Flexible radiation dosimeters incorporating semiconducting polymer thick films

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ABSTRACT
Flexible radiation dosimeters have been produced incorporating thick films (>1 μm) of the semiconducting polymer poly([9,9-dioctylfluorenyl-2,7-diyl]-co-bithiophene). Diode structures produced on aluminium-metallised poly(imide) substrates, and with gold top contacts, have been examined with respect to their electrical properties. The results suggest that a Schottky conduction mechanism occurs in the reverse biased diode, with a barrier to charge injection at the aluminium electrode. Optical absorption/emission spectra reveal a band gap of 2.48 eV for the polymer. The diodes have been used for direct charge detection of 17 keV X-rays, generated by a molybdenum source. Using operating voltages of -10 and -50 V respectively, sensitivities of 54 and 158 nC/mGy/cm³ have been achieved. Increasing the operating voltage shows that the diodes are stable up to approximately -200 V without significant increase in the dark current of the device (<0.2 nA).

Keywords: Dosimeter, X-ray, Semiconducting polymer, diode, flexible

1. INTRODUCTION

Organic materials are currently poised to open a new range of applications, including carbon-based electronics, organic sensors, and flexible display technology. [1] In particular, there has been a rapid growth in the technology sector that covers flexible, printed, and organic electronics (FPOE). [2] This has been achieved through the discovery of novel organic-based electronic materials, and via optimization of the properties of existing devices, through improvements in device architecture and fabrication. [3] Such organic materials, which include conjugated, semiconducting polymers, potentially offer device solutions that challenge those of conventional silicon-based semiconductor technologies. For example, in the past decade, exploitation of the properties of polymers has led to the development of organic sensors for radiation detection and dosimetry [4, 5] and imaging [6]. These detectors complement solid-state dosimeters based on traditional inorganic materials, [7] and emerging technologies, [8] but also present their own unique advantages over their inorganic counterparts. [9]

Specifically, the physical characteristics of polymer systems lend themselves to the production of large-area, flexible dosimeters. Large area dosimetry panels can be used in proximity to power reactors for detection of emitted radiation, offering improved solid angle coverage and sensitivity, compared to small discrete devices. Being flexible, such a large area detector panel could be formed as a tube and placed around piping to remotely monitor radioactive fluids/steam etc. Segmented (multi-channel) detectors could be formed from a large area panel, giving spatial dose information such as beam profiling. In contrast, current large area dosimeters using either gas detector or scintillation technology, tend to be bulky and difficult to install in compact locations. In this work we have developed polymer radiation detectors operating as direct detection charge-based devices, in contrast to a scintillation or electro-chemical detection method [10]. Here we report results from prototype small area (~1 cm²), flexible dosimeters, incorporating a thick (>1 μm) semiconducting polymer active layer, and test the dosimetry characteristics using soft X-rays.

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2. METHODOLOGY

2.1. Materials
The polymer used in this study was poly(9,9-dioctylfluorenyl-2,7-diyl-co-bithiophene) (F8T2, Inset Figure 2), which was used as received. Polyimide (Kapton®, 0.025 mm thick), coated on one side with aluminium (50-100 nm thick) with a nominal sheet resistance of 2.5 Ω-1, was purchased from Goodfellow Ltd., UK. Toluene (99.99%) (Sigma-Aldrich Chemical Co., UK) was used as received.

2.2. Dosimeter production
F8T2 (5 wt.% solution in toluene) was spin-cast on top of the aluminium (Al) layer of the aluminium-coated polyimide (ca. 1.5 x 1.5 cm²). The spin processing conditions for the polymer films were: 1) accelerated at 100 rpm/s to 200 rpm and held for 100 s, 2) accelerated at 100 rpm/s to 500 rpm and held for 60 s, 3) accelerated at 100 rpm/s to 2000 rpm and held for 30 s, 4) decelerated at 100 rpm/s. This procedure produced a relatively smooth polymer film with a thickness of ~10 μm. After this, the films were typically dry to the touch; a short period of drying under atmospheric conditions was however required for some films, before annealing under vacuum at 110°C for 24 h. The thickness of the polymer layers was subsequently measured using a surface profilometer (Dektak, Veeco Instruments). To complete the diode, gold (Au) electrodes (50 nm thick, 0.5 x 0.5 cm²) were thermally evaporated onto the F8T2, through a shadow mask, at a pressure of 10⁻⁶ mbar. The diodes were connected to the measurement electronics through filament wires attached by gold paste to the electrodes. Finally, the diodes were coated with paraffin wax (0CON-194 Logitech Ltd, UK) by dip coating the diode in the molten wax. Upon completion, the dosimeters were stored under nitrogen and in the dark to minimize any adverse oxidation effects.

