased from the company Unidym (Sunnyvale, CA, USA) in the form of powder. Raw SWCNTs, Pure SWCNTs, and Super Pure SWCNTs. Triton X-100 has been used as a surfactant.

2. Methods of preparation of the samples

As there were different purifications of SWCNTs, various concentrations of the surfactant and SWCNTs were used for each quality. Different concentrations of CNTs require different quantities of the surfactant. In this study the ratio by weight was the reference in the calculations. The optimum surfactant to CNT ratio has been found to be 5:1 to 10:1 by weight (Islam et al., 2003). In this work a 10:1 surfactant to CNT ratio was used to prepare all the samples. Dispersion of Triton X-100 in deionised water was prepared to suspend the single wall carbon nanotubes homogeneously. Measured quantities of the Triton X-100 and deionised water were added to a flask and a magnetic stirrer was used to stir the mixture. The dispersant bottle was placed in a cold bath, at a temperature from 3 to 6 °C and a tip sonication, Branson-Sonifier 150 was used for 30 min with a power range from 17 to 20 watt to mix the solution. If the sample is observed to include particle aggregation, centrifugation can be applied. The solution can then be filtered; here use has been made of a membrane filter, MCE MF-Millipore plain white, 0.22 μm pore size, diameter 7 mm. The buckypaper sample weights used herein were 1 mg, 4 mg and 5 mg for the raw, pure and super-pure SWCNTs respectively. The product buckypaper TL response can be compared against the typical mass of a TLD-100 (doped LiF) disc of 50 mg, a dosimeter popularly used in radiation medicine studies.

2.1. Strontium-90 source for beta irradiation of CNT samples

The various samples studied herein have been exposed to the beta-ray emissions from a strontium-90 source, the set-up being illustrated in Fig. 3. The source is retained within a plastic holder, contained within a lead-glass box to minimise radiation exposure to users. The CNTs and TLD-100 (LiF: Mg, Ti, used as a well-characterised reference TLD medium) samples have been placed in an aluminium tray. The aluminium tray is designed to hold samples of size 5 × 5 mm. As we have prepared different concentrations and quality of CNTs in the buckypaper, the edges of the tray are labelled by numbers and letters to help identify particular samples.

Buckypaper samples of various purities and concentration were irradiated in this experiment. Raw single-wall carbon nanotubes, pure single-wall carbon nanotubes, and super pure carbon nanotubes were used to form the various samples of buckypaper. The concentration of the CNTs in the dispersion used to form the buckypaper was 0.1, 0.1, and 0.05 g for raw, pure, and super pure single-wall carbon nanotubes respectively. These quantities were dispersed in 100 ml of deionized water through the use of Triton X-100. The three samples received a dose of 2 Gy each. It should be noted that the CNTs are non-transparent at the wavelengths emitted herein so that the TL signal is entirely off the top surface, the thickness of the buckypaper being immaterial.

3. Results and discussion

3.1. Raw single-wall carbon nanotubes

Fig. 4 illustrates the thermoluminescence (TL) signal from the buckypaper prior to any form of treatment, it being noted that in this instance the buckypaper was not annealed post-sample production, the background signal therefore representing the inherent defects that have been occupied as a result of issues such as strain and lattice dislocations. A time-temperature profile has been selected for the TLD reader, the set-up chosen for present measurement providing a ramp-rate of 6.5 °C s⁻¹ post pre-heat of 165 °C, with each channel number equivalent to a temperature
increment of 1.65 °C, starting at Channel Number 0 at 165 °C.

This measurement was required in order to enable comparison between the TL yield from a fresh unirradiated sample that had not been subject to any heat treatment and the TL yield from a sample treated with heat during an annealing and/or readout process. The sample consists of 0.1 g buckypaper (sample size 5 × 5 mm) formed of raw SWCNT dispersed in 100 ml of deionized water using Triton X-100. The multiple-peak signal profile is presumed to be a result of random defects created during the preparation of CNTs buckypaper samples, ranging from the superficial to deeper defects, reflected in the temperature required to enable release of trapped electron and lattice relaxation. This is supported by the fact that following annealing of the sample, the signal profile changes dramatically, the TL yield reducing by a factor of 21 (Fig. 5). The figure shows two profiles, one for the TL yield from a non-irradiated sample after an annealing process (the lower line), and the other the TL yield (represented by the prominent peak) from the sample following irradiation to a dose of 2 Gy, irradiated using the 90Sr beta source. The TL signal from the irradiated sample shows a pronounced TL response compared to that in the absence of irradiation. As previously reported, the TL signal was improved by a factor of in excess of 20 over that of the unirradiated sample. The TL yield (the so-called glow curve) was observed to be encompassed within a temperature range of 180–250 °C.

Another experiment was made in examining for the presence of any TL signal not released during the first readout procedure. Fig. 6 shows two curves, the peak illustrating the first readout and the lower line illustrating the second readout for the same raw SWCNT sample. From this, it is apparent that one heating cycle is sufficient to provide for complete de-excitation of the irradiated sample.

3.2. Pure and super-pure single-wall carbon nanotubes

Similar measurements were conducted for the pure SWCNTs and super-pure SWCNTs. Fig. 7 below illustrates the background reading for a fresh sample of the pure SWCNT that has not been exposed to radiation or heat treatment. The results are similar to that obtained for the raw SWCNT sample for both measurements, pre- and post-anneal. The TL yield from the annealed sample was practically identical to that provided by the raw SWCNT sample. However, comparing the response to irradiation of the raw and
pure SWCNT samples, the magnitude of the TL signal for the same irradiation dose has been observed to be lower for the pure SWCNT than that from the raw SWCNT, indicative of the presence of impurities in the latter.

This reduction in TL signal is expected as the former sample has been purified of iron and other elemental components. The absence of such impurity has a clear effect on the TL signal as can be seen in Figs. 5 and 6, compared with the signal obtained from the pure SWCNT buckypaper sample shown in Fig. 8.

Reduction in TL yield of some 3.8 was found for the irradiated pure SWCNT buckypaper compared with that from the irradiated raw samples as in Figs. 5 and 6.

Fig. 8 illustrates the first and second readings for the pure sample subsequent to irradiation to a dose of 2 Gy. The peak illustrates the result of the first reading cycle and the lower line illustrates that of the second read cycle, again supporting the previous sample results indicating little necessity for annealing when the sample is exposed to a dose in the range of several Gy although it would of course be important to do so for lesser doses.

