Studies of crystalline CdZnTe radiation detectors and polycrystalline thin film CdTe for X-ray imaging applications

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Abstract

The development of a replacement to the conventional film based X-ray imaging technique is required for many reasons. One possible route for this is the use of a large area film of a suitable semiconductor overlaid on an amorphous silicon readout array. A suitable semiconductor exists in cadmium telluride and its tertiary alloy cadmium zinc telluride. In this thesis the spectroscopic characteristics of commercially available CZT X- and γ-radiation detectors are established. The electronic, optical, electro-optic, structural and compositional properties of these detectors are then investigated. The attained data is used to infer a greater understanding for the carrier transport in a CZT radiation detector following the interaction of a high energy photon. Following this a method used to fabricate large area films of CdTe on a commercial scale is described. This is cathodic electrodeposition from an aqueous electrolyte. The theory and experimental arrangement for this technique are described in detail with preliminary results from the fabricated films presented. Attention is then turned to the CdS/CdTe films that are produced commercially for the photovoltaic industry. In this case the crystalline nature, surface topography and optical properties are investigated. A conclusion examines the progress that has been made towards the development of a large area flat panel digital imaging technique.
Out of the systematic disorder of research
must come the structure of science.
Anthony M D Ede
June 2001

Next time, I will use $L^A T_E X$.
Anthony M D Ede
July 2001
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Publications:

The following papers, based on work presented in this thesis have been published in the scientific literature:


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Chapter 1: Introduction

1.1 Overview

On the 5th Nov 1895 Wilhelm Conrad Roentgen was the first scientist to observe and record X-rays and was subsequently awarded the first Nobel Prize in physics. The application of X-rays to medical imaging, shortly after their discovery, has dominated this field for the intervening hundred years. Credit for its widespread adoption stems from the large amount of information that can be gained from such a simple non-invasive technique. However, conventional X-ray imaging, on film, is now ripe for a radical change, being an analogue technique in an increasingly digital environment. In addition, concerns over radiation dose to both staff and patients mean that more efficient detection of the available X-ray flux must be made.

Unlike other major present day techniques such as Computed Tomography, Ultrasound and Magnetic Resonance Imaging, conventional X-ray imaging remains a largely analogue process. Traditionally an X-ray film is held in position behind an intensifying phosphor screen, the screen absorbs X-rays, gives off light and exposes the film. Light spread in the phosphor layer prior to the exposure of the film will limit the attainable spatial resolution of the image. In digital X-ray imaging the phosphor screen is replaced with a position sensitive detection modality where the spatially resolved signal is read out by a computer.

Replacing conventional X-ray imaging with a computer controlled digital version has many advantages. Digitisation allows contrast and other aspect of image quality to be enhanced using image processing techniques. Digital radiographs could be compared more easily with those obtained from other modalities. In addition, storage and distribution of images becomes far easier over communication networks and less likely to lead to "lost films". This facilitates teleradiology, where qualified personnel could service
remote or poorly populated regions from a central facility. Greatest significance is attributed to the possibility of reducing the X-ray dose given to patients and medical staff as a result of better X-ray detection efficiency. At present 14% of the radiation dose delivered to the UK population is due to medical applications.

This thesis is part of a larger program of research to replace photographic film with a digital solid state sensor. Our goal is to simultaneously improve the quality of the X-ray image while effecting a dramatic decrease, factor 10, in X-ray dose. It will be shown that one possible replacement will be best made using films of the compound semiconductor detector CdTe or its ternary alloy CdZnTe, often referred to as CZT.

This thesis is divided into ten chapters. It is arranged as follows:

The remainder of chapter one discusses the background for this work. Descriptions of what digital X-ray imaging is and the requirements of the optimal solution, the flat panel, are made. The choice of CdTe and CZT as the interaction medium is justified. A discussion of these materials is made prior to a literature review of CZT radiation detectors.

Chapter two encompasses the relevant radiation interactions that give rise to a generated signal in the radiation detector. The required semiconductor physics is introduced. Theoretical background for some of the later measurements is also discussed.

Chapter three discusses a piece of equipment that was specifically designed and built for these experiments, the Electro-Optic Probe Station. This was used for the characterisation of the spectroscopic capabilities and semiconducting properties of the CZT detector. This instrument was remote controlled through a Visual Basic 3 computer interface and three of the programs are discussed.

Chapter four examines the spectroscopic capabilities of a gold contacted CZT detector using two radiation energy sources with principal photon lines that are comparable to the diagnostic energy range. The performance at room temperature, as a function of temperature and as a function of the interaction position between the two electrodes are investigated. The results indicate a non-conventional semiconductor radiation detector with considerable differences to the Si and Ge detectors commonly used. An investigation of the detector is then required from the following work.
Chapter 1: Introduction

Chapter five examines the semiconducting properties of the detector. This examines the electronic and optical characteristics of this material to investigate the resistivity, bandgap, composition, defect levels and carrier transport.

Chapter six complements the previous data by studying the structural properties of the CZT detector: The techniques employed are optical microscopy, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDX) and Proton Induced X-ray Emission (PIXE). The data from both this and the previous chapter provide a wealth of information concerning the nature of the detector.

Chapter seven consolidates this experimental data into a more in-depth understanding of the CZT detector than has previously been established. The relevant material properties that give rise to the experimental observations are explained. Generally there are a number of observations that can be related to an individual property. Following this the derived structure is used to understand the observed spectroscopic capabilities presented in chapter four. This concludes the work on the CZT radiation detector.

Chapter eight moves attention towards a CdTe film that could provide a digital X-ray imaging modality. This introduces the technique of cathodic electrodeposition from an aqueous electrolyte as a possible growth technique for sufficiently thick films of CdTe with the required area. The required electrochemistry, and electrodeposition of CdTe theory is introduced. The experimental arrangement and considerations that were made in its construction are described. This also includes a discussion concerning the choice of a suitable substrate and its preparation. The growth process is characterised and results from preliminary films discussed.

Chapter nine employs commercially fabricated thin films of electrodeposited CdTe in the solar cell industry for structural measurements. Experiments in this chapter examine the suitability of this structure for a future flat panel imaging array. The solar cell material consists of a glass substrate with subsequent layers of SnO₂/CdS/CdTe. The layers are characterised using selected techniques in order to monitor the bulk structure (XRD), surface appearance (SEM), stoichiometry and homogeneity (EDX) and bandgap using optical transmission with a spectrophotometer.
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Chapter ten concludes the work and reviews the contribution that has been made to the development of flat panel X-ray imaging. It also reviews the information that has been attained of the CZT radiation detector and the CdTe thin film solar cell.

1.2 Digital X-ray imaging

Here the choice of a digital detector and the medical X-ray imaging requirements are discussed. Consideration of various methods of detection for digital X-ray imaging concludes that a large area detector is most likely to produce an effective sensor [1].

Of these large area detectors, some are based on bulky but effective X-ray image intensifiers or stimulable phosphor screens that are cumbersome and time consuming to read out. Of most interest is the use of a flat panel active matrix array overlaid with a suitable photoconducting material. In this method the X-rays are converted to either light in the indirect method or electron-hole pairs in the direct method with these signal carriers being collected by the active matrix array and read out by a computer. The active matrix is a large area integrated circuit consisting of a large number of thin-film field effect transistors (TFTs) connected to individual pixel electrodes. A flat panel digital detector, in principle, could perform all current radiological modalities - radiography and fluoroscopy.

To attain a high X-ray stopping efficiency the interaction medium should be of a high density and high Z material. Such restrictions ultimately favour semiconductors and scintillators over gas chamber detectors. In addition this medium is also bulky and not considered feasible in the radiography room. Problems due to the slow components of the fluorescence in image lag may very well restrict this medium to non-fluoroscopic modes. This is a considerable disadvantage for an all encompassing radiographic modality. Assuming then a semiconductor layer of sufficient thickness for X-ray stopping efficiency and size for body imaging this medium represents the most likely candidate in future systems.

Spatial resolution losses due to the diffusion of light in the phosphor layer and the additional complication of optical coupling in the indirect method mean that the direct conversion method is preferable. In the direct conversion system the signal carriers can
be collected efficiently with negligible lateral spreading. In this case, image blurring is caused by coherent or incoherent scatter of the X-ray photon within the detector and the direction of the X-ray path relative to the photoconductor layer. This is the medium used to convert the transmitted X-ray photon to a recordable signal, electronic or optical.

Such a system is simple, compact and an elegant form of a fully digitised X-ray imaging detector. The ‘DirectRay’ system recently introduced by Sterling Diagnostic uses a-Se as a photoconductor and a-Si:H Thin Film Transistors for the Active Matrix Array [2].

However, amorphous selenium, as will be shown later, is not the best material available as an X-ray photoconductor. The choice of a-Se is based on the ease with which the layer can be deposited on the active matrix array using currently available technology. A-Se has in the past been used extensively in the photocopier industry [3]. The replacement of a-Se with a more suitable semiconductor will bring about a major improvement on this already impressive technique.

Semiconductors have a high stopping power because of their high density and Z (electron density), fast read out time, excellent interaction yield and negligible charge diffusion. In addition, for operation at room temperature there are a number of semiconductors with the required resistivity to reduce the dark current to acceptable levels. In addition there are other relevant quantities to be considered such as charge carrier mobility, defects, breakdown fields and homogeneity.

The detector should be of sufficient size to capture a shadow image larger than the body part to be imaged because of the lack of a practical means to focus X-rays. It should also possess adequate spatial resolution and must be able to accommodate the necessary dynamic range of X-ray intensities so that all relevant aspects of the anatomy are recorded with acceptable precision. Other important detector properties are: field coverage, geometric characteristics, sensitivity, noise characteristics, uniformity, acquisition speed and frame rate.

Electronic detectors for standing radiographic examinations would ideally have an active detector that is at least 43x43cm in size. In mammography a spatial resolution on the order of 50µm is thought to be necessary with a dynamic detection range of at least 4000 [4].
Also of consideration, any replacement system must be able to offer comparable or improved images to those currently achieved without a significant increase in expenditure. Certainly scanning systems exist that make use of collimators. The collimated X-ray source and detector are scanned simultaneously over the patient. However, such a system has several disadvantages including time, patient movement and X-ray tube lifetime. In addition, a replacement must possess long-term stability in the rather harsh environment of the radiology room.

1.3 The Flat Panel Detector

The direct readout flat panel detector has been identified as the most suitable solution to fulfilling the role of digital X-ray imaging. Flat panel designs for radiography, based on the use of thin-film transistors in an active matrix array readout have been described by Lee et al [5] for radiography and by Zhao and Rowlands [6] for radiography and fluoroscopy as shown in Fig 1.1.

The most common semiconductor used in thin film active matrix arrays is hydrogenated amorphous silicon or a-Si:H.
transistor sandwich. Before exposure, an electric field is applied across the photoconductor layer through a bias electrode on the top surface. Each electrode reads out the latent charge image created by the action of X-rays directly above a pixel, Fig 1.2.

During X-ray exposure, electrons and holes are released in the photoconductor which, because they are charged, can be guided directly to the surfaces of the photoconductor by the applied electric field. The latent charge image on the photoconductor surface is therefore not blurred significantly even if the plate is made thick enough to absorb most of the incident X-rays.

Because of its electrostatic field, the direct method has the potential of giving higher resolution images than phosphor based systems, even those using columnar CsI. When very large area (43x43cm) devices are required, the technology for making integrated circuits on high purity silicon cannot be used so a different approach with simpler, more modest circuitry is used. This is the active matrix, which uses cheaper substrates (glass), rather than the high purity single crystal silicon.
1.4 Photoconductor requirements

It would be instructive to consider the five primary requirements that constitute an ideal X-ray photoconductor.

Firstly, the ideal X-ray photoconductor should of course have excellent photoconductivity. This means that the amount of radiation energy $w$ required to create a single electron-hole pair, EHP, be as small as possible which requires the use of semiconductors with a small bandgap [8,9].

Second, the ideal photoconductor should have negligible dark current to reduce the effect of shot noise on the recorded charge. Low dark currents are found in materials of high resistivity due to a wide bandgap. This conflicts with the first requirement for narrow bandgap materials with low $w$ for increased sensitivity. The dark current can be limited by the use of non-injecting contacts or ideally blocking contacts, as explained in section 2.3.6. With perfect blocking contacts dark current is limited by the rate at which charge carriers are thermally generated in the bulk semiconductor.

X-ray absorption generally occurs over a substantial portion of the detector thickness. Electrons and holes, therefore, should be able to travel on average farther, before being trapped, than the thickness $L$ of the detector. If this is not the case then charge trapping will prevent the carriers from reaching the pixels. This property is characterised by the “schubweg”, which is defined as the mean distance traversed by a carrier in a field before it is trapped. The schubweg is given by $\mu \tau E$ where $\mu$ is the drift mobility and $\tau$ is the carrier lifetime (trapping time) and $E$ the electric field strength. The third requirement is that $\mu \tau E$ should be greater than $L$. The schubweg should not be confused with the carrier mean free path, which denotes the mean distance travelled between scattering events and controls the carrier mobility.

The X-ray absorption efficiency is determined by the X-ray absorption coefficient, which depends on the photon energy for a particular medium which as will be seen later favours high $Z$ materials. This is our fourth requirement.

The fifth requirement derives from the beneficial goal of minimising the radiation dose. Most of the radiation should be absorbed within the detector so that $L$ should be greater than the reciprocal of the X-ray absorption coefficient $1/\mu$ or the X-ray mean free path $\lambda$. 
These five requirements result in an important interplay and an inevitable compromise between $\mu$, $L$ and the carrier schubwegs. This is clearest for low bandgap materials with improved sensitivity but at the same time lead to larger leakage currents and increased noise. For example at an operating field of $5V/\mu\text{m}^2$, the schubwegs in device quality a-Se are typically in the range of 3-6mm for holes and 1-2mm for electrons. The absorption depth ($1/\alpha$) of 20keV photons is about 0.05mm, but it is 1mm for 60keV photons. Clearly operating at high energies requires a partial compromise between full absorption and schubweg-limited sensitivity.

There are however some overriding considerations for an X-ray photoconductor. Traditionally Si and Ge detectors are used with liquid nitrogen due to the narrow bandgap and inherently large leakage currents at even moderate temperatures. The use of LN$_2$ cooling is not thought practicable in the medical environment.

Photoconductor preparation requirements are just as important as its physical properties. If the flat panel detector is to fit into today's X-ray imaging environment, the photoconductor must be prepared in large areas (40x40cm$^2$) without loss of uniformity. Also essential are reasonable substrate temperatures, practical deposition rates for achieving thick films and practical source temperatures compatible with today's flat panel technology. Further, the deposition step must be economically competitive with other technologies.

### 1.5 Why do we consider CdTe and CdZnTe worthy of investigation?

CdTe and its ternary alloy CZT come closest to performing the task of a digital X-ray photoconductor. The high Z and high density of this material allow for good X-ray stopping power, being only slightly lower than compounds such as HgI$_2$. Physically the charge transport properties are far superior to HgI$_2$, PbI$_2$ and TlBr$_2$, which more than compensates for the extra thickness $\approx$10% required for comparable X-ray stopping efficiency.

In addition the electronic and crystalline properties of CdTe and CZT are the most understood of the candidate radiation detectors. The other candidates are in comparison
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relatively new and although the possibility exists for their increased use, research so far has not been able to improve the charge carrier properties to acceptable levels. Also, Hgl₂ is known to absorb water with time and degrade. Radiation spectra recorded with this material have also been made using crystals of reduced thickness compared to CZT as the hole trapping within the bulk imposes tighter restraints on their size than it does for CdTe.

So far the choice of a suitable photoconductor has not considered the difficulties of even producing large areas of thin film material over the area of a photographic plate \( \approx 40 \times 40 \) cm\(^2\). In the past, CdTe films have been grown mostly for the limited budget of the photovoltaic industry and as a result a large number of economical techniques are available. Films of CdTe as large as several meters squared have successfully been grown for solar cells using these techniques [10].

The ability to grow films of CdTe with techniques already understood and used in a commercial environment reinforces the decision in CdTe as the favoured choice as an X-ray photoconductor. The ability to buy radiation detectors of CZT and the free supply of CdTe films grown using electrodeposition assists in the work of this thesis.

1.6 Review of CdTe and CZT.

The room temperature lattice parameter of CdTe is the largest of any II-VI compound and for material of good stoichiometry is 6.48\( \text{Å} \) [11]. Room temperature lattice parameters for Cd\(_{1-x}\)Zn\(_x\)Te have been determined by Ben-Dor and Yellin [12]. The Cd\(_{1-x}\)Zn\(_x\)Te system forms a single phase from CdTe to ZnTe (\(a = 6.104 \text{Å}\)). The lattice parameter, \(a\), for this system is found to vary linearly with zinc concentration from \(x = 0\) to \(x = 1\), Eqn[1.1]

\[
a = 6.483 - 0.3803x
\]

For \(x = 0.2\) the lattice parameter is then approximately 6.41\( \text{Å}\).