2.3. Diode characterization
The current-voltage (I-V) characteristics of the (PI)Al/F8T2/Au diodes were examined using a voltage source-picoammeter (487, Keithley Instruments) by applying a bias voltage from 0 V to ±250 V to the gold contact, with a voltage step of 5 V. UV-visible spectroscopy (M350 double beam, Camspec, excitation by Deuterium [180-370 nm] and Tungsten-Halogen [370-1100 nm] lamps) and Photoluminescence (excitation by He-Ne laser [405 nm]) spectroscopy were completed on thin films (~200 nm thick) of F8T2 deposited on soda lime float glass (Menzel Glaser microscope slides). In the case of the UV-visible spectroscopy an uncoated piece of the float glass was placed in the reference beam of the spectrometer. Dosimetry experiments were carried out using 17 keV Kα X-rays from a molybdenum target X-ray tube (XTF5011, Oxford Instruments) operated at a 50 kV anode voltage and a variable anode current (up to 0.5 mA). Current-voltage measurements were recorded for the diodes under the irradiation of the X-rays using the voltage source-picoammeter. For comparison, measurements were completed using a Silicon PIN photodiode (S1223-01, Hamamatsu Corp.) with an active area of 0.13 cm², and thickness of 300 μm. Dose rates were measured using a dose meter (Farmer 2670, Thermo Fisher Scientific) connected to an ionization chamber (2611A, Thermo Fisher Scientific).

3. RESULTS AND DISCUSSION
The dosimeter construction is shown in Figure 1 before the addition of the encapsulation layer. The flexibility of the device is demonstrated. F8T2 has been shown to be stable with respect to X-ray irradiation, but suffers from bias stress when operated in air [11] therefore, the encapsulation layer is important. The paraffin wax encapsulation material has a low melting point (57-60°C) which means the shaped diode can be dipped in the molten wax without affecting the F8T2 active layer, which has a glass transition temperature (Tg) ~ 100°C. The use of the wax also means solvents are not present which may affect the active semiconducting polymer layer. The wax forms a barrier to atmospheric gasses, reducing any oxidation of the F8T2 under operation, and has a low electrical conductivity (10¹³-10¹⁷ Ωm⁻¹) on a par with many polymers, meaning that it does not interfere with the electrical processes occurring in the diode. The wax is also non-toxic and has a low environmental impact. Indeed, most of the materials in the diode may be recycled, which is important if large area diodes are to be produced in the future.
Fig. 1. Photograph of a flexible F8T2 dosimeter. The semiconducting polymer, F8T2, (A) is spun down onto the flexible, aluminium-coated polyimide substrate (B), and the diode is completed with an evaporated gold top electrode (C). The dosimeter is attached to a glass support (D) and the electrodes contacted to the measurement electronics through filament wires (E). While held in shape, the device can be dipped in molten paraffin wax which forms an encapsulation layer.

I/V measurements were recorded, from 0 to ±250 V, increasing in 5 V steps, with the bias voltage applied to the gold electrode (Figure 2). The plot gives a reverse bias dark current of 0.2 nA at -250 V, with a current rectification factor of ~77 between ±250 V. The diode gives conductivities of $2.7 \times 10^{-12}$ and $2.1 \times 10^{-13}$ Sm$^{-1}$ in forward and reverse bias, respectively. Examination of the reverse bias d.c. characteristics has been undertaken, using Schottky [12] and Poole-Frenkel [13] conduction mechanisms, for electric fields ($E > 10^7$ Vm$^{-1}$). Values for the relative permittivity, $\varepsilon_r$, and barrier height, $\phi_b$, calculated using these methods are given in Table 1. The permittivity value for the Schottky mechanism, which falls in the range expected for polymers [14], suggests that this method more closely matches the data in the plot, and that the conduction in these diodes is electrode limited rather than bulk limited.