Fig. 9 shows the TL yield for a fresh super-pure SWCNT buckypaper sample. The sample consists of buckypaper made of 0.05 g of Super-Pure Single-Wall Carbon Nanotubes dispersed in 100 ml of deionized water through the use of Triton X-100. The sample size was again 5 × 5 mm and again the sample was irradiated to a dose of 2 Gy using the 90Sr beta source. The graph is multi-peaked for the non-irradiated sample as obtained from raw and pure SWCNT buckypaper. However, this sample provides a greater TL yield than the pure SWCNT sample, being similar to the TL yield obtained from the raw SWCNT sample. This was not expected as the sample is super purified of impurities. However, as nitrogen is used in the process of purification of the samples, this increase is thought to be due to contamination during that process, the nitrogen atoms potentially causing increase in the trap centres in the sample.

Fig. 10 again shows two line profiles, the peak illustrating the TL yield from the super-pure SWCNT sample after exposure to 2 Gy using the 90Sr source, and the lower line illustrating the TL yield resulting from the second reading for the same sample. The TL yield from the super-pure sample is greater than the TL yield from the pure sample by factor of 2.2.

3.3. TLD-100

The response of TLD-100 (doped lithium fluoride) has been obtained for the same beta dose as that used for the SWCNT
were prepared for irradiation by a $^{90}$Sr beta emission source. TL buckypaper samples, residual clipping being observed even in selecting a factor of 10$^3$ increase in TL reader sensitivity setting, as carried out here, over that adopted for the SWCNT samples (Fig. 11).

It does need to be observed that the SWCNT samples were of lower mass than that of the TLD-100, ranging from 2% to 10% of the TLD-100 mass. Thus the mass-normalised relative response of the SWCNT to the TLD-100 were of the order of 2%.

4. Conclusion

Three types of SWCNT buckypaper, each of different purity, were prepared for irradiation by a $^{90}$Sr beta emission source. TLD-100 was used for comparison. The TL yield from the CNT samples indicate considerable potential for these media to be used as TL dosimeters, underlined by the fact that the response to varying purity buckypaper would need to be calibrated for. While the response of the buckypaper is less than that obtained from TLD-100, the results do suggest that the present preparations of CNTs have potential for use in dosimetry as in radiation therapy, a matter requiring further investigation.

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References


Lower limits of detection in using carbon nanotubes as thermoluminescent dosimeters of beta radiation

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\(^{SP_3}/^{SP_2}\) hybridization

ABSTRACT

World-wide, on-going intensive research is being seen in adaptation of carbon nanotubes (CNTs) for a wide variety of applications, particular interest herein being in the thermoluminescent (TL) properties of CNTs and their sensitivity towards energetic radiations. Using beta radiation delivering dose levels of a few Gy it has been observed in previous study that strain and impurity defects in CNTs give rise to significant TL yields, providing an initial measure of the extent to which electron trapping centres exist in various qualities of CNT, from super-pure to raw. This in turn points to the possibility that there may be considerable advantage in using such media for radiation dosimetry applications, including for in vivo dosimetry. CNTs also have an effective atomic number similar to that of adipose tissue, making them suitable for soft tissue dosimetry. In present investigations various single-wall carbon nanotubes (SWCNT) samples in the form of buckypaper have been irradiated to doses in the range 35–1.3 Gy, use being made of a\(^90\)Sr beta source, the response of the CNTs buckypaper with dose showing a trend towards linearity. It is shown for present production methodology for buckypaper samples that the raw SWCNT buckypaper offer the greatest sensitivity, detecting doses down to some few tens of mGy.

1. Introduction

Since the discovery of CNTs by Iijima (Iijima, 1991), the potential for their applications has encouraged a large numbers of studies, both across the underpinning sciences as well as across the technologies that enjoy associations with these, investigations of CNT being in terms of properties and their utilisation. In regard to the advantageous properties of CNTs, among these one can mention their unusually large electrical- and thermal-conductivities (Hone et al., 2000) as well as their very large tensile strengths (Yu et al., 2000). Concerning the latter aspect, it is to be further appreciated that the microscopic network of thin samples formed from the CNTs in the creation of buckypaper (Fig. 1) gives rise to considerable flexibility, allowing large damage-free shape change. These particular properties point in part to the possibility of CNTs being candidate media for thermoluminescence dosimetry of energetic radiations, not least for in vivo applications. A further fundamental aspect for CNTs to be potential TLD media is the need for trapping centres, forming one particular focus of present investigation. Among the alternative forms of dosimetry are also included active devices such as semiconductor diodes and graphite ion chambers, these representing electrical risks, particularly for in vivo work, also passive TLD systems based on phosphors, such as LiF, that due to their inherent hygroscopic nature also have limited prospects for in vivo applications. CNTs also have an effective atomic number similar to that of adipose tissue, making it suitable for soft tissue dosimetry.

In previous work by this group (Alanazi et al., 2016) the thermoluminescence signal was measured from samples of Single-Wall...
Carbon Nanotubes (SWCNTs) produced in the form of buckypaper, the samples being of varying purity. These aspects have been discussed in detail in the cited work. The samples (raw SWCNTs, pure SWCNTs, and super-pure SWCNTs) were irradiated by a $^{90}$Sr source to obtain various doses. In present work we have conducted further investigations of the materials, seeking to obtain a measure of the lower limit of detection (LLD) for the particular samples and their associated production methods. The doses used were in the range of 35 mGy to 1.3 Gy, the response of the CNT buckypaper against doses showing a trend towards linearity.

2. Methods of sample preparation

The buckypaper samples formed from SWCNTs were of three types: raw SWCNTs, pure SWCNTs and super-pure SWCNTs. The three different qualities of SWCNTs were purchased from Unidym (Sunnyvale, CA, USA), delivered in the form of powder. The method of buckypaper preparation was as discussed in the previously cited work (Alanazi et al., 2016). The surfactant Triton X-100 was used to disperse the SWCNTs. With deionised water a magnetic stirrer was used to maintain a suspension of the surfactant. Membrane filters (0.22 μm pore size and of diameter 47 mm; MCE MF-Millipore plain white) were purchased from Thermo Fisher Scientific (Waltham, MA, USA), filtering and accumulating the CNTs. High frequency ultrasound was used for dispersion of the mixture, use being made of a Branson tip sonication system (Danbury, CT, USA) Sonifier 150. The optimum surfactant to CNT ratio was found to be in the range 5:1 to 10:1 by weight (Islam et al., 2003). In this and previous work, a surfactant to CNT ratio of 10:1 was used to prepare the various samples. The concentration of the single-wall carbon nanotubes in the dispersion that was used to form the buckypaper were 0.1, 0.1, and 0.05 g for raw, pure, and super pure single-wall carbon nanotubes respectively. These quantities were dispersed in 100 ml of deionized water through the use of Triton X-100 as previously mentioned.