The density of CdTe is reported as 5.854±0.005gcm\(^{-3}\) [13,14] while that for Cd\(_{0.52}\)Zn\(_{0.48}\)Te is given as 5.811gcm\(^{-3}\) [14] compared with 5.636gcm\(^{-3}\) for ZnTe [15].

CdTe and ZnTe both form the diamond equivalent zinc blende structure comprised of two interpenetrating FCC crystals offset by one quarter of the crystal diagonal. The zinc blende structure of CdTe is shown in Fig 1.3 where the dark spheres
correspond to the larger Te atoms and the white ones to the smaller Cd atoms. In this structure each atom has four equidistant, nearest neighbours lying at the corners of a tetrahedron.

![Zinc blende structure of CdTe](image)

The nearest neighbour distance is \( \sqrt{3}a/4 \) and the bonding is thought to be mainly covalent although a degree of ionic bonding is believed to exist [17].

In the diamond lattice the distance between the planes is found from the relation

\[ d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]  

[1.2]

where \( d \) is the planar spacing and \( h, k \) and \( l \) are the miller indices for that plane. In the (111) direction a spacing of \( \approx 3.7 \text{Å} \) exists for Cd_{0.8}Zn_{0.2}Te.

The bandgap of Cd_{1-x}Zn_{x}Te was first established by photoluminescence studies on epitaxial layers by Niemela and Sipila [18]. The results on six compositions, with \( E_g \) in eV, are fitted by:

\[ E_g(x,300K) = 1.51 + 0.606x + 0.139x^2 \]  

[1.3]

The incorporation of zinc into the CdTe lattice has several key advantages. It substantially increases the hardness of the material, reduces the dislocation density [19] as well as increasing the bandgap. The increased bandgap of Cd_{1-x}Zn_{x}Te over CdTe reduces the shot noise in the detector and allows their use in low-photon energy dispersive spectrometers.

In radiation detector applications the incorporation of zinc does not give rise to a similar decrease in the X-ray stopping power for the material. This is due to the zinc
replacement of the lower Z Cd(48), as opposed to the higher Z Te(52). The photoelectric cross-section varies as $\sim Z^4$ so that in general, ignoring absorption edges, the atomic number of the highest atomic number element in the compound determines the absorption efficiency, not the average atomic number. This is most clearly illustrated in the comparison of InP(49, 15) and GaAs(31, 33) which both have the same average atomic number of 32 but X-ray absorption is generally much higher in InP than that of GaAs due to the In(49). At 60keV the attenuation coefficients for GaAs and InP are 10.9cm$^{-1}$ and 24.1cm$^{-1}$ respectively.

The addition of 10% zinc to the CdTe matrix only requires a thickness increase of $\approx 5\%$ for the same X-ray stopping efficiency at 60keV, whereas the resistivity is increased by an order of magnitude.

1.7 Review of CZT Radiation Detectors

Following the initial production of CdZnTe radiation detectors using the high pressure Bridgemann process [20, 21], initial progress in their development was relatively swift. Subsequently, a time of relatively slow progress was encountered as problems with sample purity, repeatability and product yield all placed limitations on the availability and use of this material for radiation detection. In recent years their progress has again picked up as the device yield of the growth process has improved.

Energy spectra from a 5mm x 5mm x 2mm Cd$_{0.6}$Zn$_{0.2}$Te detector revealed a room temperature (RT) energy resolution of 4.22keV for 59.5keV gamma rays [22]. Thinner devices (1.5mm) of the same cross section with electroless Au contacts provided room temperature (RT) energy resolutions of 2.89keV FWHM for 59.5keV and 6.9keV FWHM for 122keV gamma rays [23]. Cd$_{0.6}$Zn$_{0.2}$Te detectors with dimensions of 3mm x 3mm x 2mm have given an energy resolution of 2.5keV for 59.5keV gamma rays [24].

In addition to the typical Au or Pt contacts to CZT detectors investigations have been carried out using more novel structures. Spectrometers fabricated from 1mm thick, 10mm$^2$ area Cd$_{0.96}$Zn$_{0.04}$Te with n- and p-type HgCdTe contacts gave RT energy resolution ranging from 3.35keV to 8.66keV FWHM for 122keV gamma rays, and 6.46keV FWHM for 356keV gamma rays [25, 26].
Thicker detectors generally suffer from incomplete hole collection, thus leading to gamma ray pulse height spectra skewed towards lower energies. Several methods have been proposed to correct and reduce position dependent charge collection effects. The most promising, being pulse processing techniques [27-29] and single charge carrier sensing devices [30-34]. Presently pulse processing techniques used with a 18mm x 18mm x 2mm Cd$_{0.9}$Zn$_{0.1}$Te detector have reached a RT energy resolution of 9.3keV FWHM for 662keV gamma rays [27]. With an 18mm x 18mm x 5mm Cd$_{0.9}$Zn$_{0.1}$Te detector the RT energy resolution was 11.25keV FWHM for 662keV gamma rays [28]. Similar pulse processing techniques used for a 0.6mm thick Cd$_{0.9}$Zn$_{0.1}$Te detector at reduced temperature (-25°C) gave an energy resolution of 2.6keV FWHM for 662keV gamma rays [29]. Single charge carrier sensing devices have been used with a 5mm x 5mm x 5mm CZT detector to demonstrate a RT energy resolution of less than 16.0keV FWHM for 662keV gamma rays [33,34]. Studies by He et al [34,35] utilising collimated $^{137}$Cs gamma rays ($E_{\gamma}$=661keV) [36] indicate that the energy resolution is best for interactions occurring near the cathode. Gamma ray interactions occurring near the anode were found to degrade the overall energy resolution.

A method, which included the coupling of multiple detectors in a stack, has been shown to increase gamma ray efficiency [37]. Room Temperature Cd$_{0.8}$Zn$_{0.2}$Te detectors have recently been used successfully as thermal neutron detectors in which unique gamma ray emission lines from $^{113}$Cd(n,$\gamma$)$^{114}$Cd were clearly identified [38-40].

CZT can operate reliably at elevated temperatures, up to 50°C [41], with energy resolution for 81keV gamma rays observed to increase from 8.91keV FWHM at RT to 13.77keV FWHM at 50°C.
Chapter 2: Theory

2.1 Introduction

For any future imaging system to compare with and surpass current imaging techniques, maximum use must be made of the available X-ray flux. The conversion of the incident X-ray flux to as large a number of signal carriers as possible and their efficient collection at the electrodes is paramount.

In this chapter the relevant radiation interactions in the diagnostic energy range and the relevant semiconductor physics for effective carrier collection are discussed. Next, the mechanism of radiation detection in semiconductor detectors is described from the initial bloom of electron-hole pairs, EHP’s, around the interaction point to the collection of these signal carriers at the collection electrode.

Following this, the experimental theory required for some of the measurements carried out in chapter five are introduced.

2.2 Radiation Interactions

There are two principle processes by which X-rays in the diagnostic energy range of 20keV to 100keV can transfer energy to matter. These are photoelectric absorption and Compton scattering [1,2]. Pair production, the conversion of a photon into an electron and positron within the electromagnetic field of a nucleus or electron exhibits a threshold energy of 1.022MeV and its discussion is therefore not relevant to this study.

2.2.1 Photoelectric Absorption

The Photoelectric Effect (PE), is an interaction in which photons from an incident beam traversing a medium are absorbed by the atom. In its place a photoelectron is ejected from the atom and subsequently traverses the medium. The process is subject to the overriding condition that the incident photon energy must exceed the binding energy
Chapter 2: Theory

of the atomic electron if photoelectric absorption is to take place. The kinetic energy of
the ejected photoelectron $E$, is equal to the photon energy $h\nu$, minus the electron binding
energy $\phi$, Eqn[2.1]

$$ E = h\nu - \phi \quad [2.1] $$

The process of photoelectric absorption is shown in Fig 2.1.

![Figure 2.1: Photoelectric Effect](image)

The photon must interact with the atom as a whole as momentum and energy
considerations prevent the absorption of a photon by an electron initially free and at rest
[3]. The large disparity in the mass of the atom relative to the photoelectron means that
almost all of the initial photon energy is transferred to the photoelectron.

The probability of producing a photoelectron upon irradiation of a medium is
strongly dependent on the atomic number of the material and the energy of the primary
photons. It is highest for high Z materials and for photons of energy just above the
electron binding energy so that a sharp increase in the PE cross-section is seen as the
photon energy increases through this threshold value. The change in the PE cross section
at the binding energy of a k-shell electron in Cd, 26.7keV, is approximately a factor of 3.

The ejection of a photoelectron is followed by the transfer of an outer orbital
electron to the empty inner shell, Fig 2.1. This electron transition may be accompanied by
either the emission of an X-ray photon or the transfer of energy to another electron which
is then ejected (an Auger electron).

In the former case the photon will have energy equal to the difference in the
binding energies for the two levels and is known as a characteristic photon. This photon
is unable to interact with the same level that the photoelectron was removed from and so
may travel a greater distance in the medium than the primary, higher energy photon.
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In the case of Auger emission, the electrons possess energy equal to the difference in the original atomic excitation energy and the binding energy of the Auger electron. This process depends on atomic number, being more common for low Z materials. The probability of energy loss due to photoelectron emission over Auger emission is known as the fluorescence yield. In Cd$_{0.8}$Zn$_{0.2}$Te Auger-electron emission comprises ~20% of de-excitation processes.

The probability of photoelectric absorption is complex to calculate but can be shown to increase rapidly with atomic number, \( \approx Z^4 \), scale linearly with density, \( \approx \rho \), and decrease with increasing photon energy as \( E^{-3} \) [4].

2.2.2 Compton Scattering

In addition to the photoelectric effect it is possible for photons in the diagnostic energy range to be scattered by an atomic electron with partial transfer of the photon energy to the electron. This process is called Compton scattering (CS) and is shown simply in Fig 2.2.

![Compton Scattering](image)

In Fig 2.2 a photon of energy \( h\nu \) and momentum \( h\nu/c \) is incident upon a stationary free electron. After collision the photon is scattered at an angle \( \theta \) from the incident direction with reduced energy \( h\nu' \). The struck electron recoils at an angle \( \phi \) with energy \( E' \) and momentum \( p'/c \).

Compton scattering is more amenable to mathematical interpretation than the photoelectric effect as the principle of conservation of momentum can be applied to the electron and photon, before and after interaction. It is then possible to discern the division of energy between the two. Consideration of momentum and energy in the horizontal and
vertical directions leads to the well-known Compton scattering equation for the energy of
the scattered photon [5]

\[ h\nu' = \frac{h\nu}{1 + \frac{h\nu}{m_0c^2}(1 - \cos \theta)} \]  

[2.2]

where \( m_0c^2 \) is the rest mass of the electron.

The probability of Compton scattering depends on the number of electrons
present and therefore scales linearly with atomic number, \( Z \). The struck electron can be
regarded as free and at rest because \( h\nu \) (tens of kV) is large compared to the orbital
energies of the loosely bound outer electrons (=1eV).

Two extreme cases for the division of energy between the two radiations are then
seen to be dependent on the scattering angle. In the first for a grazing scatter where \( \theta=0 \),
\( h\nu' = h\nu \) and the energy of the electron \( E_e \) is then approximately zero. In the
backscattered photon regime at low energies \( h\nu' = h\nu \) and again the electron receives very
little energy. At increased incident photon energies the energy of the backscattered
photon tends to the limiting value of \( m_0c^2/2 \), so that \( h\nu - m_0c^2/2 \) is transferred to the
electron.

In normal circumstances, all scattering angles are possible and a continuum of
energies can be transferred to the electron, giving rise to the Compton continuum.

2.2.3 Secondary Electrons

These two processes can be considered the first stage in the transfer of energy
from an incident photon to the creation of electron hole pairs EHP’s, that generate the
signal pulse in the detector. Both processes have left an electron recoiling through the
medium. In photoelectric absorption the photon has disappeared and in Compton
scattering the photon has a reduced energy and continues to traverse the medium.

For efficient charge carrier collection and image resolution these electrons must
be stopped within a short distance and converted to EHP’s with a minimal loss of energy.
The path of energetic electrons is a tortuous one with large deflections following
collisions due to the coulomb interaction with orbital electrons of equivalent mass. A
large fraction of energy may be transferred to Bremsstrahlung, due to electron-nuclear
collisions for photons of energy greater than 1MeV.
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The energy loss per unit path length for electrons is comprised of radiative and collisional losses. Radiative losses are considered negligible for electron energies below 1 MeV [6]. For our PE and CS electrons (Emax = 90 keV and 28 keV for a 100 keV photon) energy loss is accomplished through collisions with atomic electrons in the detector.Fortunately it is found that 100 keV electrons are stopped by thicknesses of CdZnTe of the order of 20 μm [7] so that the energy spread and spatial resolution from electrons is considered negligible.

2.2.4 X-ray Attenuation

All of these processes lead to partial or complete transfer of photon energy to electron energy. In each process photons are removed from a narrow beam by a single interaction process unlike particle beams which are slowed down gradually.

Each of the interaction processes, photoelectric absorption and Compton scattering, removes a photon from the incident beam. The photon interaction and beam attenuation in matter is governed statistically by the probability per unit distance travelled that a photon will interact by one process or another. Each process possesses its own probability for interaction and for a specific medium each is dependent upon the photon energy. The sum of these interaction probabilities is known as the linear attenuation coefficient, the probability per unit path length that a photon will be removed from the incident beam with dimensions of inverse length (cm⁻¹), Eqn [2.3]

\[ \mu = \mu_{\text{PE}} + \mu_{\text{CS}} \]  

where \( \mu \) denotes the total linear attenuation coefficients as the sum of those due to each mechanism. The well-known exponential law of photon attenuation gives the number of transmitted photons as

\[ \frac{I}{I_0} = e^{-\mu t} \]  

where \( I \) and \( I_0 \) are the photon flux before and after traversing this thickness respectively and \( t \) is the absorber thickness. It follows that the quantity \( e^{-\mu t} \) is simply the probability that a normally incident photon will traverse a medium of thickness \( t \) without interaction.

The photons can be characterised by their mean free path \( \lambda \), defined as the average distance travelled in the absorber prior to any interaction and is related to the attenuation coefficient by
The value of $\lambda$ corresponds to the depth into the medium at which the number of unattenuated incident photons has fallen to $1/e$ or $\approx 36\%$ of $I_0$.

A 60keV photon traversing $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ will have a mean free path of 0.27mm compared to 13.4mm and 0.9mm in Si and Ge detectors respectively [9]. Thus $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ possesses a greater X-ray stopping power than the lower Z materials.

The linear attenuation coefficient is limited by the fact that it varies with the density of the absorber. The mass attenuation coefficient is much more widely used and is defined as

$$\text{mass attenuation coefficient} = \frac{\mu}{\rho}$$

where $\rho$ represents the density of the medium. The mass attenuation coefficient of a compound or mixture of elements can be calculated from [8]

$$\left(\frac{\mu}{\rho}\right) = \sum_i w_i \left(\frac{\mu}{\rho}\right)_i$$

where the $w_i$ factors represent the weight fraction of element $i$ in the compound or mixture.

The mass attenuation coefficients for photoelectric absorption and Compton scattering as a function of energy in $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ are shown in Fig 2.3 [9].

The abrupt changes in the photoelectric curve correspond to the K-edges for Cd, Zn and Te at 26.7keV, 9.7keV and 31.8keV respectively. The group of peaks from 3keV to 5keV are due to the L shells in Cd and Te. Also shown is a curve proportional to $E^{-3}$ which follows well the photoelectric cross section for energies above the Te K-edge.

The lower curve for Compton scattering is still an order of magnitude lower than the photoelectric absorption cross section for 100keV photons. In the diagnostic energy range photoelectric absorption is the dominant mechanism for energy transfer to matter. The linear attenuation coefficients for PE and CS in $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ are equal for a photon energy of approximately 275keV, above which CS dominates.
2.2.5 Comparison of X-ray Attenuation in High Z Semiconductors

Having decided that high Z materials are advantageous it would now be timely to compare the linear attenuation coefficients for a number of important candidates as a digital X-ray imager.

Scientifically important materials for digital X-ray imaging include CdZnTe, PbI$_2$, HgI$_2$, TlBr and amorphous Selenium. In the case of a-Se and PbI$_2$ the use of these materials in commercial or research X-ray photoconductors is already well underway [10,11]. CdTe is not included due to its similarity with Cd$_{0.8}$Zn$_{0.2}$Te in X-ray stopping power even for moderate values of $\lambda$, section 1.6. The linear attenuation coefficients for photon energies in the range of 20keV to 100keV are shown in Fig 2.4.

As expected high Z materials possess a larger linear attenuation coefficient over low Z materials. This generalisation is dependent on the photon energy relative to the k-edge of the constituents. This is perhaps most clearly shown for TlBr with a k-edge at 85.5keV, at which a factor of $\approx$4 increase in the attenuation coefficient is observed and $\mu$ for TlBr is the highest for increasing energy. Below this TlBr possesses a linear attenuation coefficient lower than both HgI$_2$ and PbI$_2$. Amorphous Selenium, the only
material commercially used as an X-ray photoconductor, has a linear attenuation coefficient an order of magnitude lower than TlBr at 100keV. In comparison the k-edge for Se at 12.7keV is too low for Fig 2.4.