Fig. 2. Semi-log current-voltage plot for a flexible (PI)Al/F8T2/Au dosimeter upon increasing the voltage from 0 to ±250 V in 5 V increments. Inset: The chemical structure of F8T2 and a diagram depicting the energy levels (in eV) in the various components of the diodes.

<table>
<thead>
<tr>
<th></th>
<th>Poole Frenkel</th>
<th>Schottky</th>
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<tr>
<td>$r^2$</td>
<td>0.9665</td>
<td>0.9971</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>397.67</td>
<td>5.49</td>
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<tr>
<td>(\phi_b/\text{eV})</td>
<td>0.464</td>
<td>0.387</td>
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Figure 3 shows the uv-visible absorption and photoluminescence spectra for the F8T2, deposited as 200 nm thick films on soda lime float glass, prior to annealing, and after annealing at 180°C for 3 hours. The short, high temperature anneal is designed to emulate the longer, lower temperature anneal of the polymer films used for the dosimetry experiments. The uv-visible absorption spectrum (Figure 3A) for the non-annealed sample shows that absorption occurs below 520 nm. The PL spectra (Figure 3B) show the laser line at 405 nm due to the exciting laser (*), and the emission spectrum of the polymer which occurs above 500 nm.

The optical absorption and emission spectra give an insight into the structure of the polymer film. Annealing the polymer increases the crystallization in this polymer. In F8T2, this increases the conjugation length in the polymer chain, and increases the luminescence output of the polymer film. The increase in the conjugation is evidenced by a bathochromic shift in the uv-visible absorption (to higher wavelengths) \[15\], and an increase in the photoluminescence from the polymer. Repeat uv-visible spectra (not shown), taken on the same (non-encapsulated) films one month later, display a small hypsochromic shift (<5 nm) indicating some increase in disorder in the polymer film over time.

As well as the shift in the spectra, both spectra display the formation of a double peak after annealing. Doping is known to affect the absorption and photoluminescence spectra of polymers in a way similar to that seen here. [16, 17] In these reports, the spectra in each case change from having one peak in a doped state to having two peaks when the polymer is in an undoped state. In our work, two peaks occur in both the absorption and photoluminescence spectra upon annealing the F8T2 (Inset Figure 3) suggesting that a reduction in doping of the polymer film occurs, possibly through the elimination of solvent molecules left over from the solution processing.

The UV-visible spectroscopy and photoluminescence spectroscopy have been used to estimate the F8T2 band-gap energy, \(E_g \approx 2.48 \text{ eV}\), which is similar to that reported in the literature. [18] Using the Fermi level energies of the metals and the F8T2 conduction band energy level reported by Bernardo et. al [18] an energy level diagram can be constructed for the diode (Inset Figure 2). If we assume that the F8T2 is a p-type polymer, as with most semiconducting polymers, [19] and that the gold electrode forms an ohmic contact to the F8T2 (due to the similarities in the energies of the Fermi levels of the metal and that of the semiconductor; the latter of which lies just above the highest occupied molecular orbital (HOMO) level of the p-type F8T2) a depletion layer forms in the polymer at the low Fermi energy, aluminium contact. Upon formation of the depletion layer, band bending occurs which acts as a barrier to hole injection into the aluminium. This can be used to explain the I/V characteristics (Figure 2). Application of an increasingly negative bias to the gold electrode (diode in reverse bias) increases the size of the depletion layer, the hole current is minimized and consequently the current remains low. Application of an increasingly positive bias to the gold (diode in forward bias) decreases the size of the depletion layer and the hole current increases. As the dark current is low in reverse bias (<1 nA), the reverse biased diode was used for dosimetry experiments.
Figure 4 gives an indication of the performance of the F8T2 dosimeter when it is positioned in a beam of 17 keV X-rays from a molybdenum source. The current output of the dosimeter increases as the intensity of the incident X-rays increases from a dose rate of 12 to 61 mGy/s (Figure 4A). Three cycles of the measurements are shown. After a period of ~180 s to confirm the linearity of the background current, a dose period of 25 s is alternated with a period of 25 s with no dose applied. Figure 4B shows the effect of the applied bias on the signal output at increasing dose rate ($DR$) for three repeat measurements. The effective noise level due to the background dark current is $\sim 1 \times 10^{-11}$ A. Increasing the voltage applied to the gold electrode from -10 to -50 V produces an approximately 3-fold increase in the X-ray induced photocurrent, increasing the sensitivity ($s$) of the device from 54.2 to 158.2 nC/mGy/cm$^3$ respectively, where:

$$s = \frac{dI}{dDR}$$

$V$ is the volume of the polymer film between the electrodes ($= 2.25 \times 10^{-4}$ cm$^3$), and $dI/dDR$ is the slope of the curve with the dose rate $DR$ measured in mGy/s. The increase in applied voltage on the reverse biased diode increases the electric field in the diode and consequently causes charge carriers produced by the incident X-rays to be more easily swept out of the diode. This results in the increased photocurrent produced as the operating voltage is increased.

![Figure 4](image)

**Fig. 4.** (A) Temporal plot showing three trails of increasing current output with increasing dose rate (12.0, 24.2, 36.5, 48.8 and 61.0 mGy/s) for a (PI)Al/F8T2/Au dosimeter, operated at -10 V (top) and -50 V (bottom), irradiated by 17 keV X-rays through the gold contact. (B) Current versus dose rate plots for the dosimeter with -10 V (solid line) and -50 V (dashed line) operating voltage applied: the data are the average of 3 measurements taken from Figure 4A.

Figure 5 shows the increase in signal output when the operating voltage applied to the diode is increased (to -300 V). The operating voltage is applied for 25 s prior to irradiation, and for 25 s after irradiation, before switching to the next operating voltage. The dark current is measured as the average current from the two 25 s periods of applied voltage either side of the X-ray exposure. Irradiation of the diode at each operating voltage occurs for 25 s at an X-ray dose rate of 61 mGy/s. The output current increases from 1.2 to 13.6 nA when increasing the voltage from -10 to -300 V respectively (Figure 5A). Plotting the output current and the dark current, measured for each operating voltage, shows that although the output current increases, there is an accompanying increase in dark current (Figure 5B). This appears to affect the output signal at high voltages (above -200 V) when the dark current increases from <1 % to ~6 % of the signal output.
Fig. 5. (A) Temporal plot of current increase for a (PI)Al/F8T2/Au dosimeter at different operating voltages (10, 20, 30, 40, 50, 75, 100, 150, 200, 250, 290, 300 V) irradiated through the gold contact by 17 keV X-rays at 61 mGy s\(^{-1}\). (B) Current versus applied voltage plot, using the data in (A), showing the signal current (▲) and the dark current (●). Inset: Semi-log plot of the data in (B) showing the increase in dark current in more detail (and which may be compared with the reverse bias current (negative voltages) in Figure 1).

4. CONCLUSIONS

We have demonstrated the sensitivity and linear dosimetric response of F8T2 semiconducting polymer diodes as X-ray detectors. Scaling up the dimensions of these flexible radiation dosimeters will open potential application fields in such areas as medical dosimetry, security and the nuclear power industry. The linear dosimeter response (Figure 4), which is based on electrical detection of the charge carriers produced in the semiconductor, will also allow for real time monitoring of the applied dose. Flexible, segmented organic dosimeters can be used for patient dosimetry, for example during cancer therapy or X-ray diagnostics, by forming large area detector panels as tubes around areas of the patient's body, such as a limb, providing spatial dose information. Alternatively, portal imaging of passengers, baggage or vehicles, in security applications, would benefit from large area flat-panel X-ray detectors, increasing throughput when compared to using small area, hand-held dosimeters.

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