Surface roughness and variability in the buckypaper samples as shown in Fig. 2 indicate considerable variability in the amount of CNTs deposited in the surface of buckypaper. Normalization for surface roughness can be expected to lead to reduction in the variability in response to dose.

2.1. Strontium-90 source for beta irradiation of CNT samples

Exposure of the CNTs samples was carried out in the radiation laboratory, University of Surrey. A $^{90}$Sr beta source of approximate activity 95 MBq was used to irradiate the various CNTs samples, raw, pure, and super-pure. In order to minimise exposure to the user, the source was located within a box shielded by lead. The samples were positioned in a rotating disk that can accommodate 26 individual samples within it, each labelled to identify the individual samples. The set-up is as shown in Fig. 3. The different qualities of single-wall carbon nanotubes have been exposed to the beta-ray emissions to provide doses of 0.02, 0.035, 0.627, 0.836, and 1.245 Gy.

3. Results and discussion

3.1. Glow curve of the CNTs samples

Fig. 4 above shows the glow curves obtained for the irradiated CNT buckypaper samples for doses within the quoted range, the TL yields being observed to be encompassed within the temperature range 180–250 °C. The absence of noticeable differences in shape or distribution of TL yield with dose is indicative of an essentially identical trap centre activation energy distribution over the particular dose range. The temperatures have been made to ramp from room temperature to the maximum value of some 397 °C at a ramp rate at 6.5 °C per second, leading to an ability to discern above-background glow curves for doses down to 35 mGy, extending to 1.3 Gy, allowing the samples to be considered to be of utility for radiotherapy dosimetric applications. Thus said, we have also observed a reproducible hyper-response at 0.2 Gy of the order of four times greater than that obtained at any other dose within the dose range. The more general trend, in response to the
various doses, in the absence of this hyper-response was found to be linear across the dose range (Fig. 5), albeit with considerable variability; further investigation is required in seeking to understand the origin of the hyper-response. Note should be taken that each point in the graph is the mean of three measurements made on three individual samples irradiated under the same conditions.

3.2. Energy response

In Fig. 4 the lower line in the graph represents the dose response for the super-pure SWCNTs, that above it the dose response for the pure SWCNTs and the upper line represent the dose response for the raw SWCNTs. The inset to the figure displays the hyper response observed at 0.2 Gy. As can be seen in the graph the dose response is generally proportional with dose, trending toward linearity for the three samples, raw, pure, and super-pure single-wall CNTs. The raw sample provides the greatest response, a matter supported by Energy Dispersive X-Ray Analysis (EDX) examining the purity of samples provided by the manufacturer. Fig. 5 shows EDX analysis for the raw SWCNTs, the Fe content in the raw sample being some 17.2 wt%, considerably greater than that for the pure and super-pure samples, at 11.7 and 7.6 wt% respectively. These quantities are a reflection of the number of trapping centres within each sample. As such, the raw samples produce a commensurately large TL yield; conversely the super-pure samples, greatly purified from impurities, produces a commensurately low TL yield.

Other contributions to the TL yield can be interpretation to a rise as a result of hybridization between the carbon atoms themselves and between the carbon atoms with other atoms within the sample. Changes in the state of the electron orbitals, in particular SP² and SP³ bonds, cause the electron orbitals to change from SP² to SP³ hybridization, the latter having greater energy level. When there is sufficient energy to break this hybridization, photons will be released.

From EDX analysis for the raw, pure, and super-pure SWCNTs (Fig. 6 and Table 1), the weight percentage of carbon were found to be 68.2%, 72.1%, 74.1% respectively. The remaining impurities are dominated by Fe and O₂. Fluorine, Al, SiO₂, and Ca were found in amounts of less than 1%. The oxygen weight percentage for the raw, pure, and SP SWCNTs were 13.5%, 15.1%, 15.5% respectively. These impurities contribute to the charge centres localization and induce the SP² to SP³ hybridization as mentioned earlier. 3.3. X-ray photoelectron spectroscopy

To account for the change in the ratio of the SP² to SP³ hybridization before and after irradiation, XPS (Beamson and Briggs, 1992) analyses were performed on a ThermoFisher Scientific (East Grinstead, UK) Theta Probe spectrometer. XPS spectra were acquired using a monochromated Al Kα X-ray source (hν=1486.6 eV). An x-ray spot of ~400 µm radius was employed. Survey spectra were acquired employing a pass energy of 300 eV. High resolution, core level spectra for C1s and O1s were acquired with a pass energy of 50 eV. High resolution, core level spectra for Fe2p and Si2p were acquired with a pass energy of 50 eV. Quantitative surface chemical analyses were calculated from the high resolution, core level spectra following the removal of a non-linear (Shirley) background. The manufacturer Avantage software was used, incorporating the appropriate sensitivity factors also correcting for the electron energy analyser transmission function. The best fit C 1s

Fig. 4. TL yield for the CNTs (the glow curve), encompassed within the temperature range 180–250 °C.

Fig. 5. Comparison between the energy response for raw, pure, and super-pure (SP) SWCNTs. The TL yield divided by 1 million to normalize the numbers on the scale of Y-axis. The inset displays the hyper-sensitivity observed at low doses.
(Kaciulis, 2012) was acquired with a centre peak binding energy for the SP2 of 284.4 eV and with a shift of 0.4 eV. The SP3 peak was located at binding energy 284.8 eV.

The results show an increase in the SP3/SP2 hybridization ratio for a sample exposed to a dose of some 0.4 Gy. As can be clearly seen in the displayed example of the peak fitted for C 1 s for the super-pure SWCNTs sample, Figs. 7 and 8 display the peak associated with the SP3 and SP2 hybridization before (Fig. 7) and after (Fig. 8) irradiation. This increase in the SP3 hybridization has been found in the pure and raw samples, with quantitative data provided in Table 2 showing the increase in the SP3/SP2 hybridization ratio for the sample after irradiation.

From Table 2, SP3/SP2 hybridization ratio pre-irradiation for the raw, pure, and super-pure SWCNT samples were 44%, 22%, and 25% respectively, increasing post-irradiation by factors of 1.8, 1.9, and 2.7 respectively.

This change in the orbitals within the carbon atoms leads to increased molecular strain, reflected in the molecular binding energy.