This is principally why the research described here is being carried out. If the a-Se layer can be replaced with a higher Z semiconductor then the X-ray stopping power will be enhanced. The TlBr layer could also be much thinner, for the same degree of X-ray attenuation, so that generated EHPs would have a far smaller distance to travel and the charge collection efficiency may then be increased. Clearly the possibility of a replacement photoconductor has some very important implications.

The characteristic photon energy for a tungsten X-ray tube is ≈60keV at which 600μm of CZT is required to absorb 90% of this radiation. In comparison 12cm of silicon would be required for the same X-ray stopping power. A 40x40cm² silicon X-ray photoconductor of thickness 12cms would weigh approximately 45kg, quite some mass. The alternative CZT photoconductor would weigh approximately 0.6kg, a far more convenient mass.
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2.3 Semiconductor Physics

In many radiation detection applications the use of a solid detection medium is highly desirable. Detection of higher energy radiation becomes possible, as solid densities are some three orders of magnitude larger than gases. Scintillation detectors have many steps prior to signal collection, each of which contributes noise, limiting their ultimate efficiency. Semiconductor detectors effectively have a single charge generation stage, compact size (cm³), relative fast timing (<1μs) and excellent energy resolution (0.2% for Si or Ge at 77K for the 241Am 59.5keV γ-ray).

Use of semiconductors with a large bandgap and very high atomic number, Z>40, offers further benefits with improved X-ray stopping power and room temperature operation. Perhaps the most exciting recent development in room temperature radiation detectors is the use of CZT crystals on the earth-orbiting dual satellite X-ray telescope Swift by NASA [12]. In this section the required semiconductor physics for X- and γ-radiation detectors are discussed.

2.3.1 Band Structure

For an isolated atom the orbital electrons have only discrete energy levels. As a large number of atoms are brought together to form a solid the Pauli exclusion principle requires that these energy levels split, as no two electrons can have the same set of four quantum numbers. The discrete energy levels then spread out into a range of sub-levels so close together that they form an energy band. The energy band into which the ground state (fully occupied at absolute zero), and the band corresponding to the level immediately above this band, i.e. the first excited state (empty at absolute zero) are known as the valence band and the conduction band respectively.

In conductors the valence band is not fully occupied and electrons close to the top of this band may easily attain sufficient energy to transfer to higher energy levels. In insulators and semiconductors the valence and conduction bands are separated by a forbidden energy gap or bandgap, denoted by $E_g$. The band diagram for a semiconductor is shown in Fig 2.5.

In semiconductors the bandgap is typically 1eV wide. Insulators are normally defined as those materials whose bandgap is in excess of 5eV, i.e. diamond 5.47eV [13].
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A Cd$_{0.8}$Zn$_{0.2}$Te crystal of volume 125mm$^3$ (5x5x5mm) will contain a total of $5.8 \times 10^{20}$ atoms possessing $2.8 \times 10^{22}$ energy levels. Bands are typically 1eV wide so that the inter level spacing within a band can be as small as $3.6 \times 10^{-22}$eV.

![Semiconductor band structure](image)

Except at absolute zero when the conduction band is completely empty, there is a finite probability that some electrons will acquire sufficient thermal energy to jump from the valence band to the conduction band generating free carriers.

### 2.3.2 Extrinsic Semiconductors

The band diagram shown in Fig 2.5 describes an intrinsic semiconductor, one in which the material is pure and free of defects. In reality, though, semiconductor properties are controlled by the trace amounts of impurities, either desired or undesired, that persist in even the purest of material. Defects in the crystal lattice, such as vacancies, also play an important role in the charge flow through a semiconductor. Defects and impurities are collectively termed imperfections.

These imperfections in the crystal lattice contribute energy levels to the bandgap region of the intrinsic semiconductor. The nature of these levels is dependent upon the nature of the defect and the bulk material. Impurity atoms that can easily donate an electron to the conduction band are known as donors and the resultant energy levels are called donor levels. An example of a donor level can be found in the addition of phosphorus (Group V) to silicon (Group IV). The phosphorus is a substitutional impurity forming four covalent bonds with the surrounding silicon atoms in the diamond lattice. The remaining fifth electron is then loosely bound to the parent atom and therefore easily...
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excited into the conduction band. Hence donor levels are typically sited close to the conduction band edge.

If an impurity atom is present that results in the absence of a bonding electron a vacancy is formed. This vacancy is not a hole as it is bound to the impurity atom but, at any temperature above absolute zero, an electron from a neighbouring atom can fill the vacancy, leaving a hole in the valence band. These imperfections are called acceptors as their associated energy levels accept electrons excited from the valence band. An example of an acceptor level can be found in the case of boron (Group III) doping of silicon. The boron impurity atom like phosphorus will substitute a silicon site but will not be able to form the required four bonds so that a vacancy in the lattice bonding exists.

It is often convenient to regard this situation as an acceptor atom with a positive hole orbiting around it such that an energy $E_a$ is required to free the hole from its parent impurity. In reality, of course, $E_a$ is the energy required to excite an electron from the valence band to the energy levels associated with the acceptor atoms. An impurity atom that loses its associated hole will become a negatively ionised impurity.

The presence of donor and acceptor levels in the bandgap is illustrated in Fig 2.6. At absolute zero, Fig 2.6a, donor and acceptor levels are filled and the ability for these charges to move to either band is zero. At any temperature above this (b) it becomes possible for transitions to occur between these levels and the band edges.

![Diagram of donor and acceptor levels](image)

Fig 2.6
Acceptor and donor levels in an extrinsic semiconductor at a) 0K and (b) elevated temperature
2.3.3 Intrinsic Carrier Transport

The stimulation of electrons from the valence band to the conduction band leads to a nearly full valence band and a nearly empty conduction band. When an electron makes an inter-band transition an empty energy level or "hole" is left in the valence band which can be considered in the same manner as an electron except of course for the positive charge. If an electric field is now applied to the sample, electrons in the conduction band and holes in the valence band will drift in opposite directions and both then contribute to the sample conductivity, Fig 2.7.

\[
\sigma = \sigma_{\text{hole}} + \sigma_{\text{Electron}}
\]

\[
\sigma = ne\mu_e + pe\mu_p
\]

where \( n \) and \( p \) are the concentrations per unit volume of conducting electrons and holes. The electron and hole mobilities, \( \mu_e \) and \( \mu_h \) respectively with units \((\text{cm}^2/\text{Vs})\), are defined by

\[
v_e = \mu_e E
\]

\[
v_h = \mu_h E
\]

in which case \( v_{eh} \) (\text{cm}^{-1}) is the electron or hole velocity and \( E \) the electric field strength (Vcm\(^{-1}\)). In an intrinsic semiconductor (free of impurities) the number of electrons and holes are equal and so Eqn[2.9] can be simplified to
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\[ \sigma_i = n_i e (\mu_e + \mu_h) \]  

[2.11]

where \( i \) denotes intrinsic.

It is clear from Eqn[2.9] that the concentrations of electrons in the conduction band and holes in the valence band will influence the value for the electrical conductivity of semiconductors. Electrons are fermions and using Fermi-Dirac statistics the number of electrons in the conduction band is given by

\[ n = CT^2 \exp\left(\frac{E_c - E_f}{kT}\right) \]  

[2.12]

where \( E_f \) is the appropriate fermi level and the constant term \( C \) includes the electron effective mass. For intrinsic semiconductors \((n=p=n_i)\), \( E_f = E_{f_i} = E_g/2 = (E_c-E_v)/2 \) giving

\[ n_i = CT^2 \exp\left(-\frac{E_g}{2kT}\right) \]  

[2.13]

The intrinsic conductivity can thus be written as

\[ \sigma_i = n_i e (\mu_e + \mu_h) = CT^2 e (\mu_e + \mu_h) \exp\left(\frac{-E_g}{2kT}\right) \]  

[2.14]

The temperature variation of the conductivity depends both on the thermal excitation of electrons into the conduction band and on the variation of the mobilities, \( \mu_e \) and \( \mu_h \), with temperature. The mobilities at all but the lowest temperatures are largely determined by lattice scattering of the charge carriers and hence, as might be expected decrease with increasing temperature. In simple terms the mobilities are expected to vary with temperature as

\[ \mu = CT^{-\frac{3}{2}} \]  

[2.15]

where \( C \) is a constant, due to the change in lattice scattering dependence on temperature.

2.3.4 Extrinsic Carrier Transport

In extrinsic semiconductors the charge carrier transport properties are somewhat complicated by the presence of energy levels within the bandgap. Principally the capture of free carriers leads to recombination or trapping. These effects are illustrated in Fig 2.8.
Intrinsic generation in Fig 2.8(a) corresponds to the thermal excitation of an electron from the valence band to the conduction band. Extrinsic excitation corresponds to the raising of an electron from an imperfection to the conduction band as in Fig 2.8(b), or the raising of an electron from the valence band to an imperfection in Fig 2.8(c). The latter two processes are known as detrapping as they involve the removal of charge carriers from the imperfection or trap.

A free electron may be captured at an imperfection as in Fig 2.8(d), or a free hole may be captured at an imperfection as in Fig 2.8(e).

The capture process is described through a capture coefficient $\beta$ such that the rate of capture $R$ of a species with density $n$ by a species with density $N$ is given by

$$ R = \beta n N $$ \hspace{1cm} [2.16]

When capture of an electron (or hole) leads to recombination with a hole (or electron), a recombination process has occurred. The lifetime of a free carrier, $\tau$, i.e., the average time the carrier is free before recombining, is given by

$$ \tau = \frac{1}{\beta N} $$ \hspace{1cm} [2.17]

Comparison with Eqn[2.16] shows that the rate of capture (in this case the rate of recombination) is equal to $n/\tau$. Since in the steady state the rate of generation must be
equal to the rate of excitation $G$ (per unit volume per second), we obtain the following basic relationship.

$$n = G \tau$$  \hspace{1cm} [2.18]

The average density ($m^{-3}$) of a species present at a given time is given by the product of the rate of generation ($m^{-3}s^{-1}$) and the average lifetime of that species(s). If more than one recombination process is present then the individual recombination rates add.

From Fig 2.8 a captured carrier at an imperfection may do one of two things: (I) recombine with a carrier of the opposite type, or (II) be thermally excited back to the energy band before recombination can occur. In the latter case the imperfection is called a trap and the capture and release processes are called trapping and detrapping. This is shown in Fig 2.8(f).

In the former case in which recombination occurs, the imperfections are known as recombination centres.

The nature of these imperfections is dependent on the energy $E_d$ or $E_a$ and the material temperature, which determines the probability of a captured carrier to detrapp before recombining. A level that at room temperature behaves as a trap may become a recombination centre at lower temperatures as the probability of thermal excitation is decreased. There therefore exists a temperature region for each imperfection at which recombination and detrapping are both possible. The distinction between traps and recombination centres is then based on the probability of occurrence for each process. The most probable outcome describes the nature of the imperfection.

2.3.5 Optical Properties

So far electron excitation and conductivity have been discussed with regard to thermal effects alone. Electron excitation can also occur as a result of an electron in the valence band absorbing a photon of energy $h\nu > E_g$ and subsequently moving to the conduction band. Such a process is called optical absorption and is an important and well-known characteristic of semiconductors. If the photon has energy less than $E_g$ then it will not be absorbed whereas if the energy is above $E_g$ then there is a probability that absorption will occur. The energy of the incident radiation is given by [15].
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The photon energy at which absorption occurs is therefore the bandgap energy. Substitution of typical bandgap energies of 1.45eV and 1.1eV (CdTe and Si at 300K) into Eqn[2.19] gives 855nm and 1130nm for the absorption edges.

In a direct bandgap semiconductor such as CdTe no phonon involvement is required and the probability of optical absorption is far higher than for indirect semiconductors such as silicon and germanium.

Optical absorption is described through the absorption coefficient \( \alpha \). If we ignore reflection and interference effects for light of intensity \( I_0 \) incident on the surface of a material of thickness \( d \) with absorption coefficient \( \alpha \), the intensity of the transmitted light \( I \) is given by Beer’s law [16].

\[
I = I_0 \exp(-\alpha d) \tag{2.20}
\]

For a direct bandgap semiconductor the absorption coefficient depends only on the bandgap and incident photon energies [17].

\[
\alpha^2 = (h\nu - E_g) \tag{2.21}
\]

Direct optical transitions are characterised by a rapid increase in \( \alpha \) for \( h\nu > E_g \) to values of the order of \( 10^6 - 10^7 \text{m}^{-1} \) so that only a film of thickness 1\( \mu \)m would be required to absorb \( \approx 90\% \) of this radiation. From Eqn[2.21] it can also be seen that as the photon energy increases, \( \alpha \) will continue to increase so that higher energy photons will be stopped within a shorter distance of the surface. The form of Beer’s law is similar to the well known exponential dependence of radiation penetration into a medium and similarly the mean free path of optical photons is given by the inverse of the absorption coefficient, 1/\( \alpha \). Absorption involving imperfections is called extrinsic optical absorption and the absorption probability is proportional to the density of the absorbing centres.

2.3.6 Metal Semiconductor Contacts

In order to construct a practical radiation detector, some means must be provided to collect the electrical charges created by the radiation at either boundary of the semiconductor material. The effects that occur at the interface between a metal and a semiconductor depend on the work functions of the two materials. When the two are
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placed in direct contact the difference in work functions $\Delta \phi$ is taken up by bending of the valence and conduction bands, Fig 2.9.

There are four cases of metal-semiconductor contact worth distinguishing, depending on whether the metal or semiconductor has the larger work function and whether the semiconductor is p- or n-type. Two of these lead to rectifying or Schottky barrier contacts and two to non-rectifying or ohmic contacts. When the two materials make contact, the fermi levels must be equal at thermal equilibrium. In addition, the vacuum level must be continuous. Let us look at the case of the n-type semiconductor when the metal work function $\phi_m$ is both smaller and larger than the semiconductor work function $\phi_s$.

For the case of $\phi_m < \phi_s$ on a n-type semiconductor forms an ohmic contact. The main feature of this contact is that there is no potential barrier between the metal fermi level and the bottom of the semiconductor conduction band. The work function is the energy difference between the Fermi level and the vacuum level. In the semiconductor the value of $\phi_s$ depends on the doping and the kind of crystal [18]. Also shown is the electron affinity $q\chi$, which is the energy difference between the bottom of the conduction band edge and the vacuum level in the semiconductor.

The ohmic contact for a n-type semiconductor and a metal where $\phi_m < \phi_s$ is shown in Fig 2.9 [19]. The IV profile for this contact varies as the square of the voltage [20].

![Diagram](Fig 2.9)

An ohmic contact between a metal and an n-type semiconductor

In the case of $\phi_m > \phi_s$ there exists a potential barrier between the fermi level of the metal and the conduction band of the semiconductor, Fig 2.10 [21].
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![Diagram of Schottky barrier between an n-type semiconductor and a metal]

The quantity $\phi_D$ shown in the figure is the diffusion potential and $q\phi_D$ is equal to the difference between the work functions of the metal and semiconductor. The barrier height is larger than this by the amount $(E_C - E_F)$. Using the electron affinity $\chi_s$ then the barrier height can be expressed as $q\phi_B = (q\phi_m - \chi_s)$.

Electrons in the metal that are entering the semiconductor are faced by a potential barrier and their flux is reduced by a factor of $\exp\left\{\frac{(E_m - E_B)}{kT}\right\}$ by comparison to the case when there is no barrier. Those carriers with sufficient energy to overcome this barrier form the thermionic emission current $J_s$ given by,

$$J_s = A^* T^2 \exp\left\{-\frac{\phi_B}{kT}\right\} \quad [2.22]$$

where $A^*$ is called the effective Richardson constant [22] in units of $AK^{-2}cm^{-2}$ with a value of $120AK^{-2}cm^{-2}$ for electron emission from a clean metal surface. $T$ is the absolute temperature.

If the metal is positively charged, the energy levels in the semiconductor are raised and, more electrons flow into the metal and the current increases exponentially. This is called the forward bias direction. If the metal is negative, the barrier height is unaffected and a small current independent of the applied voltage is observed.

The actual value for the reverse bias current is the sum of the thermionic emission current and the bulk generated current in the semiconductor,
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\[ J_{\text{TOT}} = A' T^2 \exp\left(\frac{-\phi_e}{kT}\right) + \frac{V}{\rho d} \]  \[2.23\]

where \( \rho \) is the bulk resistivity for the semiconductor.

2.4 Semiconductors as Radiation Detectors

In this section the development of an EHP pulse and its collection at the electrodes is discussed.

When ionising radiation (particle or photon) passes through a semiconductor radiation detector the production of many electron-hole pairs occurs at the points of interaction. The quantity of practical interest for detector applications is the average energy expended by the primary charged particle to produce one electron-hole pair. This quantity denoted by \( w \) and loosely called the w-value is observed to be largely independent of the radiation type. The dominant advantage of semiconductor detectors lies in the relatively small value of \( w \) compared to other detection mediums such as gas counters. Thus in semiconductor detectors a greater number of EHP’s are produced. In a typical gas converter, every keV of incident radiation will produce 40e of charge carriers while in a semiconductor such as Ge it will produce 300e of charge carriers [23].