With the sample heated to temperatures > 250 °C, SP3 hybridization can change to SP2 hybridization, with energy release in the form of photons. This luminescence has been observed by the group of Chruścińska, referred to them as relaxoluminescence (Chruścińska et al., 2006). While this relaxoluminescence contributes to the thermo-

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**Table 1**

Quantitative EDX Results for raw, pure and super-pure SWCNT, obtained using an accelerating potential of 15 kV and magnification power of 50.

<table>
<thead>
<tr>
<th>Elements Line</th>
<th>Raw sample</th>
<th>Pure sample</th>
<th>Super-pure sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%Norm.</td>
<td>wt% Err</td>
<td>wt%Norm.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>wt%Norm.</td>
</tr>
<tr>
<td>C K</td>
<td>68.22 ± 0.35</td>
<td>± 0.35</td>
<td>72.14 ± 0.35</td>
</tr>
<tr>
<td>O K</td>
<td>13.54 ± 0.28</td>
<td>± 0.28</td>
<td>15.51 ± 0.21</td>
</tr>
<tr>
<td>Al K</td>
<td>0.16 ± 0.02</td>
<td>± 0.02</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>Si K</td>
<td>0.31 ± 0.02</td>
<td>± 0.02</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td>Ti K</td>
<td>0.59 ± 0.04</td>
<td>± 0.04</td>
<td>0.31 ± 0.02</td>
</tr>
<tr>
<td>Fe K</td>
<td>17.18 ± 0.27</td>
<td>± 0.27</td>
<td>11.71 ± 0.26</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

---

**Table 2**

Percentage change in the ratio of hybridization from SP2 to SP3 (SP3 / SP2) for the raw, pure, and super-pure SWCNT samples pre and post irradiation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Raw SWCNTs</th>
<th>Pure SWCNTs</th>
<th>Super-Pure SWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-irradiation</td>
<td>44%</td>
<td>22%</td>
<td>25%</td>
</tr>
<tr>
<td>Post-irradiation</td>
<td>80%</td>
<td>43%</td>
<td>69%</td>
</tr>
</tbody>
</table>

---

**Fig. 6.** Energy Dispersive X-Ray Analysis (EDX), showing the various elements present in the raw SWCNT samples.

**Fig. 7.** X-ray Photoelectron Spectroscopy for the super-pure SWCNTs sample pre-irradiation, showing the separate SP2 and SP3 peaks.

**Fig. 8.** X-ray Photoelectron Spectroscopy for the super-pure SWCNTs sample post-irradiation. The peak of the SP3 and SP2 are displayed.
luminescence signal it remains apparent that greater contribution can be obtained through the addition of impurity to the samples, as clearly shown from the response of the raw SWCNT sample.

4. Conclusion

Three types of single-wall CNTs were formed into buckypaper, with each of different impurity and prepared for irradiation using a $^{90}$Sr source. The samples, irradiated to different doses from 35 mGy to 1.245 Gy, show the TL yield from the single-wall CNT buckypaper samples to be generally proportional to the dose deposited in the sample, albeit with an as-yet unexplained hyper-sensitivity at 0.2 Gy. While SP$^3$ to SP$^2$ hybridization in carbon provides a strain-related contribution to the TL signal from irradiated samples, the greater contribution to the overall TL signal can be obtained from impurity, in the present case predominantly from Fe. The general response indicates considerable potential for the raw CNT media to be used in radiotherapy dosimetric applications, although there remains a need to develop means for control of surface roughness of the buckypaper CNTs in order to obtain more uniform response.

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References


Novel dosimetric study of the sp² to sp³ hybridisation ratio in free-standing carbon nanotubes buckypaper

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Carbon nanotubes

ABSTRACT
Over the past several years a great deal of research has focused on the adaptation of carbon nanotubes (CNTs) for a wide range of applications, including as gas detectors, in energy storage, for various photonics purposes, also as radiation sensors. In previous studies by this group, investigating thermoluminescent (TL) properties, the sensitivity of CNTs towards ionising radiations has been observed using beta radiation at dose levels from fractions of a Gy and more. Strain and impurity defects in CNTs give rise to substantial TL yields, the extent to which electron trapping centres exist varying inversely with the quality of CNT, from super-pure to pure to raw. In present study the contribution to TL of beta particle irradiated CNTs has been investigated with respect to changes in the lattice atomic orbitals, pointing to the possibility of a new radiation dosimetry method. The surface-sensitive method, one highly suited to the thin (few tens of µm thick) CNT samples produced in the form of free-standing buckypaper, is based on use of the X-Ray Photoelectron Spectroscopy (XPS) technique, evaluating sp² to sp³ hybridisation. The CNT samples have been examined subsequent to irradiation using a relatively large activity ⁹⁰Sr/⁹⁰Y radionuclide source (Eβ = 0.546 MeV/2.28 MeV), delivering doses in the range 0.2–6 Gy, in all three qualities sp² to sp³ hybridisation being observed to increase with dose deposition. Considerable advantage is seen in making use of such thin CNTs in dosimetry, rendering them particularly suitable for beta particle soft tissue dosimetry.

1. Introduction
In previous investigations (Alanazi et al., 2016b) various single-wall carbon nanotubes (SWCNT) samples in the form of buckypaper have been irradiated to doses up to 1.3 Gy, use being made of a ⁹⁰Sr beta source, the TL response of the CNT buckypaper showing linearity with dose. For the presently adopted buckypaper production methodology it has been shown that raw SWCNT buckypaper provides the greatest sensitivity, detecting doses down to some 30 mGy. In present study, as an alternative technique to TL, the change in carbon orbital bonding from sp² to sp³ (referred to as hybridisation) has been investigated as a novel method of dosimetry. In this, use has been made of X-Ray Photoelectron Spectroscopy (XPS), values of hybridisation increasing with deposited dose. The novel application, making use of thin (few tens of microns) free-standing CNTs is eminently suitable for skin dosimetry, the method of analysis being one that is well established (Mezzi and Kaciulis, 2010).

1.1. X-ray photoelectron spectroscopy (XPS)
XPS is well known for its ability to provide chemical state information, relying in the main on initial state effects (as in the case of polymers) or sometimes final-state effects that can become very strong in the case of some metal oxides. XPS in its usual mode of operation considers the chemical shift of core level electron orbitals, as we do in this paper. Being a relaxation process XPS can lead to the generation of...
X-ray induced Auger electron transitions (known as X-AES). As an Auger transition is a three-electron process, for carbon materials the valence electrons are involved as the transit and emitted electrons. This means that the chemical effects present in the valence band electrons are also present (in a heavily convoluted manner) in the CKLL transition (where the L electrons are of course valence electrons). In order to extract such information a common approach, described in detail by (Mezzi and Kaciulis, 2010) is to take the first differential of the CKLL Auger spectrum and define a so-called D-Parameter. This is the distance (in electron volts) between the maximum and minimum excursions in the CKLL Auger spectrum. Such a measurement has been shown to be extremely sensitive to carbon hybridisation, as a result of the influence of the C2p and C2s electrons in the Auger transition. As many authors have shown there is a linear relationship between the value of the D-Parameter and the extent of sp2 and sp3 hybridisation (see for instance, Caschera et al., 2013; Kaciulis, 2012; Mezzi and Kaciulis, 2010). We have used this method to illustrate subtle changes that occur on the surface of the CNT as a function of treatment.

Use of XPS enables exploration of the effects of ionising radiation on the structure of CNTs. In particular, XPS is a surface sensitive technique that provides quantitative spectroscopic measurements of elemental composition, also providing information on the chemical/electronic configurational state of the surface of the target medium. XPS spectra are acquired by exposure of the material to X-ray radiation, simultaneously measuring the kinetic energy and number of electrons that travel from the upper-most surface of the material (0–10 nm) via use of an electron energy analyser detector. The technique requires relatively high vacuum conditions (~1 x 10−7 millibar) and reference to the D-Parameter, the latter based on separation of the two maxima observed in the X-ray excited carbon KLL transition. This has been used to estimate the hybridisation ratio (sp2/sp3), representing the change in orbital bonding with respect to dose received. Fig. 1 illustrates hybridisation of the carbon atom orbitals. The study has been carried out for three different purities of CNT sample, raw, pure and super-pure, each exposed to various doses.

2. Experimental

The XPS technique has been used to explore the surface structure samples of single-wall carbon nanotubes (SWCNTs) of various degrees of purity, raw, pure and super-pure. In present investigations the buckypaper samples have been irradiated with beta-particle ionising radiation, use being made of a 90Sr irradiator. The rationale for this choice has been to ensure dose deposition throughout the buckypaper, of purity, raw, pure and super-pure. In present investigations the SWCNT samples have been measured at various doses (i.e. 100, 200 and 500 Gy) and reference to the D-Parameter is made of the fact that graphite is 100% sp2 while diamond is 100% sp3, both used as reference values for the sp2 and sp3 ratio such that any D-Parameter value. Here use has been made of the fact that graphite is 100% sp2 while diamond is 100% sp3, both used as reference values for the sp2 and sp3 ratio such that any D-Parameter value can be assessed using the plot of Fig. 4, showing the fractional change from sp2 to sp3, typically referred to as hybridisation, can be assessed using the plot of Fig. 4, showing the degree of sp2 to sp3 hybridisation. For all three qualities of CNT, the ratio sp2/sp3 shows an exponential-like dose-dependent response (see for example, Fig. 3), the functional dependency differing from sample to sample, a reflection of sample variation, including level of impurity, thickness and surface roughness. Fitting by non-linear least-squares to the proposed exponential form shown in Eq. (1) has been carried out, aided in so doing through use of the Python package SciPy data analysis toolkit "Jones, 2001" in evaluation of the parameters A, b and c. The correlation coefficient R2 and test of significance p has been quoted in each case. Specifically, fitting has been made to equations of the form:

\[ y = Ax^{b} + c \]  

with y the D-Parameter, x the dose and A, b, c constants for the particular sample and type (raw, pure or super-pure). Such exponential behaviour has also been reported by (McEnaney and Wickham, 1996) in their study of degradation of nuclear graphite properties.

3. Results

For all three qualities of CNT, the ratio sp2/sp3 shows an exponential-like dose-dependent response (see for example, Fig. 3), the functional dependency differing from sample to sample, a reflection of sample variation, including level of impurity, thickness and surface roughness. Fitting by non-linear least-squares to the proposed exponential form shown in Eq. (1) has been carried out, aided in so doing through use of the Python package SciPy data analysis toolkit "Jones, 2001" in evaluation of the parameters A, b and c. The correlation coefficient R2 and test of significance p has been quoted in each case. Specifically, fitting has been made to equations of the form:

\[ y = Ax^{b} + c \]  

with y the D-Parameter, x the dose and A, b, c constants for the particular sample and type (raw, pure or super-pure). Such exponential behaviour has also been reported by (McEnaney and Wickham, 1996) in their study of degradation of nuclear graphite properties.

3.1. Raw single-wall carbon nanotubes samples

For preparation of raw sample A, use was made of 0.1 g of CNT, 80 ml of deionised (DI) water and 1 g of Triton X-100 (TX-100) to act as surfactant, see (Alanazi et al., 2016a) for more details of the method of preparations. The curve fitting parameters were: [A = 3.5 eV, b = 0.38, c = 17.5 eV]. Each data point presented in Fig. 3 is the average of three separate measurements, the standard error in D being 0.2 eV.

The fractional change from sp2 to sp3, typically referred to as hybridisation, can be assessed using the plot of Fig. 4, showing the percentage sp2 associated with each D-Parameter value. Here use has been made of the fact that graphite is 100% sp2 while diamond is 100% sp3, both used as reference values for the sp2 and sp3 ratio such that any D-Parameter value can then be measured accordingly. As can also be seen in Fig. 3, measured D-Parameter values associated with given doses can be projected in Fig. 4 to calculate the sp2 to sp3 hybridisation. Table 1 shows the quantitative data for raw sample A, the change of hybridisation and D-values associated with the deposited doses being provided. The D-Parameter values for the sample at zero and at 5.85 Gy
were 21.1 eV and 17.8 eV respectively.

Fig. 5 displays the D-Parameter value vs dose for raw sample D, being of the same purity category as that of sample A but differing in regard to the preparation process, with a greater quantity of SWCNTs being used; 0.14 g of CNTs, with 100 ml of DI-water and 1 g of Tx-100. The resulting equation fitting parameters were: \([A = 3.1 \text{ eV}, b = 0.53, c = 18.1 \text{ eV}]\), with again each data point representing the average of three measurements and a standard error in D of 0.2 eV. The decrease in the value of the D-Parameter with dose is similar to that seen in raw sample A, indicative of a technique robust against such concentration variations.