The increased number of EHP’s has two beneficial effects on the attainable energy resolution. Statistical fluctuations in the number of charge carriers produced become a smaller fraction of the number as the number is increased. At low energies, the energy resolution may be limited by the electronic noise in the preamplifier so that the increased charge per photon leads to a better signal to noise ratio.

In practice \( w \) is a material property found to increase with the semiconductor bandgap. For many semiconductors \( w \) has been shown to depend on the bandgap energy \( E_g \) and approximately follow Klein’s rule [24],

\[ w \approx 2.8 E_g + E_{\text{phonon}} \] \[2.24\]

In direct semiconductors \( E_{\text{phonon}} \) is expected to be small so that

\[ w \approx 3E_g \] \[2.25\]

The values for \( E_g \) of all compound semiconductors means in practice that all have \( w \) values 1-2eV larger than those of Si and Ge. This loss in the number of generated
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charge carriers and therefore energy resolution is an inherent price to pay for the use of room temperature semiconductors. However the value of \( w \) for compound semiconductors is still about 20 times lower than that for the thallium activated sodium iodide scintillator, NaI(Tl) [25].

Following the formation of EHP's within the semiconductor bulk the applied electric field draws these carriers to the collection electrodes where they form the signal pulse. The ability of both carriers to move within the semiconductor affects the response time of the detector and the obtainable energy resolution. An unfortunate trend exists for semiconductor detectors whereby high Z materials, improved X-ray stopping power, show inferior charge transport properties. For Ge (32), the mobility of electrons is 3800cm\(^2\)/Vs at 300K with values of 1000cm\(^2\)/Vs for CdTe (48,52) and 100cm\(^2\)/Vs for HgI\(_2\) (80,53). Silicon is somewhat of an exception to this rule where the electron mobility is 1350cm\(^2\)/Vs.

The application of an external electric field to the semiconductor will result in a small, but finite leakage current. Random fluctuations in the leakage current will tend to obscure the small signal current from an ionisation event so that the leakage current must be reduced as much as possible. The use of detector cooling for the narrow bandgap semiconductors of Ge and Si or the use of high bandgap materials such as CdTe (1.45eV) or HgI\(_2\) (2.1eV) can overcome this problem.

2.5 Experimental Background

In chapter four a large number of electronic and optical measurements are carried out on the CZT crystals. The theoretical background for these measurements is described here.

2.5.1 Photoluminescence (PL)

Photoluminescence or PL describes the process by which light of one energy may be given off from matter under the excitation of light of a different but higher energy.

In semiconductors super bandgap radiation will excite electrons from the valence band across the bandgap to the conduction band. Once there they rapidly lose energy through exciting lattice vibrations – i.e. to heat until they reach the bottom of the conduction band. Simultaneously holes in the valence band will be rising to the top of the
valence band. The electron can then return to the top of the VB to fill the hole state again, in the process emitting a photon characteristic of the bandgap energy.

Other sources of luminescence arise from defects within the bandgap resulting in sub-bandgap energy radiation being observed. CdZnTe, being a direct semiconductor, will absorb light within the first μm of the surface, and the fluorescence will then be characteristic of the exposed surface.

2.5.2 Photoreflectance (PR)

In Photoreflectance or PR a modulating electric field is used to perturb the crystal band structure which can be observed through its effect on simple reflection from the sample. Fundamental parameters such as band edges and energy levels can therefore be deduced. The effect of an externally applied perturbation is outlined here and a more thorough account of photoreflectance can be found in Garawal [26].

A uniform flux of photons entering an absorbing medium of thickness d will be reduced to I at the exit side. This can be expressed in terms of the attenuation coefficient, \( \alpha \), of the medium,

\[
\ln \left( \frac{I_0}{I} \right) = \alpha d
\]  

[2.26]

where \( \alpha = \omega \epsilon_2(\omega)/nc \) [26] and \( \omega \) is the frequency of the radiation and \( \epsilon_2 \) is the complex component of the dielectric function, \( \epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \), of the solid. If absorption is defined such that it excludes reflection and scattering losses, it is reasonable to state that absorption is caused by electronic transitions. Thus the physical quantity most related to these transitions is \( \epsilon_2 \).

In a semiconductor the Fermi level is pinned to the surface states at the solid/air interface. Charge is therefore trapped in these states resulting in the generation of an internal electric field. Application of an external electric field to the semiconductor leads to modulation of the built-in electric field with the minority carriers going to the surface.

At the surface the photogenerated carriers recombine with the charge trapped in the surface states and so reduce the built-in field. In electroreflectance the periodic application of the external electric field is directly applied through an electrical contact to the material. In the case of PR, carriers are produced by absorption of the laser light directed at the sample. Modulation is therefore produced by modulating the laser beam.
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Bottka and Glosser [27] have shown that a one-to-one correspondence between electroreflectance (ER) and photoreflectance (PR) exists. PR can therefore be described as a contactless form of ER.

2.5.3 Photocurrent versus Wavelength

The absorption of super bandgap ($hν>E_g$) radiation by a semiconductor has been described previously. Briefly, in an intrinsic direct bandgap semiconductor the absorption coefficient of this radiation is typically $10^5\text{cm}^{-1}$. The photocurrent variation with increasing photon energy will show a marked increase at the bandgap energy. This will also be shown in the variation by several orders of magnitude of the absorption coefficient.

This standard semiconductor behaviour is somewhat complicated here due to the passivated surface of our detectors. The passivation of the surface leads to a large number of recombination centres that act to limit the mobilities of charge carriers in this region to effectively zero. The lifetime of carriers in this region is of the order of nanoseconds. Super bandgap radiation, absorbed within 2μm s of the surface, will generate charge carriers in a region with poor charge transport properties. Sub-bandgap radiation will penetrate into the bulk of the crystal. The shaded regions indicate the passivated surfaces for this situation in Fig 2.11.

![Fig 2.11](image)

Photon absorption dependence on energy
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The photocurrent in the $h\nu > E_g$ region will then to some extent be reduced by this surface layer. This effect will be more apparent for photons of increasing energy as the attenuation coefficient $\alpha$, increases with photon energy Eqn[2.21] so that as $h\nu$ increases the photocurrent decreases. As the thickness of the passivated surface is unknown, the number of super bandgap photons that successfully traverse this region is also unknown. The photocurrent in this region is not easily modelled and is dependent upon $\alpha(\lambda)$, photon flux and the depth of the surface layer.

Sub-bandgap radiation traversing the crystal entirety may then be absorbed through levels within the bandgap and through edge absorption from thermal broadening, $kT$, of the band edges. At 300K ($kT \approx 0.025\text{eV}$) and for CZT with an anticipated bandgap of 1.55eV a spread of $\pm 15\text{nm}$ s in the band edges is expected. Absorption within the bulk material will allow the charge carrier lifetime to increase by three orders of magnitude [28]. The size of the photocurrent in this region is then dependent upon $\lambda$, photon fluence, the defect levels involved and their concentration. Sub-bandgap radiation will have an attenuation coefficient several orders of magnitude lower than super bandgap radiation. The absorption of sub-bandgap radiation in the passivated layer is considered negligible compared to the bulk absorption because of the relative thickness involved, $<1\mu\text{m}$ and $5000\mu\text{m}$'s respectively.

2.5.4 Multiple Reflections in Absorbing Media

In later experiments the transmission of sub-band gap radiation through a CZT detector is observed. Changes in the refractive index at both air/CZT interfaces must be taken into account to accurately measure the refractive index and absorption constants for CZT at these wavelengths.

If the incident, reflected and transmitted components for a particular photon energy can be found then the refractive index and extinction coefficient are obtainable.

The refractive index of a surface being acted on by optical radiation at normal incidence is related to the reflection coefficient by [29]

$$ r = \frac{(n-1)^2}{(n+1)^2} \quad [2.27] $$

36
where \( n \) is the refractive index and \( r \) is the reflection coefficient. The transmission coefficient is related to the absorption coefficient by

\[
t = (1 - r)^2 \exp(-\alpha d)
\]  

[2.28]

where \( \alpha \) and \( d \) are the absorption coefficient and sample thickness respectively.

Eqn[2.27] indicates that both CZT/Air interfaces will give rise to two Fresnel reflections. Our detector has parallel faces and for \( h\nu < E_g \) the expected low attenuation may give rise to multiple reflections from both surfaces. This scenario is shown in Fig 2.12 with the magnitude for each reflection and transmission shown.

The sum of the transmission coefficients is then

\[
T = I \left[ (1 - r)^2 e^{-\alpha d} + (1 - r)^2 r^2 e^{-3\alpha d} + ... \right]
\]  

[2.29]

where \( I \) is the incident beam intensity. The sequence is that of a geometric progression where the sum to infinity of the individual transmissions gives the total transmission \( T \) as

\[
T = \frac{(1 - r)^2 e^{-\alpha d}}{1 - (r e^{-\alpha d})^2} I
\]  

[2.30]

Similarly, the reflection coefficient is given by

\[
R = I \left[ r + (1 - r)^2 r e^{-2\alpha d} + (1 - r)^2 r^3 e^{-4\alpha d} + ... \right]
\]  

[2.31]

The bracketed term represents the result of the initial reflection from the surface upon striking the crystal, \( r \), and the sum of the multiple reflections from the medium. These multiple reflections as before form their own geometric progression. In this case the total reflection is given by
Chapter 2: Theory

\[ R = \left[ r + \frac{(1-r)^2 re^{-2ad}}{(1-r^2 e^{-2ad})} \right] I \] \hspace{1cm} [2.32]

It is therefore possible using the above formulas and knowing the reflection coefficient from our crystals to work out the refractive index for sub-bandgap radiation.

2.5.5 Thermally Stimulated Current

In extrinsic semiconductors the rates of detrapping-trapping and recombination for a particular energy level are dependent on the sample temperature.

Briefly, at elevated temperatures charge carriers held within the defect levels are more likely to undergo thermal detrapping and so the energy levels are more likely to display trapping-detrapping processes as opposed to recombination. At lower temperatures the energy level behaves as a recombination centre as trapped carriers are less likely to escape.

The ability of these energy levels to trap charge at low temperatures and allow their escape can be exploited to investigate the depth of these energy levels. A charge trapped at 77K is less likely to de-trap than one trapped at 300K. If a semiconductor is held at 77K and the concentration of filled traps increased through photon excitation, then upon heating, the conductivity will show rapid increases when the probability for escape from a specific trap is increased. The process by which this happens is approximately twenty times the value of $kT$ at this temperature [30]. This process is shown in Fig 2.13 for two donor levels at depths from the conduction band of $E_1$ and $E_2$, where $E_1 < E_2$.

\[ \text{(a) } T_1 \hspace{1cm} \text{(b) } T_2 \hspace{1cm} \text{(c) } T_3 \]

Fig 2.13

Temperature dependence of de-trapping and recombination at $T_1 < T_2 < T_3$

At sufficiently low temperatures Fig 2.13(a) the rate of thermal excitation from both trapping centres is negligible and recombination dominates. As the temperature is increased Fig 2.13(b) both traps will show an increase in the rate of thermal de-trapping
but the rate due to $E_1$ will be higher than that due to $E_2$. The dark conductivity then begins to rise due to an increase in the number of free carriers above that due to band to band transitions. As the number of filled traps of energy $E_1$ is decreased the increase in the dark conductivity will slow down and the dark conductivity will show a peak as the chances of thermal excitation are dramatically reduced. Further increases in temperature will decrease the conductivity in a small temperature range as no carriers remain trapped.

At increased temperatures the same effect may be seen from the deeper trap $E_2$. A second peak will then be observed due to this deeper energy level. The resultant plot of dark current versus temperature is shown in Fig 2.14 and consists of the thermal detrapping current associated with each trap superimposed on the exponentially temperature dependent crystal dark current, Eqn[2.14]. In this figure the peaks due to both energy levels are well separated and are very much larger than the semiconductor dark current.
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2.6 Discussion

In this chapter the interactions of X- and γ-radiation with solid media and the creation of a proportionate number of EHP’s has been described. The required semiconductor physics and the behaviour of semiconductors as radiation detectors was introduced. Following this, the necessary experimental theory was presented. It is now time to focus on a major piece of experimental apparatus that was used for these investigations, the electro-optic probe station.
Chapter 3: The Electro-Optic Probe Station

3.1 Introduction

In the course of this work a piece of equipment, the electro-optic probe station, was constructed to allow a large number of investigations to be carried out on CZT detectors with minimal changes in equipment. The probe station was initially designed to carry out electronic and optical investigations before being adapted for use in the characterisation of the radiation detection properties of a CZT detector. In this chapter the design and experimental descriptions of the probe station are discussed.

3.2 Overview

The Electro-Optic probe station was situated in a light tight room with remote control facilitated with a PC. Remote operation was essential due to the sensitive nature of CZT to vibration and light and allows the use of high powered laser sources. The probe station is mounted on a pneumatically raised optical bench to improve vibration isolation. This is particularly important considering the piezoelectric nature of CZT whereby a potential difference is generated between opposing faces due to mechanical stresses such as vibration. The Electro-Optic probe station can be considered in several key parts; cryostat, optics, electrical measurements and computer control.

3.3 Cryostat

A photograph of the cryostat with key parts labelled is shown in Fig 3.1. The CZT crystal is held in a modified Oxford Instruments Microstat\textsuperscript{N} optical cryostat. The crystal is placed in a machineable ceramic ($\rho > 10^{16}\Omega\text{cm}$) holder with BeCu sprung contacts at either end for electrical contact. Care was taken to avoid scratching the crystal contacts.
Chapter 3: The Electro-Optic Probe Station

upon insertion. The ceramic sample holder was then coupled to the cryostat cold finger. The cryostat is held on micro positioners allowing X-Y movement of the crystal with a travel of 25mm and a resolution of 10μm in both directions.

The cryostat has a temperature range of 77K to 500K adjusted by an ITC502 temperature controller. The temperature of the cold finger is measured with a calibrated Pt resistor and assured to an accuracy of ±0.1K. Liquid nitrogen is pumped around the cold finger by a diaphragm pump with the flow adjusted by a needle valve on the output line. The desired temperature is achieved by balancing the nitrogen flow with the ohmic heating from a resistance heater attached to the cold finger.

Evacuation of the cryostat is achieved by a Pfeiffer 50ls⁻¹ mini turbo pump backed with an Edwards 2m³h⁻¹ rotary pump. A base pressure of 3E-6mbar was routinely achieved following slight heating of the cold finger to hasten out-gassing of absorbed water vapour. Vibrations from the turbo pump and rotary pump, following several
restrictive measures were found not to give rise to any piezoelectric effects in the crystal. Care was also taken to avoid earth loops from the turbo pump and ITC502 controller.

During our initial experiments it was found that the temperature of the crystal was somewhat different to that of the cold finger due to the poor thermal conductivity of the sample holder (1.5 W m\(^{-1}\) k\(^{-1}\)). Combined with the relative proximity of the cryostat’s outer wall to the crystal surface, \(\approx 2\) mm, these factors lead to erroneous results. Use of a calibrated k-type thermocouple positioned on the crystal and a high resistance, voltage measurement unit allowed an accurate measurement of the crystal temperature to be attained simultaneous to the recording of relevant data. The thermocouple was calibrated against the reading on the ITC502 controller prior to the recording of experimental measurements.

3.4 Optics

Optical probing of the crystal can be achieved by a Tungsten-Halogen light source coupled with an Ealing 27-5248 infrared diffraction monochromator, continuous wave or pulsed laser.

The 50W Tungsten-Halogen light source provides broad band uniform illumination to 2\(\mu\)m and the monochromator was fitted with 300\(\mu\)m entry and exit slits giving a spectral resolution of \(\pm 2.5\) nm [1] over the wavelength range of 750nm to 1700nm. A Schott glass colour filter [Ealing RG715] was placed on top of the cryostat entrance window to remove the second order radiation that is characteristic of this type of monochromator. Use of a spectrophotometer revealed that the filter possessed a sharp cut-on at 650nm with uniform transmission close to 100\% above 715nm. Achromatic lenses were used throughout the optical path to reduce chromatic aberration. The wavelength accuracy of the monochromator was assured using sources of known wavelength; a Hg vapour lamp that has an infra red line at 1014nm and a 850nm semiconductor laser. The spectral output of the source and monochromator combination as a function of wavelength was evaluated using a Si PIN diode of known spectral response. The intensity of the light at the exit slit of the monochromator was found to be approximately 6\(\mu\)W for an area of 1.5mm\(^2\) over the wavelength range.
Chapter 3: The Electro-Optic Probe Station

The lasers that were available were a 337.1nm 20mW N₂ laser which could be coupled to a dye laser, an infrared 850nm, 1mW continuous wave or pulsed semiconductor laser that can be pulsed using the TTL control signal and a 635nm, red, 1mW continuous wave semiconductor laser.

Focusing the light onto the crystal surface required the use of an a-Si:H array held at the same height as that of the crystal top surface. Light reflected back from the array was captured by a CCD camera and the image viewed using a high resolution TV screen. The magnification that was possible with this arrangement was approximately 800 times. In this manner it was possible to obtain a laser spot some 50μm wide. The monochromatic light was limited by the output slits to a 300μm by 5mm strip beam with a power concentration of 2μWmm². A schematic of the Electro-Optic probe station is shown in Fig 3.2.

![Fig 3.2 Electro - Optic Probe Station Schematic](image)

3.5 Electrical Measurements

Current and voltage measurements from the sample were usually recorded using a Hewlett Packard HP4156A Semiconductor Parameter Analyser or HPPA. This instrument has 4 Source Measurement Units (SMU’s), 2 Voltage Measurement Units
Chapter 3: The Electro-Optic Probe Station

(VMU’s) and 2 Voltage Source Units (VSU’s). A VMU was used to measure the signal from the thermocouple on the crystal. The maximum voltage that can be supplied by the SMU’s is 200V with a current resolution of 10fA in the instrument.

Electrical signals were always carried by Triaxial cables to limit capacitance effects that would otherwise result across the dielectric insulation. The cables were either allowed to relax elastically prior to measurements or were taped down. Care was also taken to star ground all apparatus and avoid earth loops. In the absence of a crystal a 200V bias produced current fluctuations of only a few 10 s of femtoamps and never exceeded 100fA. A photo of the Electro-Optic Probe Station is shown in Fig 3.3.

![Photograph of the Electro-Optic Probe Station](image)

Fig 3.3
Photograph of the Electro-Optic Probe Station

### 3.6 Computer Control

The control programs to remotely operate the electro-optic probe station from the externally held PC were written in Visual Basic 3 specifically for each individual
experiment. The VB3 front panel for each experiment was written so that no codes must be entered to perform an experiment. Instead a more user-friendly approach using an object orientated front panel was taken. This allowed direct entry of experimental parameters into text boxes. This allowed excellent control of the experiment with relative ease. Constraints were included in all the programs so that equipment was not damaged or the experimental procedure compromised through the setting of incorrect conditions.

The HP4156A Semiconductor Parameter Analyser, an Oxford Instruments ITC502 Temperature Controller, Tektronix TDS544A digitising oscilloscope and a Tektronix AFG2020 Function Generator are controlled through a GPIB interface card. The monochromator is controlled through the computer serial port and two stepper motors through their own card.

3.7 Program Overview

Each of the programs had several key points in common. In the first instance all were designed with easy to use front panels free of coding and interlocks ensuring the use of parameters within the capability of utilised equipment. All programs recorded the experimental information such as the date, time and equipment settings in a sequential data file with the obtained data. The data was also processed with error statistics being applied to obtain such things as the standard deviation and standard error in the mean for repeated measurements. These were then recorded in the same data file simultaneously. Confidence was assured by taking preliminary data directly from an instrument and separate statistical analysis confirmed the computed values as accurate. Most of the programs also included a continually updated experimental report window, which allowed the user to gain the status of the experiment and to allow for problems to be identified. The programs were completely autonomous allowing the user to leave the room and return following completion. This was most useful as some of the experiments lasted as long as 12 hours or more. It is important to note that these experiments are not exclusive to CZT radiation detectors of specific dimensions alone but may be adapted for other samples of different compositions or configurations. A brief discussion of three key computer programs is now made.
3.7.1 Current v's Voltage

The resistivity of CZT is known to be approximately $10^{11}\Omega\text{cm}$. The maximum E-Field that could be applied across the cubic 5mm thick detectors was 400Vcm$^{-1}$. In this event the expected currents are of the order of 1nA. Such low current levels require the use of triaxial cables and good experimental practice. In addition, multiple measurements improve the sensitivity. In the computer program the recorded results are analysed using statistical techniques that examine the accuracy of the recorded result, principally by evaluating the standard error in the mean, the sum of the standard deviations divided by the number of samples.

The front window for this experiment is shown in Fig 3.4. This experiment used the HP4156A instrument alone. The experimental windows are white with the labels in yellow for distinction. The mode, function and source (V or I) for each of the four source measure units, SMU’s, is at the top left. Principally the input values were checked against those allowed by the maximum power of the instrument. The minimum and maximum voltages are shown on the right hand side. The program automatically checks the number of steps for acceptability. The current integration time option boxes are at the bottom left and the associated white boxes indicate the defaults. The status of the GPIB card can be monitored from this window using a command button. The Run button starts the experiment.

The use of the HP4156A to record the IV characteristics is similar for all the other experiments and the description of its settings is not repeated.
3.7.2 Photocurrent v's Wavelength

In this experiment the CZT detector is irradiated with optical photons using focused monochromatic light. The change in generated current across the detector as a function of photon wavelength is measured at a constant E-Field by the HP4156A. The front window for this experiment is shown in Fig 3.5.

The monochromator settings are shown on the top right. The choice of monochromator, visible or infrared, is a primary concern. The monochromator start, end and step size are then checked. All inputted values are checked following entry and prior to the experiment commencing. A further option is shown that allows the monochromator to be controlled by the user. This is permitted only after a successful initialisation. The user can set the required wavelength directly. This proved useful when examining interesting properties of the detector. It also creates a more flexible program. The default file name is mono.dat, which records the wavelength, current and its standard error.
3.7.3 Current versus Wavelength and Temperature

In this experiment the current as a function of wavelength is recorded over a temperature range. Three pieces of equipment are used, the HP4156A, monochromator and the ITC502 temperature controller. All experimental variables are grouped in these three categories from left to right across the window. The front panel is shown in Fig 3.6.
Fig 3.6
ITC502, monochromator and HP4156A experimental front panel

All inputted values are checked in the initialisation procedure. In addition it is now possible to set specified wavelengths and temperatures following successful initialisation of both instruments. The default file name is All.dat, which records the temperature, wavelength, current and its standard error.

3.8 Discussion

This chapter has reviewed the design considerations, and described the component apparatus of the electro-optic probe station in detail. In the next chapter the spectroscopic capabilities of a CZT radiation detector are assessed using this experimental set-up.
Chapter 4. CZT as a X- and γ-Radiation Detector

4.1 Introduction

This chapter determines the X- and γ-radiation spectroscopy characteristics of a gold contacted CZT detector. Three main experiments are performed. Firstly the room temperature spectroscopy capabilities are studied. Next the temperature limits for effective operation are determined. Lastly, the spectroscopic dependence on interaction position is studied to quantify the effect of carrier transport properties on the obtained radiation spectra.

The radiation sources used are Americium 241 and Cobalt 57 with principal photon energies at 59.5keV and 122keV respectively. Such energies are comparable to the characteristic photon energy of tungsten (=69.5keV) [1] and a higher energy that is indicative of the Bremsstrahlung tail from the X-ray tube. Prior to the experiments the growth and physical characteristics of the CZT detector is described.

4.2 Background: Growth and Physical Characteristics

The radiation detectors used in these experiments were supplied by eV products, a division of II-VI Incorporated. They are cubic in shape with vertices of 5mm. Two opposing faces are metalised with either Au or Pt contacts and the remaining sides are passivated. Some detectors were received with a protective polymer coating on the non-metallised surfaces to aid mechanical strength.

The crystals are grown using the High Pressure Bridgman, HPB technique from highly pure starter materials [2-8]. Following growth, contacts are made by deposition from either a AuCl₃ solution or Pt sputtered with a Xe glow discharge. The contact layers are believed to be typically 5-10nm thick [9]. Final heating of the detectors “activates”
them useable [9]. The zinc concentration within the detector is quoted by the manufacturers to be approximately 10% yielding a bandgap of 1.58eV, Eqn[1.3].

4.3 Room Temperature Radiation Detector Characteristics

The increased bandgap (\(E_g = 1.6\)eV) and large Z (=50) of \(\text{Cd}_{1-x}\text{Zn}_x\text{Te}\) enables the detection of higher energy radiation than traditional Si and Ge detectors permit, at room temperature with sufficient resolution for spectroscopy applications. It is unfortunate that due to inferior carrier transport properties in CZT that the spectral resolution is generally below that of Si and Ge detectors. Principally, the spectral resolution in CZT is limited by the poor hole transport properties, so that any photopeak exhibits a low energy tail due to incomplete hole collection within the amplifier shaping time. Irradiation is usually carried out through the detector cathode to reduce the hole transit path length and collection time, improving the charge collection efficiency.

4.3.1 Experimental Set-up

The experimental set-up is shown in Fig 4.1. The detector was held in a brass holder with a beryllium entrance window and irradiation was carried out through the cathode. Later measurements found that the electrical resistivity of the detector is dependent on the E-field direction, section 5.2. The crystal was operated in the high resistivity orientation to reduce the dark leakage current and subsequently the shot noise.

The detector was capacitively coupled to an eV products 550 charge sensitive pre-amplifier. A Canberra 2022 shaping amplifier was connected to a multiple channel analyser within a computer. The computer program PCAII was used to collect the spectra. The power supply used to generate the E-Field was a Canberra 3122D. The gain on the shaping amplifier was 1000 and the shaping time could be varied between 0.5, 1.0, 2.0, 5.0 and 10\(\mu\)s.

Two sources were used to compare the detector performance at a range of energies, \(^{241}\text{Am}\) and \(^{57}\text{Co}\) with activities of 0.4MBq and 0.37Mbq respectively. Americium 241 decays through alpha emission to the daughter nucleus Neptunium 237 emitting two relatively intense gamma rays at 23.4keV and 59.5keV, together with a number of characteristic L X-rays from the Np decay product. Cobalt 57 decays to \(^{57}\text{Fe}\)
Chapter 4: CZT as a X- and γ-Radiation Detector

with the emission of two higher energy γ-rays at 122keV and 136keV and a relatively low energy line at 14.4keV.

The principal photon energies of 59.5keV and 122keV have mean free paths of 0.28mm and 1.5mm respectively in CZT [10]. The 5mm thickness of our detectors means that ≈100% and 93.5% respectively of this radiation will be absorbed in the crystal. This compares with thicknesses of ≈85mm and ≈15mm required to achieve the same absorption efficiency for the 122keV line in silicon and germanium detectors respectively.

Following the application, or change in the E-Field, the detector was allowed one hour for its resistivity to attain equilibrium.

4.3.2 Americium 241 Spectra

The 59.5keV photopeak was visible for E-fields as low as 400Vcm⁻¹ due to the high probability for absorption close to the cathode. A lower energy peak and a large background in the intervening region accompanied this. Improvements in the spectra were observed for increasing E-field strengths. Principally, an increase in the 59.5keV centroid channel number and the separation of the lower energy peak into the 23.5keV γ-ray, Np L-shell X-rays and the Cd and Te escape peaks.

A spectra recorded with an E-field of 2kVcm⁻¹ and a shaping time of 0.5μs is shown in Fig 4.2. The spectra is typical of any found in the literature [11-15]. The γ-ray
Chapter 4: CZT as a X- and γ-Radiation Detector

photopeaks at 59.5keV and 23.4keV, the Np L_{α,β} X-rays and the Cd and Te escape peaks are all clearly distinguishable. The best spectra in terms of higher peak channel number and resolution for $^{241}\text{Am}$ were always recorded at a shaping time of 0.5μs.

The 59.5keV photopeak possesses a FWHM of ≈5% which is found to be entirely consistent with values found elsewhere of 6% [11,12], 4.8% [13], 4.2% [14] and 8% [15]. The peak to valley ratio for the 59.5keV peak is 100:1 due to the low background noise. The low energy side of the photopeak constituents 56% of the FWHM, a fact related to poor hole transport in the detector despite irradiation through the cathode. Low energy peaks are also visible from the Np product indicating the good resolution that is achievable with these detectors.

![Fig 4.2](image)

$^{241}\text{Am}$ Spectrum obtained using a CdZnTe crystal at room temperature

Increases in the shaping time above 0.5μs were found to degrade the spectral resolution at elevated E-field strengths. Reversal of the E-field direction so that irradiation was through the anode did not give a recordable spectrum other than low energy noise. This is clearly linked to the inferior charge transport properties of holes to electrons in CZT.
Chapter 4: CZT as a X- and γ-Radiation Detector

In cathodic irradiation with $^{241}$Am the application of high E-fields ($E > 1 \text{kVcm}^{-1}$) is sufficient to limit the effect of poor hole transport properties. As will be discussed in more detail later, section 4.5.1, there is a depth within the detector corresponding to the point where hole and electron transit times are equal. In CZT this point is 0.45mm from the cathode at which point the transit times for both charge carriers are approximately 0.5μs for an E-field of 1kVcm$^{-1}$. At this depth ≈80% of the surface incident 59.5keV photons will have been absorbed with a 98% chance of photoelectric absorption being the interaction mechanism.

More evidence therefore of the effect of bias and shaping time on charge collection efficiency would be achieved with photons of increased penetration depth.

4.3.3 Cobalt 57 Spectra

The principal photon energy of 122keV from Co$^{57}$ has a mean free path of 1.5mm in CZT. At this depth with an E-Field strength of 1kVcm$^{-1}$ on a 5mm thick detector the charge carrier transit times are $\tau_e=0.14\mu s$ and $\tau_h=1.5\mu s$. The probability of photoelectric absorption as a percentage of the interaction probability for a non-elastic interaction is 92% [10].

For cathodic irradiation with $^{57}$Co, a minimum field of 800Vcm$^{-1}$ was required to extract a reasonable spectra. This compares to 400Vcm$^{-1}$ for the 59.5keV peak from $^{241}$Am. The spectra recorded for E-fields of 1kVcm$^{-1}$ and 2kVcm$^{-1}$ with a shaping time of 0.5μs are shown in Fig 4.3. Both were calibrated using the 122keV and 136keV lines.

Both spectra possess the separated photopeaks due to 122keV and 136keV $^{57}$Co photons with the expected low energy tail to the 122keV peak. At higher field strengths ($E > 1.2 \text{kVcm}^{-1}$) the Cd and Te escape peaks are observed superimposed on the 122keV low energy tail. The FWHM for the 122keV peak at 2kVcm is 7%. This compares with 2.4%[13], 3.5% [16], 4.4% [17], 6.1% [18] and 7.1% [19] reported elsewhere. At 2kVcm$^{-1}$ the peak count is increased by 10%, with a slightly reduced background over the lower field strength. The peak channel number for the 122keV peak are 1510 and 1592 respectively indicating an increase by 5% due to improved charge collection efficiency at higher E-Fields.
Chapter 4: CZT as a X- and γ-Radiation Detector

In Fig 4.4 the peak channel number is shown at E-Fields for shaping times of 0.5, 1.0 and 2.0μs. For E-Fields at, or above 1kVcm⁻¹ the peaks channel number is greater for shorter shaping times. The difference between the peak channel number for 0.5μs and that for 1.0μs and 2.0μs increases for larger E-Fields. Below 1kVcm⁻¹ a cross over is seen at 900Vcm⁻¹ where the 1μs shaping time yields a larger value for the peak channel number. This is linked to the increased carrier transit times at lower E-Fields so that a sizeable number reach the electrodes outside of the 0.5μs shaping time.

The energy resolution (FWHM in keV) of the 122keV photopeak as a function of E-Field for three different shaping times is illustrated in Fig 4.5. The FWHM attained using 0.5μs and 1.0μs shaping times is very similar over the E-Field range and considerably lower than that attained using 2.0μs. The FWHM for 0.5μs and 1.0μs shaping times decreases by 50% over the E-Field range.
The similarity between the shorter shaping times are believed to again illustrate the longer hole transit times from 122keV photon interactions. Here, the hole transit time is sufficiently large that a considerable portion of the signal is collected outside of the 0.5μs shaping time. After 1μs only a very small signal is collected resulting in the poor resolution for 2.0μs. This late signal is due to trapping-detrapping phenomena in the bulk material. The comparable energy resolution in keV is essentially a percentage of the 122keV peak. As the FWHM values are very similar and there are large differences in the peak channel numbers for 0.5μs and 1.0μs shaping times the resolution is enhanced for the shorter of the two.

Clearly Fig 4.5 shows the improvement in energy resolution for higher E-fields and shorter shaping times. A fact more clearly seen here than for the Americium spectra, reflecting the increased penetration depth of the 122keV photon.
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The FWHM however is not the best indication of tailing available. In Fig 4.6 the energy resolution is therefore measured as the two Half Width Half Maximum (HWHM) values that comprise the FWHM.

At 1kVcm⁻¹ the low energy side comprises ≈85% of the FWHM compared to ≈65% at 2kVcm⁻¹. The low energy side of the FWHM decreases by ≈50% and the high-energy side by only ≈10% for the larger bias. Clearly most gains are made on the low energy side as a result of improved charge collection efficiency at the larger E-field strength.