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% sp²</th>
<th>% sp³</th>
<th>D-value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>84.1</td>
<td>15.9</td>
<td>21.1</td>
</tr>
<tr>
<td>0.21</td>
<td>80.1</td>
<td>19.9</td>
<td>20.8</td>
</tr>
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<td>0.63</td>
<td>74.5</td>
<td>25.5</td>
<td>20.3</td>
</tr>
<tr>
<td>1.05</td>
<td>68.9</td>
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<td>19.8</td>
</tr>
<tr>
<td>3.50</td>
<td>55.7</td>
<td>44.3</td>
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</tr>
<tr>
<td>5.85</td>
<td>46.8</td>
<td>53.2</td>
<td>17.8</td>
</tr>
</tbody>
</table>

Table 1

Quantitative results for raw sample A for different doses.
variation. Fig. 6 exhibits the dose-dependent measured D-Parameter values for raw sample D as a function of sp².

Table 2 shows the quantitative data for raw sample D; at zero and at 5.85 Gy the D-values were 21.1- and 18.3 eV respectively.

Fig. 7 shows the D-Parameter values vs dose for raw sample H, formed using 0.12 g of CNTs, 100 ml of DI-water, 1 g of Tx-100, with associated fitting parameters \([A = 3.5 \text{ eV}, b = 0.59, c = 17.6 \text{ eV}]\). Again, each data point is the average of three measurements, the standard error again being 0.2 eV. The fitting parameter values lie between those of A and D as expected of a medium of intermediate concentration of SWCNTs. Fig. 8 displays the percentage sp² associated with each dose dependent D-Parameter value.

Table 3 provides quantitative data for raw sample H, with D-Parameter values at 0 and 5.85 Gy of 21.1- and 17.7 eV respectively.

### 3.2. Pure single-wall carbon nanotubes

Fig. 9 shows the D-Parameter values vs dose for pure sample B1, of

Table 2

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of sp² hybridisation</th>
<th>% of sp³ hybridisation</th>
<th>D-Parameter value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>81.7</td>
<td>16.3</td>
<td>21.1</td>
</tr>
<tr>
<td>0.21</td>
<td>82.8</td>
<td>17.2</td>
<td>21.0</td>
</tr>
<tr>
<td>0.63</td>
<td>75.1</td>
<td>24.9</td>
<td>20.3</td>
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<td>1.05</td>
<td>67.4</td>
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<td>19.6</td>
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<td>3.50</td>
<td>56.8</td>
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<td>5.85</td>
<td>52.5</td>
<td>47.5</td>
<td>18.3</td>
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</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of sp² hybridisation</th>
<th>% of sp³ hybridisation</th>
<th>D-Parameter value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>84.1</td>
<td>15.9</td>
<td>21.1</td>
</tr>
<tr>
<td>0.21</td>
<td>78.4</td>
<td>21.6</td>
<td>20.6</td>
</tr>
<tr>
<td>0.63</td>
<td>71.6</td>
<td>28.4</td>
<td>20.0</td>
</tr>
<tr>
<td>1.05</td>
<td>64.8</td>
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</tr>
<tr>
<td>5.85</td>
<td>45.5</td>
<td>54.5</td>
<td>17.7</td>
</tr>
</tbody>
</table>

Fig. 7. Dose dependent D-Parameter values for raw sample H, made using 0.12 g of CNTs, with 100 ml of DI-water and 1 g of Tx-100, \([R^2 = 0.941, p = 0.005]\).
comparative purity compared to that of raw and super-pure using the Energy Dispersive X-ray (EDX) facility of a Scanning Electron Microscope as in Table 4 below.

For preparation of pure samples B1 use was made of 0.05 g of CNTs, 100 ml of DI-water and 0.5 g of Tx-100. With this change in preparation the resulting equation fitting parameters were: \(A = 6.3 \text{ eV}, b = 0.20, c = 14.9 \text{ eV}\), with each data point the average of three measurements and with standard error 0.2 eV. The value of the D-Parameter decreases with dose in similar fashion to that previously described but with fitting parameter A differing by approaching a factor of 2 compared to the raw samples, a matter that will be more fully rationalised in the discussion section. The situation is that larger mean D-Parameter values are obtained at the lower dose point values compared to the raw samples, a matter that will be more fully rationalised in the discussion section. For preparation of pure samples B1 use was made of 0.05 g of CNTs, 100 ml of DI-water and 0.5 g of Tx-100. With this change in preparation the resulting equation fitting parameters were: \(A = 6.3 \text{ eV}, b = 0.20, c = 14.9 \text{ eV}\), with each data point the average of three measurements and with standard error 0.2 eV. The value of the D-Parameter decreases with dose in similar fashion to that previously described but with fitting parameter A differing by approaching a factor of 2 compared to the raw samples, a matter that will be more fully rationalised in the discussion section. The situation is that larger mean D-Parameter values are obtained at the lower dose point values compared to the raw samples, a matter that will be more fully rationalised in the discussion section. The situation is that larger mean D-Parameter values are obtained at the lower dose point values compared to the raw samples, a matter that will be more fully rationalised in the discussion section.

Table 4

<table>
<thead>
<tr>
<th>Raw samples</th>
<th>Pure samples</th>
<th>Super-Pure samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element/Line</td>
<td>Norm. wt%</td>
<td>Norm. wt% Err</td>
</tr>
<tr>
<td>CK</td>
<td>68.2 ± 0.3</td>
<td>72.1 ± 0.4</td>
</tr>
<tr>
<td>O K</td>
<td>13.5 ± 0.1</td>
<td>15.5 ± 0.2</td>
</tr>
<tr>
<td>Al K</td>
<td>0.16 ± 0.1</td>
<td>0.10 ± 0.15</td>
</tr>
<tr>
<td>Si K</td>
<td>0.31 ± 0.1</td>
<td>0.10 ± 0.15</td>
</tr>
<tr>
<td>Ti K</td>
<td>0.59 ± 0.1</td>
<td>0.30 ± 0.15</td>
</tr>
<tr>
<td>Fe K</td>
<td>17.2 ± 0.3</td>
<td>11.7 ± 0.4</td>
</tr>
</tbody>
</table>

Table 5

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of sp(^2) hybridisation</th>
<th>% of sp(^3) hybridisation</th>
<th>D-Parameter value (eV)</th>
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</thead>
<tbody>
<tr>
<td>Zero</td>
<td>85.2</td>
<td>14.8</td>
<td>21.2</td>
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<tr>
<td>0.21</td>
<td>81.8</td>
<td>18.2</td>
<td>20.9</td>
</tr>
<tr>
<td>0.63</td>
<td>77.3</td>
<td>22.7</td>
<td>20.5</td>
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<tr>
<td>1.05</td>
<td>71.6</td>
<td>28.4</td>
<td>20.0</td>
</tr>
<tr>
<td>3.50</td>
<td>48.9</td>
<td>51.1</td>
<td>18.0</td>
</tr>
<tr>
<td>5.85</td>
<td>35.2</td>
<td>64.8</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Table 6