The high energy side of the peak shows negligible variation over the E-Field range. The low energy HWHM however starts at very large values (>10keV) and converges towards the value of the high energy side with increased E-Field strength indicating that the tailing effect is gradually reduced but not overcome.
Chapter 4: CZT as a X- and γ-Radiation Detector

Similar measurements with a 1mm thick CdTe detector at −20°C using $^{57}$Co found that the energy resolution component due to the high and low sides can converge at sufficiently high field strengths, 10kV cm$^{-1}$ [20]. In this case the tailing effect is finally defeated.

4.3.4 Miscellaneous Experiments

What follows is a series of experiments that examine a few interesting aspects of our detectors. These are the polarisation effects, resolution and peak pulse height versus time and the detector orientation. In these experiments only the $^{241}$Am source was employed.

There is a substantial amount of literature concerning the polarisation effects in CdTe and HgI$_2$ detectors [21-24]. Generally the count rates and peak positions were found to vary with time. This time dependence has been attributed to space charge effects due to the fabrication process. Maintaining the crystal at an E-Field of 1kV cm$^{-1}$ for six hours at 300K showed no changes in the obtained spectral capabilities. This agrees with the work of other authors who showed that CZT detectors do not exhibit short term polarisation effects [3].
Following the change in the E-Field across the CZT detector in chapter 5 the resistivity of the detector is found to vary with time. The change in leakage current will give rise to changes in the shot noise component of the peak broadening. To assess this change an E-Field of 2kVcm\(^{-1}\) was applied to a CZT detector at 300K and the resultant spectra recorded at five minute intervals. Only changes between the first two spectra could be ascribed to variations outside of experimental tolerances. The change seen was an increased peak channel number and peak height for the second spectra. The variations in time of the resistivity have been reported elsewhere [25] to occur over a fifteen minute period following a change in E-Field. In our case the variation was seen over an hour or more. These authors however did not quantify the effect of an unstable resistivity on the spectroscopic properties of CZT detectors.

The resistivity of the detector was also found in chapter 5 to depend on the E-field direction. The difference in resistivity being approximately 10% between directions. Variation in the orientation was found not to lead to any noticeable changes in the attained spectra over the E-Field range, upto 2kVcm\(^{-1}\). This may indicate that the changes in resistivity are too small to be of consequence in this case. However, some evidence clearly indicates that in a more severe case it determines if any spectra at all may be attained [9].

### 4.4 Spectroscopic Temperature Dependence

The wider bandgap (1.6eV) and related higher resistivity (\(\rho = 10^{10}-10^{11}\Omega\text{cm}\)) of CdZnTe spectrometers delivers improved room temperature operation compared to CdTe (1.45eV, \(\rho=10^8\Omega\text{cm}\)). An evaluation of their temperature dependent performance is still useful in establishing an operational temperature range. A number of processes; charge trapping and de-trapping, mobility-lifetime product and the generation-recombination rate in the bulk are dependent on the detector temperature. A complicated interplay of these factors will be important in determining the detectors effective working range.

In this section two experiments are performed using the 0.4MBq \(^{241}\text{Am}\) source. Firstly, successive radiation spectra at 200K are obtained as a function of time following the application of an E-field. Secondly, the radiation spectra in the temperature range of 240K to 360K are recorded to establish the temperature limits for effective operation.
Chapter 4: CZT as a X- and γ-Radiation Detector

4.4.1 Experimental Set-up

The experimental arrangement is illustrated in Fig 4.7. The CZT detector was aligned vertically, cathode uppermost, in the optical cryostat. The crystal was orientated in the high resistivity direction. Irradiation was carried out using the 0.4MBq $^{241}$Am point source placed atop the cryostat. Aluminium foil was used to prevent extraneous light from affecting the measurement with negligible effect on the photon flux [10].

In this experimental set-up, vibrations from the nitrogen and rotary pumps were subdued and the electrical interference from the temperature controller was removed. In the absence of the source at an E-field of 1kVcm$^{-1}$ the MCA recorded no visible spectra.

For this experiment a shaping time of 0.5μs and gain of 1000 were used with an E-field strength of 1kVcm$^{-1}$. The gain of the shaping amplifier was a thousand.

4.4.2 Americium Spectra versus Time at 200K

Before evaluating the spectroscopic dependence on temperature it would be interesting to investigate the time dependence of a low temperature measurement. The crystal was held at the temperature of 200K with the $^{241}$Am source in place and no external field applied. Following the application of a 1kVcm$^{-1}$ E-Field, three spectra were recorded at five minute intervals, Fig 4.8. The cessation of one spectrum was quickly followed by the commencement of the next.
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A dramatic difference in the three spectra as a function of time is clearly seen. In the first spectra a photopeak is observed which is almost non-existent in the second spectra. In the third spectra only low energy noise is observed with no photopeak. Subsequent spectra recorded only low energy noise.

During the recording of the first spectra the peak shape was clearly observed to become more asymmetric with time, i.e. the low energy side of the FWHM increased. The centroid channel for the first spectra is 422 compared to 750 with a FWHM of 5% for this E-Field strength at 300K.

At these reduced temperatures the crystal is rendered unusable within ten minutes of E-field application. Application of the E-Field in the absence of the source, ten minutes prior to irradiation, was found to also render the crystal unusable.

This result is at odds with the traditional semiconductor detectors such as Si and Ge, which rely on being cooled to a lower temperature (77K) for effective operation. In the case of CZT detectors the decrease in shot noise is not the only relevant parameter for their operation at reduced temperatures.
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4.4.3 Americium Spectra versus Temperature

The temperature response of the CZT detectors under irradiation was recorded in the temperature range of 240K to 360K (-33 to 87°C) using the same arrangement as Fig 4.7. An E-field of 1kVcm\(^{-1}\) was applied to the detector and a shaping time of 0.5μs was used. The spectra were recorded for ten minutes. Fig 4.9 shows a three dimensional plot of pulse height spectra versus channel number at nine temperatures using \(^{241}\)Am. The shaping amplifier gain was set at 1000.

![Graph showing pulse height spectra versus channel number at different temperatures with \(^{241}\)Am](image)

Fig 4.9  
\(^{241}\)Am pulse height in the temperature range 240 to 360K

A drastic reduction in the 59.5keV photopeak is observed at temperatures less than 280K. For temperatures below this the photopeak becomes absorbed in the low energy noise and the detector is unusable. For higher temperatures the photopeak begins to fall off at 360K with a similar decrease in the resolution, Fig 4.9.
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The plot clearly indicates that at temperatures below 290K, the 59.5keV photopeak is considerably reduced and that at 240K the spectra consists of low energy noise only. In the temperature range 280K to 340K a plateau of best spectroscopic performance is observed with the pulse height, peak channel and FWHM being relatively invariant.

Fig 4.10 shows the FWHM(keV) and peak counts as a function of temperature. The FWHM is observed to be essentially unchanging in the temperature range of 280K to 330K before increasing sharply for temperatures outside this range. The number of counts recorded is also seen to be very similar in this region, before falling outside of this. Accounting for the changes in peak channel number and FWHM with temperature, the FWHM was minimised at 300K. This indicates the optimisation of CZT to work at this temperature.

![Resolution (keV) for Am spectra as a function of temperature](image)

The spectroscopic temperature dependence of CZT detectors to high energy photons has been reported elsewhere [12,26-28]. Cooling of the detectors has principally been undertaken to reduce the dark leakage current to a few picoamps for the measurement of soft X-rays. Reduction in the leakage current allows the use of higher E-
Field strengths. The higher E-Fields allow for more efficient charge collection since the transit time of the carriers is inversely proportional to the E-Field inside the detector.

In an experiment using $^{55}$Fe the detector was cooled to $-40^\circ$C using peltier coolers and the FWHM was measured to be 240eV. The energy resolution of the $^{55}$Fe photopeak (at 5.9keV) was found to degrade with increasing temperature [26].

In addition the performance of Cd$_{0.8}$Zn$_{0.2}$Te and CdTe was also reported by Egarievwe et al [27]. For temperatures in the range of 25-70°C, the peak positions in the CZT was found to vary much less than in CdTe. Further, the CZT detectors also exhibited little deterioration in the energy resolution up to 60°C. The IV profile was nearly identical in their sample following the temperature cycling.

Temperature cycling of CZT detectors was also undertaken by Glick et al [28]. A detector was heated to 85°C for 15hr before cooling to room temperature. Spectra were recorded using $^{241}$Am before and after this thermal cycling and they were found to be nearly identical.

The temperature response of a CdTe detector grown by HPB has been reported by C. J. Johnson et al [12]. Spectra from $^{241}$Am were recorded using a 10x7x2mm$^3$ detector in the temperature range of $-60^\circ$C to 40°C with an E-Field of 1kVcm$^{-1}$. A drastic reduction in the pulse height of the 59.5keV photopeak was observed at temperatures less than $-25^\circ$C and the FWHM was found to be optimal at about $-20^\circ$C. This phenomena was attributed to either defect trapping properties that are effecting the carrier transport properties or that the internal field distribution is reduced at lower temperatures.

A comparison was made with the temperature dependence of electron and hole charge collection on E-Field due to LED illumination [12]. The maximum collected electron charge has a maximum at about $-20^\circ$C, which is in agreement with the pulse height analysis investigations. The hole signal was maximum between 0 and $-20^\circ$C and decreased by about an order of magnitude at $-60^\circ$C. This large reduction in hole current is most likely attributed to a deep hole trap in the bulk material [12].

The loss of spectroscopic abilities for higher energy radiation in $^{241}$Am (at 59.5keV) than in $^{55}$Fe (at 5.9keV) would indicate that the effect is a bulk property and not due to the contact barriers. This applies if the defect levels or the internal field are responsible for limiting the charge collection efficiency at reduced temperatures.
Chapter 4: CZT as a X- and γ-Radiation Detector

4.5 Variation of Interaction Position

Some features of the spectra attained from CZT detectors; pulse height, energy resolution are strongly affected by the charge collection efficiency. Therefore low charge mobility and trapping-detrapping phenomena can degrade the performance. The distance a signal must travel from the point of interaction to the collection electrode therefore governs the degree of signal degradation. Classical irradiation through the cathode, Electrode Irradiation (EI), is sufficient for low energy X-rays where problems with hole collection due to trapping are reduced. However, at increased photon energies ≈100keV where the mean free path is \( \lambda \approx 1.1 \text{mm} \) in Cd_{0.8}Zn_{0.2}Te the spectroscopic performance is severely degraded owing to the lower mobility of holes.

4.5.1 Theory

To study the effect of interaction position on spectroscopic performance an alternative irradiation configuration can be used, that is denoted as Side Irradiation or SI. In SI the photon enters the crystal through one of the passivated surfaces with the direction of travel perpendicular to the direction of the E-field vector. The two irradiation configurations are shown in Fig 4.11 [29].

![Diagram of irradiation configurations EI and SI on a detector.](image)

In electrode irradiation, EI, the energy resolution is governed by the individual signals having a density distribution governed by the exponential absorption law in the detector, i.e. the highest density of charge carriers is generated close to the irradiated electrode. In SI the signals will have a constant density distribution within the detector.
Thus in SI it is expected that an enhancement in the low energy peak and a reduction of the high energy peak will occur. This effect is expected to be more pronounced at lower incident photon energies.

The charge collection efficiency is dependent on the point of interaction within the detector and the lower $\mu\tau$ product for holes indicates that the least favourable point of interaction is therefore close to the anode. At this point the holes must traverse the entire length of the detector prior to collection at the cathode. In this case the collection time for holes is [29]

$$\tau_{\text{max}} = \frac{d}{v_h} = \frac{d}{\mu_h E} = \frac{d^2}{\mu_h V_b}$$  \[4.1\]

where $d$ is the distance between electrodes (0.5 cm), $V_b$ the bias voltage, $E$ the field strength (V cm$^{-1}$) and $v_h$ the hole speed (cm s$^{-1}$). Derivation of Eqn[4.1] is made from the general formula

$$v_h = \mu_h E$$  \[4.2\]

an expression valid for E-fields up to several kV cm$^{-1}$.

As the point of interaction moves from the anode to cathode the collection of holes is improved. At a certain point the collection time of holes and electrons will be equal and in this case

$$\tau_{\text{min}} = \frac{x_m}{v_h} = \frac{(d - x_m)}{v_e}$$  \[4.3\]

Substitution of $1/v_h$ from Eqn[4.1] gives

$$\tau_{\text{min}} = \frac{x_m d}{\mu_h V_b}$$  \[4.4\]

where $x_m$ is the distance from the cathode. Here the point of interaction for equal collection is [29]

$$x_m = \frac{d \mu_h}{(\mu_e + \mu_h)}$$  \[4.5\]

derived from Eqn[4.4] and using Eqn[4.3]. This assumes that a uniform field exists across the detector.
Chapter 4: CZT as a X- and $\gamma$-Radiation Detector

It is therefore possible with the use of a suitable collimator between the source and the detector to restrict interaction to a particular region of the detector. It is apparent that pulses generated in the region $x=x_m$ are most useful for spectroscopic applications.

The ratio $[29]$

$$\frac{\tau_{\text{slow}}}{\tau_{\text{fast}}} = \frac{\mu_e + \mu_h}{\mu_h}$$  \hspace{1cm} [4.6]

is a measure of the intrinsic time spread function of the detector due to the mobilities of both charge carriers and is independent of detector dimensions. The lower the ratio the better the time response with a limiting value of 2 for $\mu_e = \mu_h$. For currently available CZT detectors this ratio is approximately 11 which is somewhat worse than Ge ($\approx 3$) or Si (3.8) detectors. It is however better than HgI$_2$ for which the ratio is approximately 23.

4.5.2 Experimental Set-up

The experimental set-up is similar to that used in section 4.4 with irradiation now carried out through a passivated surface. In this case the BeCu sprung contacts are aligned horizontally and a collimator is positioned between the detector and the source, Fig 4.12. The 5mm thick brass ($Z\approx 30$) collimator, sufficient to absorb $>99.9\%$ of this radiation, has a slot hole of 5mm x 0.2mm.
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The position of interaction was varied by movement of the cryostat using the micropositioners. The cryostat maintained the crystal temperature at 300K. The shaping time and gain were 0.5μs and 1000 respectively. The applied E-Field was 2kVcm⁻¹.

4.5.3 Results

The peak channel number and the FWHM (in keV) are shown as a function of interaction distance from the cathode up to ≈2mm. Beyond this point the quality of the spectra was so poor that such figures could not be computed.

Clearly the peak channel number is maximum closest to the cathode before falling gradually (<1mm) and then more rapidly (>1.5mm). This is clearly linked to the loss of hole signal with distance from the cathode. The FWHM also increases significantly with distance from the cathode due to the same reason.

![Fig 4.13](image)

Energy Resolution (FWHM) in keV as a function of position

The work of Bertolucci et al [30] with ²⁴¹Am also showed a radical difference between cathodic and anodic irradiation with side irradiation being an intermediary. In this case E-Fields of 350Vcm⁻¹ were applied across the 1cm thick detector. For cathodic irradiation an acceptable photopeak with a peak to valley ratio of 13:1 and a FWHM of 6% were produced. Anodic irradiation yielded no photopeak. In lateral irradiation the
incomplete charge collection process produced a plateau that took the 59.5keV peak to valley ratio to 1:7. In this case the FWHM is 7%.

Aurrichio et al [31], using $^{37}$Co side irradiation on a 3x5x2mm$^2$ detector found similar results to those that are seen here. The centroid channel for the photopeak was seen to decrease with distance from the cathode. This change was only small for distances less than 0.3mm and then falling off sharply. The FWHM was also seen to increase over the same distances. In this thin detector energy spectra were obtained across the entire thickness of the detector.

The point of optimal interaction distance from the cathode could not be resolved other than to say that it is very close to the cathode, within 200μm.

### 4.6 Discussion

In this chapter a number of experiments have been carried out to examine, in depth, the spectroscopic capabilities of a Au contacted CZT radiation detector. At room temperature the detectors were found to posses excellent spectroscopic abilities for the 60keV photon energy and below. This was established at a shaping time of 0.5μs with a minimum E-Field of 400Vcm$^{-1}$. At higher photon energies of 122keV the spectra clearly showed a large amount of low energy tailing to the principal photopeak. This was considerably reduced but not overcome at increased field strengths. The effect of shaping time was more clearly seen here.

No polarisation effects or change in the spectroscopic performance were found to depend on time.

The effect of detector temperature was the most revealing characteristic found in this chapter. At 200K the spectra was found to degrade completely within 15 minutes of the E-Field being applied. The detector was also found to be unusable outside the temperature range of 280K to 360K. This result is at odds with the traditional semiconductor detectors of Si and Ge, which require cooling to 77K for effective operation.

The positional dependence of interaction revealed that moving the point of interaction away from the cathode soon resulted in a deterioration of the detection capabilities.
Chapter 4: CZT as a X- and γ-Radiation Detector

The results reported here reveal that CZT is not a simple semiconductor radiation detector. To fully understand the mechanism behind the observed phenomena a more detailed understanding of the material properties is required. This is carried out in the following two chapters.
Chapter 5: Electronic and Optical Measurements of a CZT Radiation Detector

5.1 Introduction

The literature is replete with examples of radiation spectra attained using CZT detectors, usually following the variation of a manufacturing process [1-16]. There is though a lack of coherent explanations for the observed spectroscopic characteristics of these detectors. This chapter investigates the electronic and optical properties of a CZT radiation detector so that a model for the observed spectroscopic behaviour can be established. This model is discussed in chapter seven.