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of sp(^2) hybridisation</th>
<th>% of sp(^3) hybridisation</th>
<th>D-Parameter value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>81.8</td>
<td>18.2</td>
<td>20.9</td>
</tr>
<tr>
<td>0.21</td>
<td>77.3</td>
<td>22.7</td>
<td>20.5</td>
</tr>
<tr>
<td>0.63</td>
<td>73.9</td>
<td>26.1</td>
<td>20.2</td>
</tr>
<tr>
<td>1.05</td>
<td>69.3</td>
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</tr>
<tr>
<td>3.50</td>
<td>50.0</td>
<td>50.0</td>
<td>18.1</td>
</tr>
<tr>
<td>5.85</td>
<td>37.5</td>
<td>62.5</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Fig. 10. Percentages of sp\(^2\) associated with the D-Parameter values for pure sample B1.

Fig. 11. D-Parameter values vs dose for pure sample B2, prepared using 0.05 g of CNTs, 100 ml DI-water and 0.5 g of Tx-100, \(R^2 = 0.991, p < 0.001\).

Fig. 12. The percentages of sp\(^2\) associated with the D-Parameter values for pure sample B2.

Parameter values at zero and at 5.85 GY were 20.9 eV and 17.0 eV respectively (Fig. 12).

Fig. 13 shows the D-Parameter values vs dose for pure sample F, a sample of similar impurity to that of the B samples as in Table 4. For its preparation the following quantities were used: 0.03 g of CNTs, 50 ml DI-water and 0.3 g of Tx-100. The resulting equation fitting parameters...
were: \[A = 20.8 \text{ eV}, b = 0.03, c = 0.0 \text{ eV}\]. Each data point is the average of three measurements and the standard error is 0.2 eV for all samples. The fitted curve shows a greater degree of linearity compared to pure samples B1 and B2, with the fitting of the curve restricted to just the first two terms of the exponential expansion. Fig. 14 displays the measured D-Parameter values associated with given doses together with the \(sp^2\) to \(sp^3\) hybridisation.

Table 7 shows the quantitative data for pure sample F. The change of hybridisation and D-Parameter values associated with the deposited doses are shown. The D-Parameter values for the sample at zero and at 5.85 Gy were 20.7 eV and 17.8 eV respectively.

### 3.3. Super-pure single-wall carbon nanotubes samples

Fig. 15 shows the D-Parameter values vs dose for super-pure sample G1. Sample preparation was similar to that for pure sample F, using: 0.03 g of CNTs, 50 ml DI-water and 0.3 g of Tx-100. The resulting equation fitting parameters were: \[A = 41.8 \text{ eV}, b = 0.02, c = 2.04 \text{ eV}\], again with each data point being the average of three measurements and standard error of 0.2 eV. The fitted curve for the G1 sample shows a greater degree of linearity compared to the raw samples and pure samples B1 and B2, with a similar trend to that observed for the pure sample F. Fig. 16 displays the measured D-Parameter values associated with given doses together with the \(sp^2\) to \(sp^3\) hybridisation.

Table 8 shows the quantitative data for super-pure sample G1. The D-Parameter values for the sample at zero and at 5.85 Gy were 20.5 eV and 18.9 eV respectively.

Fig. 17 shows the D-Parameter values vs dose for super-pure sample G2. For preparation of the super-pure sample G1 similar quantities to that for pure sample F were used, as follows: 0.03 g of CNTs, 50 ml DI-water and 0.3 g of Tx-100. The resulting equation fitting parameters were: \[A = 58.4 \text{ eV}, b = 0.14, c = 16.3 \text{ eV}\]. Each data point presented is the average of three measurements and the standard error is 0.2 eV. The fitted curve for the G2 sample shows similar curvature to that of pure samples B1 and B2 and the raw samples. Table 9 shows the quantitative data for super-pure sample G2. The

### Table 7

Quantitative results for pure sample F for different doses.

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of (sp^2) hybridisation</th>
<th>% of (sp^3) hybridisation</th>
<th>D-Parameter value (eV)</th>
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</thead>
<tbody>
<tr>
<td>Zero</td>
<td>79.5</td>
<td>20.5</td>
<td>20.7</td>
</tr>
<tr>
<td>0.21</td>
<td>78.4</td>
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<td>20.6</td>
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<tr>
<td>0.63</td>
<td>76.1</td>
<td>23.9</td>
<td>20.4</td>
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<td>1.05</td>
<td>74.4</td>
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<td>3.50</td>
<td>58.5</td>
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<tr>
<td>5.85</td>
<td>46.8</td>
<td>53.2</td>
<td>17.8</td>
</tr>
</tbody>
</table>

### Table 8

Quantitative results for super-pure sample G1 for different doses.

<table>
<thead>
<tr>
<th>Dose (Gy)</th>
<th>% of (sp^2) hybridisation</th>
<th>% of (sp^3) hybridisation</th>
<th>D-value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>77.3</td>
<td>22.7</td>
<td>20.5</td>
</tr>
<tr>
<td>0.21</td>
<td>76.1</td>
<td>23.9</td>
<td>20.4</td>
</tr>
<tr>
<td>0.63</td>
<td>75.0</td>
<td>25.0</td>
<td>20.3</td>
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<tr>
<td>1.05</td>
<td>73.9</td>
<td>26.1</td>
<td>20.2</td>
</tr>
<tr>
<td>3.50</td>
<td>65.9</td>
<td>34.1</td>
<td>19.5</td>
</tr>
<tr>
<td>5.85</td>
<td>59.1</td>
<td>40.9</td>
<td>18.9</td>
</tr>
</tbody>
</table>
D-Parameter values for the sample at zero and at 5.85 Gy were 20.3 eV and 18.1 eV respectively (Fig. 18).

4. Discussion

By projecting the D-Parameter values in association with dose, a process exemplified in the graph of Fig. 3 and graphs thereafter, one can observe a regularity of change in the percentages of sp² and sp³. In particular, the sp² hybridisation, expressed as the ratio sp²/sp³, reduces for increasing radiation dose, a behaviour that has been observed for all of the samples investigated herein, be they raw, pure or super-pure. Similar such behaviour in terms of the reduction of sp² has previously been observed in the study of (Bardi et al., 2017), for samples of SWCNT exposed to x-ray radiation, at doses of 20 cGy and 45 cGy, for a technique based on measurement of accumulated charge. The Bardi study investigated changes in the structure of the SWCNT in powder form, investigations focusing both on change of structure and the effect on raw SWCNTs as a potential device in active dosimetry, such as that of the ion chamber. Apparent from present analysis is that the reduction in sp² varies from sample-type to sample-type (raw, pure and super-pure) being attributable to the level of impurity, thickness and roughness of the surface, affected as these are by the process of sample preparation.

Fig. 3 has depicted the relationship between the deposited dose and the change in the D-Parameter value (sp²/sp³) for raw sample A. Over the dose range from zero up to 5.85 Gy, the D-Parameter value shows exponential reduction with increasing deposited dose. The change of sp² to sp³ has subsequently been evaluated using the plot of Fig. 4, illustrating the percentages of sp² associated with particular D-Parameter value, also making use of the fact that graphite is 100% sp² while diamond is 100% sp³. In accord with this, test has been made of whether any dose dependent D-Parameter value can be measured from the linear fit between the diamond and graphite, a matter that has been demonstrated not only for all of the raw samples, but also for all of the other sample types tested herein, as further summarised below. From the results for the raw samples it has further been shown that there is a standard exponential reduction in D-Parameter value with deposited dose. The change in D-Parameter value can be measured with deposited dose, indicative of the degree of sp² to sp³ hybridisation. For the raw samples the D-Parameter value varied from 21.1 eV to 17.7 eV. At zero dose the carbon nanotube walls contain carbon bonding of some 84% sp² and 16% sp³ hybridisation. Depositing 0.21 Gy of beta particle dose is seen to lead to a reduction of sp² from 84% to ~ 80% and enhancement of sp³ to 20%.

When comparing the raw sample dose-dependent D-Parameter value curves against those for the pure and super-pure samples, with increasing purity it can be seen that the curves trend towards a more linear dependency. This phenomenon, attributed to the impurities in the raw samples, accords with EDX analysis, showing the raw samples to have greater amounts of iron in them than the pure and super-pure, at 17.2%, 11.7% and 7.6% respectively.

For graphite, the lowest energy required for carbon atom displacement, on the c-axis direction, was found by (Banhart et al., 1997) to be...
15–20 eV. Another study suggests the threshold energy required for carbon atom displacement in graphite 15–17 eV (Krasheninnikov and Nordlund, 2004). Yet another threshold value for carbon atom displacement for SWCNT was reported to be 16.9 eV (Cress et al., 2010). Simmons reported the value to be 25 eV in neutron damaged graphite, cited in (Marsden, 1996). Conversely, for diamond, another form of carbon, the displacement threshold has been reported to be 30–48 eV (Bourgoin and Massarani, 1976; Koike et al., 1992). Thus said, graphite is formed from two different chemical bonds on each plane, a van der Waals bonds that links the basal planes and covalent bonds that work within the planes; Banhart has subsequently pointed out that SWCNTs are the smallest graphite-based structure, their specific geometry allowing them to be unaffected by van der Waals forces (Banhart, 1999).

From these studies in graphite it has been estimated by the group of Banhart that the threshold energy required to displace a carbon atom in the walls of the SWCNTs is in the range 15–20 eV, estimated assuming the lack of van der Waals bonds between the graphite layers in the SWCNTs (see Fig. 19). Such atomic displacement can be expected when the beta particles emitted from the 90Sr source (maximum energy 0.546 and 2.28 MeV respectively for 90Sr and 90Y) interact with the SWCNT samples.

In regard to the results for the pure samples it can be seen that again there is an exponential reduction in the D-Parameter value with deposited dose, the D-Parameter value change varying progressively from 21.2 eV to 16.8. For these samples, as a function of dose deposited in the sample, sp2 hybridisation is again observed to alter (with associated proportionate increase in sp3). Thus for example, while at zero dose the carbon nanotubes walls contain 85.2% sp2 (14.8% of sp3), dose deposition of 0.21 Gy leads to reduction of sp2 from 85.2% to ~ 81.8% and enhancement of sp3 to ~ 20.9%.

As commented upon before, comparing the pure sample dose-dependent D-Parameter value curves against those for the raw samples, with increasing purity it can be seen that the curves trend towards a more linear dependency, the fitted curves now showing a high degree of linearity when comparing to for instance the samples B1 & B2. In the associated regard to the carbon concentration in the raw and pure samples, these were found to be 68.2% and 72.1% respectively.

In regard to the results of the super-pure samples, it can be seen that the super-pure samples can again be depicted in terms of an exponential reduction, limited in number of terms. D-Parameter value continuing to be associated with progressive change with increase in deposited dose. The D-Parameter value for these samples has been observed to range from 20.3 to 18.1 eV. At zero dose (as that for an annealed sample) the D-Parameter value is some 20.3 eV, corresponding to 74.7% sp2 and 25.3% sp3. The dose-dependent response of the super-pure samples is similar to that for the pure samples (the D-Parameter value decreasing with dose and for the fitted curve for the super-pure sample G2 this shows similar linearity with that to the pure samples B1 & B2). The more limited curvature than that seen for the raw samples can be neglected in a linear approximation, given consideration of the errors associated with the measurements.

To sum up, the XPS study discussed herein show results with a clear relationship between deposited dose and enhancement of sp3 hybridisation. The D-Parameter value decreases (hence sp3 hybridisation increases) with dose deposited in the samples. It is further clear from the above discussion and also with reference to the summary results of Table 10, showing the fitting parameter values for the various samples A (raw) to G (super-pure), that relation (1) provides for a threshold energy, the sum of each of the energy values leading to a mean value of (20.9 ± 0.3) eV. This can be related to the estimate of the group of Banhart (1997) (1999) for the threshold energy in the range of 15–20 eV that is required to displace a carbon atom in the walls of the SWCNTs. These results suggest the use of XPS to provide for a new technique for radiation dosimetry. However, as it is a surface analysis technique, this would seem to limit the application to relatively low penetration radiation, potentially including alpha (for ultra-thin CNTs) and beta particles and low-energy photons. Thus said, the limitation points to considerable potential for the use of this novel soft tissue equivalent technique in estimating skin dose in personal dosimetry (noting that the previous work of Bardi (2017) has shown measurable effects at mGy levels) and when electrons or ions are used to treat superficial tumours.

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References