The properties discussed in this chapter are the detector resistivity, contact barrier, semiconductor bandgap, defect energy levels and carrier transport properties. For direct comparison the device studied is the same 5mm cubic detector that was used in the radiation spectra measurements in chapter four. Most of the experiments are performed using the Electro-Optic probe station, which was described in chapter three. Additional experimental arrangements are discussed where necessary.

In order to build a cohesive model of a material where the electronic properties are not well documented it was decided to start with those experiments that studied the most basic property of the detector. The simplest measurement that can be undertaken of the detector is the electrical resistivity, easily evaluated by recording the current versus voltage profile.

5.2 Resistivity of a CZT Radiation Detector

The electrical resistivity of the detector was measured using the Electro-Optic probe station and current measurements as a function of E-Field recorded using the HPPA. It was noticed that the dark current observed at an E-field strength of 400Vcm\(^{-1}\) exhibited a time dependent component. Before accurately recording the IV profile this
variation with time of the integrated current and therefore the detector resistivity must be quantified.

### 5.2.1 Current versus Time

The nature of the current variation was such that the detector resistivity appeared to increase with time, i.e. $dI/dt < 0$. This change was clearly observable on the HPPA display screen and at a temperature of 300K it could take up to one hour for the current to attain equilibrium. This behaviour is not encountered with Si or Ge detectors. This repeatable behaviour was found to be dependent on the sample temperature.

Extraneous effects such as capacitance effects in the measurement cables and thermal fluctuations were quickly discounted. Prior to crystal insertion the capacitance of the wires gave rise to currents that decreased within ten seconds of the potential difference being applied. The temperature of the crystal was monitored with the thermocouple to ensure accuracy.

By subtracting the equilibrium current at each temperature and expressing the remainder as a percentage above the equilibrium value, allowed direct comparison of this variation at different temperatures. The current variation as a percentage above the final steady state value is shown in Fig 5.1 for three temperatures. The time $t=0$ corresponds to the application of the 400Vcm$^{-1}$ E-field. For each sample point the current was integrated over a period of 320ms.

At 280K and 320K the dark current decreases more rapidly following the application of the E-field than it does at 300K. All temperatures in the range 280K to 320K were measured with a step size of 5K. The slowest decrease in current was found to be at 300K where the dark current continues to fall at $t>30$ mins.

The results indicate that to effectively record the IV profile at 300K, a hold time is necessary, following the application of the E-Field and prior to recording the data, of at least one hour. A further delay time is necessary between variations in the E-field. As will be seen later other effects are observed at or below 300K.

Comparison with the literature reveals that the time dependence of resistivity has been seen elsewhere [17]. In this work the stabilisation time for CdTe detectors was 10-15min compared to 1hour in CZT. This may hint at a deeper charge trap in CZT than CdTe. These authors however did not quantify the effect of an unstable resistivity on the
spectroscopic properties of CZT detectors. The spectroscopic characteristics were found not to have a time dependent component outside of 10 minutes at 300K.

Further experiments, where applicable, used suitable hold and delay times to prevent erroneous results due to current instabilities. A similar feature was also seen during optical excitation measurements.

5.2.2 Current versus Voltage Profile (IV)

The IV profile in both E-field directions to 400Vcm$^{-1}$ with a step size of 0.4Vcm$^{-1}$ at 300K is shown in Fig 5.2. The IV profile was recorded with a hold time of two hours and a one minute delay time between each voltage measurement. At each step the current was recorded for a total time of 320ms. The profile indicates a non-linear region in the low E-field regime, $<$40Vcm$^{-1}$, with the current magnitude being dependent on the E-field direction.
The corresponding resistivities were taken from the gradients in the 300Vcm\(^{-1}\) to
400Vcm\(^{-1}\) region to avoid the non-linearity at low E-Field strengths. The two curves give
values for the detector resistivity of 1.47E+11\(\Omega\)cm and 1.61E+11\(\Omega\)cm in the high and
low resistance orientation respectively. The line of best fit that was obtained using a \(\chi^2\)
test was very close to the measured data with the correlation for the forward and reverse
orientations being 0.999967 and 0.999965 respectively. The high values for the resistivity
are close to those predicted through theoretical consideration of a perfect crystal
indicating an intrinsic or very nearly perfectly compensated material [18].

The resistivity of Cd\(_{1-x}\)Zn\(_x\)Te detectors has been studied elsewhere [19-21]. Butler
et al [19] measured the resistivities of Cd\(_{1-x}\)Zn\(_x\)Te with x=0.04 and x=0.2 as 2.5x10\(^{10}\)\(\Omega\)cm
and 2.5x10\(^{11}\)\(\Omega\)cm respectively. Johnson et al [20] have reported resistivities of 10\(^{11}\) on
HPB CdTe so that a higher value for Cd\(_{0.8}\)Zn\(_{0.2}\)Te would be expected. Resistivities of
\(\approx 10^{11}\) have also been reported by Verger et al [16] and Parsons et al [21].

The non-linearity at a low E-field is a combination of contact barrier phenomena
superimposed on the crystal dark current. The generation-recombination current that
constitutes the crystal dark current dominates the crystal conductivity. The combination
of the contact generated current and bulk resistivity of the material mean that the number of free carriers within the material cannot be determined until the barrier heights are evaluated. The resolution in the voltage in this experiment is insufficient to determine the barrier height.

Johnson et al [20] found that those detectors that displayed the S-shaped curve around a zero electric field were more likely to produce detectors with good spectroscopic performance, although no model was suggested to explain this observation.

The IV plot, with its S-shaped curve, is not that of a true ohmic contact confirming the existence of a contact barrier at the Au/CZT interface [21] and in this sample the conductivity is asymmetric.

5.2.3 Hysteresis Phenomena

The HPPA is capable of recording the current in one E-field direction before returning in an identical step size to the initial field strength. This is known as a double sweep. Considering the observed time dependent current variation it was felt interesting to see if any changes were seen between increasing E-Field and decreasing E-Field strengths.

![Graph](image)

**Fig 5.3**

Hysteresis type effect in a CZT detector at 300K
Chapter 5: Electronic and Optical Measurements of a CZT Radiation Detector

A double sweep of the E-field strength was made of the detector from 0Vcm\(^{-1}\) to 400Vcm\(^{-1}\) in steps of 5Vcm\(^{-1}\) before returning to 0Vcm\(^{-1}\) in the same step size. At each step, the current was integrated for a time of 20ms. The resultant double sweep at 300K in the forward bias direction is shown in Fig 5.3 where the arrows indicate the direction of the E-field variation. Clearly there is quite some degree of difference between the observed conductivity in the primary, increasing E-Field, and secondary, decreasing E-Field, sweeps. At the half way point, E=200Vcm\(^{-1}\), the secondary sweep is \(-16\%\) below that of the primary sweep.

The difference in current magnitude for the two sweeps was found to be dependent on the rate of change of the E-field and the sample temperature. Decreased rates of measurement through smaller step sizes or longer delay times led to a reduction in the difference between the two sweeps. At elevated temperatures the difference was seen to reduce for the same measurement parameters.

In Fig 5.4 double sweeps for the high and low resistance orientations are seen that clearly show the same phenomena is observed for both E-field directions with the return sweep being the lower current for both. The orientation then seems to only determine the magnitude of the dark current.
In contrast, if the E-field started from the highest E-Field strength then the return sweep was at higher current values.

**5.2.4 Summary**

In these experiments the detector resistivity has been seen to depend on time following the E-field application and its direction across the detector. In the former case this has also been seen to have a temperature related component. In the latter a difference of up to 10% is seen in the conductivity between the increasing and decreasing voltage sweeps. These properties are not observed on traditional semiconductor detectors such as LN$_2$ cooled Si or Ge.

Further experiments, where applicable, used suitable hold and delay times to prevent erroneous results, which included some of the later optical measurements.

These results are clearly important for spectroscopic applications where the increased dark current will lead to an increase in the shot noise from the detector and ultimately degrade the attainable resolution. A search of the literature has found only a few references that discuss the effect of the IV profile on spectroscopic resolution [20,21]. Certainly with our semiconductor detectors the energy resolution was not found to alter measurably with time. No changes in the spectroscopic performance were observed as a result of a change in the detector orientation.

The IV profile exhibits a non-linearity for E-field strengths below 40Vcm$^{-1}$ hinting at non-ohmic behaviour at the Au/CZT interface. It is now imperative to focus down upon this region.

**5.3 The Gold – CZT Contact**

The asymmetric contact barriers gave rise to the non-linear regions in the low E-field region, forming a S-shaped curve about 0Vcm$^{-1}$. The barriers could not be evaluated accurately in the previous measurements due to insufficient voltage resolution. Focusing down the IV profile to a narrower range of E-field strengths, centred at 0Vcm$^{-1}$, will allow the attainment of more relevant data. It was also noticed in the course of these experiments that the Au/CZT interface displayed a photovoltaic type effect.
Chapter 5: Electronic and Optical Measurements of a CZT Radiation Detector

5.3.1 Narrow Range IV Measurement

The experimental arrangement for the large IV measurement is sufficient to allow its use here for lower magnitudes of current. The E-field was varied from $-10 \text{Vcm}^{-1}$ to $10 \text{Vcm}^{-1}$ with the current integrated for 640ms at each of the 100mVcm$^{-1}$ steps. This allows the E-field direction to be reversed and the observed asymmetric resistivity to be more closely examined. A hold time of two hours was used prior to recording measurements with a one minute delay time at each step.

The resulting voltage scan with the linear extrapolations from the large range IV data from 300Vcm$^{-1}$ to 400Vcm$^{-1}$ and corresponding barrier heights calculated from the y-axis intercepts in Eqn[2.22] are shown in Fig 5.5.

![Fig 5.5](image)

Small range IV plot with intercepts and barrier heights

The repeatable S-shaped nature of the IV profile is more clearly illustrated at these lower E-field strengths. The appearance of the graph is one of increasing resistance, i.e. an increase in V does not result in a proportionate rise in I. Instead, the rate of change of I, $\Delta I$, decreases with increasing E-field.

Either side of the origin the S-shape is slightly different. For the forward bias direction, $E<0 \text{Vcm}^{-1}$, the change in $\Delta I$ is smaller than for the reverse bias orientation,
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$E > 0 \text{Vcm}^{-1}$. This indicates that the barrier heights are non-identical as suggested by the non-symmetrical conductivity. The extracted barrier heights of 0.99eV and 1.02eV are similar with the lower barrier height related to the increased current flow in one detector orientation. The ratio of $\exp(\phi_B/kT)$ for $\phi_B = 0.99eV$ and 1.02eV is $\approx 1/3$ so that the thermionic emission current density is three times that at one contact than the other.

Non-linear IV behaviour in CZT detectors has been linked previously with detectors of superior spectroscopic performance by Johnson et al [20], although no model was suggested to explain this correlation. In [20] 50% of the detectors were tested and 82% of those that could be described as spectrometer grade were ones that possessed increasing resistance with increasing E-Field. These detectors had resistivities of $\approx 10^{11} \Omega \text{cm}$, which is the same as those used in this study.

5.3.2 Photovoltaic Phenomena

If a Schottky barrier exists at the Au/CZT interface it will give rise to an internally generated E-field. In the absence of an externally applied E-field, generation of electron-hole pairs via photon excitation in this region will generate a photocurrent. To investigate the possible existence of a contact barrier charge carriers were generated through optical absorption in the contact region under a 0Vcm$^{-1}$ external E-field.

A 1mW 850nm infrared semiconductor laser in continuous wave mode collimated to a slot beam of 200$\mu$m by 5mm provided excitation, Fig 5.6. Later measurements of the photocurrent versus wavelength showed that carriers generated in the surface region have inferior charge carrier transport properties to those generated in the passivated surface. Hence the need for sub-bandgap radiation that will give rise to carriers within the bulk material through thermal broadening of the band edges. The HPPA maintained the E-field at 0Vcm$^{-1}$. The micro-positioners on the Electro-Optic probe station allowed for the point of interaction to be accurately varied between the contacts.

Initial illumination of the contact region generated a current of approximately 100pA. This is easily recorded with the HPPA. Also shown in Fig 5.6 is the direction of the observed photocurrent during illumination where the electron current was observed to flow away from the contact region.
The micro-positioners allowed the point of interaction to be varied between the contact regions. In Fig 5.7 the observed photocurrent versus interaction position is shown. The point of interaction was varied in 50µm steps with the crystal allowed a delay time of 300 seconds at each step. The current was recorded for 640ms and the results are the average of 100 of these measurements at each position.
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The graph clearly shows the existence of similarly sized photocurrents (≈300pA) generated in both contact regions and falling off with distance from the contact. The photocurrent levels though do not decrease identically for both contacts being non zero at the halfway point, 3mm. More detailed work is required to explain why photocurrents can be generated so far from either of the contact regions. A second mechanism is thought to be involved which comes from the scattering of the photons from changes in the refractive index.

Previous work on the photovoltaic phenomena of gold contacted CZT detectors has employed a $^{55}$Fe source irradiating a contact. In the absence of an external E-Field a current of 2.5pA was created [22].

5.3.3 Summary

Although the contact barrier phenomena has been reported previously [20] the asymmetry that gives rise to differences in the resistivity has not. The contact region has been shown to have contacts of approximately 1eV in height and the photovoltaic evidence confirms the existence of a contact barrier giving rise to an internally generated field. Individually the photovoltaic effect does not prove the existence of a contact barrier as an ohmic contact under the right conditions may display the same effect [20]. Combined with the S-shaped curve in the narrow range IV profile this would reinforce the existence of a Schottky barrier at each electrode.

A small amount of work has been found that the non-linear IV profile yields improvements in the radiation spectra [20]. Having identified the barrier heights at the interface and the orientation in determining the conductivity it would be useful to look at the bulk material properties and in particular the semiconductor bandgap. This is a fundamental parameter for semiconductor detectors, determining the operating temperature range because of the contribution of shot noise due to thermally generated charge carriers.
5.4 The Bandgap of CZT

The bandgap of semiconductor radiation detectors is fundamental to their operation. In the case of Si and Ge, $E_g$ is 1.1eV and 0.7eV respectively [23], liquid nitrogen cooling is essential for their use due to the large number of free carriers that exist at room temperature. The bandgap is the dominant factor in determining the resistivity of intrinsic or well compensated semiconductors.

Evaluating the bandgap of a CZT detector is a semiconductor property essential to understanding the spectroscopic behaviour. The attained bandgap can be used to give the incorporated Zn concentration from Eqn[1.3]. Further, the Zn concentration is known to vary along the length of the HPB CZT boule [24,25]. Variations in the Zn content can cause a large variation in the bandgap and in the number of photogenerated carriers per incident gamma ray, Eqn[2.25].

In this section, four experiments are carried out to evaluate the bandgap of CZT radiation detectors. These are; photocurrent versus photon wavelength, dark current versus temperature, photoluminescence (PL) and photoreflectance (PR). The first two are carried out on the same detector as before enabling the continued direct comparison. The latter two require cleaving of a crystal to produce a fresh surface free of gross contamination and defects. This is done using a previously damaged detector. The manufacturers quote a good repeatability between batches of these detectors and errors are not thought to arise through inconsistency.

A discussion compares each technique in terms of accuracy and ease of set-up as well as commercial viability for verifying a homogeneous Zn concentration.

5.4.1 Photocurrent versus Wavelength

The absorption of super bandgap ($h\nu>E_g$) radiation by a passivated direct bandgap semiconductor has been described previously in section 2.5.3. Briefly, a direct bandgap semiconductor the absorption coefficient in this region is typically $10^5$ cm$^{-1}$ [26]. The photocurrent variation with increasing photon energy will show a marked increase at the bandgap energy as free carrier generation becomes possible through intrinsic optical absorption.
A preliminary wavelength scan at $E=400\text{Vcm}^{-1}$ simultaneous to the measurement of the crystal photocurrent indicated the suppression of super bandgap radiation and the existence of a long wavelength tail.

This experiment was carried out using the Electro-Optic probe station. Irradiation was carried out through the side of the detector with an initial photon wavelength of 850nm. Prior to experiment the point of interaction was varied using the linear positioners and the photocurrent continuously monitored using the HPPA. This allowed the position corresponding to maximum collected photocurrent to be located with an accuracy of $\approx 50\mu\text{m}$. This point was observed to be very close to the cathode, $<0.5\text{mm}$. This is believed to be linked to the poor hole transport properties compared to electrons in CZT.

In this experiment optical radiation gives rise to changes in the charge carrier concentration and time dependent current variations must be considered. An E-field of $400\text{Vcm}^{-1}$ and an incident photon wavelength of 750nm were maintained for two hours prior to the recording of experimental data. The wavelength was scanned from 750nm to 1050nm in 1nm steps. The delay time required prior to the current measurement for each wavelength was found to be only two minutes as variations in the photogenerated current were only small.

The photocurrent and transmission curves for the detector at 300K as a function of photon energy are shown in Fig 5.8. The transmission curve was attained using a computer controlled Camspec m350 double beam UV-IR spectrophotometer. The reflection that occurs at the two air/CZT interfaces has been corrected using the value for the refractive index attained in section 5.5.1 at a wavelength of 850nm of 2.9. The dispersion that occurs is thought to be negligible in such a small wavelength range [27].

In the high absorption region I, the photoconductivity is controlled by the surface lifetime. In the intermediate range of region II there is still strong absorption and the photoconductivity is controlled by the bulk lifetime, with a maximum occurring when the absorption constant is approximately equal to the reciprocal of the sample thickness [26]. In the low absorption region III the photoconductivity is also controlled by the bulk lifetime but decreases with increasing wavelength as the absorption coefficient decreases.
The photocurrent spectrum clearly shows a peak at 817nm. The short wavelength side shows as expected the observed photocurrent being suppressed due to the absorption of higher energy photons in the passivated surface. A much smaller peak at 790nm could not be explained. The long wavelength tail was expected from earlier measurements and clearly indicate that for these wavelengths, even 0.4eV below the expected bandgap, that an interaction mechanism exists.

The peak photocurrent is, as expected, a compromise between interaction depth and interaction probability in the bulk material. Also the peak wavelength is close to the theoretical limit of 813nm due to thermal broadening, $kT$, of the band edges. These two unknowns make it impossible to evaluate a reliable measurement for the bandgap using this method. A best fit made to the leading edge of the photocurrent peak has an intercept on the x-axis of 800nm or 1.55eV which is well within the expected range. This result is not thought to be considered accurate for the reasons outlined above.

Bube [26] has developed a model for such a situation of passivated surfaces and based on this the peak wavelength of 817nm corresponds to the maximum occurring
when the absorption coefficient is equal to the reciprocal of the sample thickness, $\alpha_{0.17} \approx 2\,\text{cm}^{-1}$.

The higher wavelengths are featureless, other than the gradual decrease as the probability of photoexcitation is reduced. Thermal broadening of the band edges is insufficient to account for the observed photocurrent at wavelengths some way from the bandgap.

The transmission data clearly shows the total absorption of photon wavelengths below 824nm (1.5eV) rising suddenly and then continuing to rise more gradually at higher wavelengths. This is clearly linked to the band edge of CZT at which the highly attenuating intrinsic absorption occurs. The maximum recorded transmission, taking into account Fresnel losses at the two Au/CZT interfaces, never exceeds 40%.

The continued existence of photocurrent at 1050nm, 0.4eV below the expected bandgap, indicates that extrinsic absorption may be occurring within the material.

An interesting comparison can be made between the two curves. The lines cross at $\approx 840$nm where the recorded photocurrent is 4nA and the transmission is 20%. At 1050nm the photocurrent is 0.5nA and the transmission is 35%. Although the generated current and therefore the absorption fall by a factor of 8 the increase in transmission does not match this, not even doubling. A second mechanism is thought to be involved, limiting the observed transmission.

This mechanism is optical scattering within the crystal due to changes in the refractive index for a photon as it traverses the medium. Scattered photons that leave the sample along a different path to the principal beam are lost from, and reduce the transmission measurement. Scattering may arise through changes in the composition or crystal orientation. As will be seen later these causes can be linked to results recorded by XRD.

5.4.2 Darkcurrent versus Temperature - The Arrhenius Plot

In the CZT detector the total leakage current is a combination of two effects. These are excitation over the contact barrier and thermal generation of charge carriers across the bandgap in the bulk. In section 5.2 at E-Field strengths of 400Vcm$^{-1}$ the second of these dominated the conductivity. The contribution of both components to the dark current Eqn[2.23] can then be simplified [22] to,
where $J$ is the current density, $T$ the sample temperature in K, $E_g$ the bandgap, $k$ is Boltzmann's constant and $C$ is a constant. Subsequent rearrangement gives,

$$\ln\left(\frac{J}{T^{3/2}}\right) = -\frac{E_g}{2kT} + \ln C$$  \[5.2\]

A plot therefore of $\ln(J/T^{3/2})$ against $1/T$ will yield a straight line with a gradient proportional to $E_g$ and an intercept of $\ln C$ on the y-axis. Such a plot is known as an Arrhenius plot. The bandgap is assumed to be invariant to temperature, i.e. $dE_g/dT=0$.

The dark leakage current was recorded using the HPPA at temperatures in the range of 300K to 380K, in 10K steps using the optical cryostat. Excessive heating was avoided so as not to alter the contact or bulk nature through diffusion of electrode gold.

The crystal was maintained for one hour at each temperature with the experimental E-Field of 400Vcm$^{-1}$ applied. This ensured that the crystal temperature was stable, checked using the thermocouple, and that current-time variations were removed from the experiment. A total of one thousand current measurements were recorded at each temperature in a time of approximately ten minutes. Each current measurement involved the integration of the collected charge for 640ms. The Arrhenius plot for a CZT crystal is shown in Fig 5.9 with the statistical best fit based on the $\chi^2$ parameter.

From the straight line fit a bandgap of 1.57eV±0.02eV was established with a correlation coefficient of 0.9996. The intercept of $\ln C$ on the y-axis was found to be 3.6E-2. The result here is in good agreement with the theory due to the excellent correlation coefficient and there is no reason to doubt the attained value of $E_g$ due to the relative simplicity of this experiment.

This method was found to become unreliable for temperatures below 290K where the experimental values deviated strongly from those predicted by the theory. There are two possible reasons for this. In the first the assumption of bulk dominating contact generated current may no longer apply at these depressed temperatures. Alternatively the bulk material may possess temperature dependent defect trapping properties that alter the
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theoretical concentration number of charge carriers. This may also affect the carrier lifetimes and mobilities [20].

![Arrhenius plot and best fit line for CZT](image)

As a final remark, no change in the resistivity of the detector was seen upon cooling to 300K. Johnson et al [20] investigated changes in the radiation spectroscopy characteristics with temperature cycling and found the spectra to be identical before and after heating. This may then have a clear link to high temperature applications.

5.4.3 Photoluminescence (PL)

The theory of Photoluminescence or PL was discussed in chapter 2. CdZnTe is a direct bandgap semiconductor which will absorb almost all, >90%, of super bandgap light photons within the first μm of the surface and the fluorescence will then be characteristic of the exposed surface. The sample used in this case was from a damaged CZT crystal that was cleaved prior to the measurement to reveal a fresh specularly smooth surface free of gross contamination and mechanical defects. This allowed the crystal bulk and not the passivated surface to be interrogated by the laser beam.

The set-up is shown in Fig 5.10. A 35mW red 633nm He-Ne laser steered onto the sample with a mirror provided excitation. The spot size is approximately 5mm wide.
The photoluminescence is emitted into all directions from the sample (into $4\pi$) and a small part is collected by the PL optics. The crystal is orientated so that specularly reflected light is prevented from entering the PL optics. A high pass filter for the infrared (>750nm) attenuates any scattered laser light.

The PL is focused down onto the entrance slit of a Jobin-Yvon H-series Monochromator. Entrance and exit slit widths can be varied from 0.1mm to 2mm with a resolution of 8nm per millimetre of slit width. A photomultiplier tube, PMT, is coupled closely to the exit slit and the resultant current fed to a Princeton Applied Research model 5209 lock in amplifier. The photomultiplier is limited to wavelengths shorter than 850nm and is not considered reliable for wavelengths longer than 840nm.

Signals from the chopper and the PMT were fed to the lock in amplifier which multiplies only those signals of equal frequency and phase to the chopped laser beam. The chopper frequency was set to 333Hz removing mains noise from the amplifier output. The lock-in amplifier is able to integrate the current over time, defined by a time constant, for increased sensitivity. This can be further enhanced by a similar time constant function within the PC.

Fig 5.10
Photoluminescence Setup
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The optics arrangement was aligned using a ruby sample that has a strong sharp signal at 692nm due to the chromium impurity in the aluminium oxide.

For this experiment, monochromator slits 0.1mm wide were used and a resolution of 0.8nm was attained. The lock in amplifier had a sensitivity of $3 \times 10^4 \, \text{VA}^{-1}$ and a time constant of three seconds. A further time constant of ten seconds was used on the PC. The wavelength range of 700nm to 850nm was scanned a total of ten times with the final results being the average of the readings. The resultant room temperature photoluminescence curve is shown in Fig 5.11.

![Photoluminescence spectrum at room temperature from CZT](image)

Clearly the spectra consists of a single peak centred at 792nm. The FWHM for this peak is 20nm and the attained bandgap and error is $1.57 \pm 0.02 \, \text{eV}$. This is felt reliable due to the simplicity of the results for interpretation. A number of positions across the surface were investigated and no deviations from the spectra shown were seen. Thermal broadening of the bandgap will contribute to the peak width, $\pm 15\,\text{nm}$ or $12\,\text{meV}$.

### 5.4.4 Photoreflectance (PR)

A second method for determining the bandgap of a semiconductor is possible with minimal rearrangement using the same apparatus as for PL. This is Photoreflectance or
PR, which was described in chapter 2. One serious problem in PR is the detection of unwanted PL from the sample, which adds to the background signal and can at low temperatures dominate the PR signal. However since the PR measurement was performed at room temperature and pressure, the low temperature effects are not important. PL may be reduced by using low focal length optics or by appropriate “cut out” filters in front of the detector. In this set-up the former was used. The light collection optics was arranged to be well spaced so that the solid angle of collected PL light from the sample was very small. The magnitude of the PL signal was determined prior to recording the PR and found to be below the background noise of the system. The experimental set-up is shown in Fig 5.12.

![Fig 5.12 Schematic of PR experiment](image)

In this experiment the chopper frequency and time constants were those reported for the PL experiment. The wavelength was varied a total of twenty five times and the resultant spectra is an average of the attained data. The monochromator slit width was 1mm. The resultant photoreflectance spectra is shown in Fig 5.13.
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Fig 5.13
PR spectra at room temperature 1mm slits and 25 scans for CZT

The room temperature PR spectra for a CZT crystal consists of a single peak centred at 793nm, clearly due to the bandgap. The remainder of the spectra is entirely featureless other than the edge of the peak due to spectral reflection of the interrogating laser beam at 650nm. The FWHM for the CZT peak is 13nm and the attained bandgap is 1.57eV±0.01eV.

The peak wavelength is very close to that observed for the photoluminescence, 792nm, indicating the excellent agreement between the two when considering the effect of experimental error.

5.4.5 Summary

Four experiments have been used to find the bandgap of a CZT radiation detector. In the case of the photocurrent versus photon wavelength the passivated surface of the detectors common to these materials was found to render these experimental results unusable for determining the bandgap. The depth of this layer and more directly the degree of attenuation in this region are unknown and their effect on the photocurrent can not be taken into account. It was clear though that the value was approximately 800nm, 1.55eV. The transmission data that was shown indicated that less than 40% of incident
photons left the detector along the primary photon path. This coincided with a drastic drop in the photocurrent that in this region is due to extrinsic absorption only.

This is believed to be due to scattering of the optical photons within the bulk material due to changes in the composition or crystal orientation. In later measurements, section 6.5, a XRD pattern of a CZT crystal reveals a number of orientations within a single crystal.

The Arrhenius plot for temperatures above 290K revealed a bandgap of 1.57eV. The experimental data had excellent agreement with the theory, correlation coefficient of 0.9996, indicating that at these temperatures the thermally generated current in the bulk dominated over that due to excitation over the contact barriers. Below 290K the experimental results deviated from theoretical predictions which is believed to be related to the temperature dependent charge carrier properties. This is expanded upon in chapter seven.

PL and PR investigations were performed on a different sample. They produced values for the bandgap of 1.57±0.02eV and 1.57±0.01eV which are in excellent agreement with each other. Both experiments allowed scanning the interrogating laser beam across the sample surface to reveal homogeneous material. The PL has the advantage of an easier set-up while the PR has a more accurate result.

The excellent agreement in bandgap between the PL and the PR on cleaved detector and the Arrhenius plot on a working detector indicates good consistency in the growth process between different boules of the material.

The bandgap of 1.57eV indicates a zinc concentration of 9.7%. This is within the limits quoted by the suppliers of 8% to 12%.

Of the successful techniques PL seems to be the most preferred for a number of reasons. It is easier to set-up than the PR experiment, which has additional complications due to the complexity of the theory to this technique. Also PL can also be used at a range of temperatures to study the effect of temperature on the bandgap and to the identification of energy levels within the bandgap. In comparison the Arrhenius measurement at low temperatures was found to lead to spurious results. On a commercial quality control basis the bandgap of a cleaved CZT boule could be found most easily using scanning PL.
5.5 Defect Levels

In the previous sections the resistivity, contact barrier and bandgap measurements have supplied evidence for the existence of defect levels within the CZT radiation detector. In this section three experiments are performed that provide evidence for the existence of defect levels within the material.

Usually the identification of energy levels and their density within the semiconductor requires the use of advanced experimental techniques such as PL at 4K [28-34] or photoinduced current transient spectroscopy, PICTS [33,36]. Neither of these are available to us. The study of energy levels is then restricted to qualitative evidence for their existence.

In this section the refractive index and attenuation coefficient for sub-band gap radiation for 850nm (1.46eV) photons is found. Next the photoresponse of the crystal to various photon wavelengths is evaluated. Finally, thermally stimulated current measurements are undertaken that assess the ability for the detector to trap carriers and the change in the conductivity that occurs upon heating.

5.5.1 Optical constants of Sub-Bandgap Radiation

During our experiments with infrared radiation certain wavelengths, λ >850nm, were seen to traverse the detector crystal. The radiation spot could be seen on the far side of the detector using a phosphor card infrared sensor. This included those crystals that had been wrapped in a protective coating on the passivated surfaces.

This should not be surprising. It has already been seen that the crystals possess a very high resistivity, indicating excellent crystallinity i.e. free of defects. In addition the onset of optical transmission for photon wavelengths above 824nm, section 5.4.1, was seen.

It has also been seen in our photocurrent measurements that radiation even several hundred nanometers below that of the bandgap will still cause photoexcitation. Such an interaction will lead to the attenuation of the sub-bandgap radiation flux. The degree of attenuation is expected to be much below that of super bandgap radiation as direct band to band transitions are no longer possible. The defect ionisation will depend on the capture cross section and ionisation depth.
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The absorption of sub-bandgap radiation will attenuate the incident photon flux through the usual exponential dependence with depth. The attenuation coefficient in this case will be some way below that of super-bandgap radiation at $10^5 \text{cm}^{-1}$[26]. The measurement of the linear attenuation coefficient for sub-bandgap radiation is then of interest. If 10% of the incident radiation is able to penetrate the crystal entirety then, considering reflection from the two CZT/air interfaces the attenuation coefficient is more than four orders of magnitude lower, $\approx 1 \text{cm}^{-1}$.

It is therefore possible using the principles described in section 2.5.4 and establishing the reflection coefficient from our crystals to evaluate the refractive index for sub-bandgap radiation.

The experimental arrangement is shown in Fig 5.14. The monochromator was found to provide insufficient illumination for accurate transmission measurements to be made at a range of wavelengths. Instead the 1mW 850nm semiconductor infrared laser was employed. The laser power being approximately 500 times that of the monochromator output at 850nm. The output from two silicon photodiodes of known spectral response measured the transmission and reflection power. This was recorded using two Voltage Measurement Units on the HPPA.

The incident laser power was measured in the absence of a crystal with a silicon photodiode and neutral density filters of known optical density to prevent current saturation.

Using the theory of multiple reflections, the refractive index and the absorption coefficient were found to be 2.9 and 0.9cm$^{-1}$ respectively. The refractive index indicates a primary reflection on first meeting the CZT surface of $\approx 24\%$, Eqn[2.27]. Following
reflections within the bulk this rises to 29%, Eqn[2.32]. This attenuation coefficient means that ≈64% of the incident radiation is lost in traversing the detector due to absorption and scattering.

5.5.2 Photocurrent Response

In the previous section the optical constants, n and α, were found for a photon wavelength of 850nm. Evidence for the presence of defect levels may also arise through the change in photocurrent due to extrinsic absorption. This is assessed here.

Following the application of an E-field in section 5.2 the detector resistivity was found to increase with time, i.e. dI/dt < 0. Changes in the resistivity as through photoexcitation may exhibit the same time dependence.

In this experiment the crystal was maintained at 300K in the cryostat. Photoexcitation was carried out by the monochromator with the applied E-Field of 400Vcm\(^{-1}\) and the current recorded by the HPPA. The light was focused upon the centre of the crystal so as not to adversely effect the contact barrier height. The intensity of illumination, <1mW, is sufficiently small not to perturbate the E-field. The E-Field was maintained for one hour prior to measurements being recorded. The dark current was 0.94nA. The experiment involved continuous current measurements for three minutes, the middle minute of which excitation was carried out. Each current measurement integrated the collected charge for 640ms. This was done for a variety of wavelengths in the sub-bandgap (λ>800nm) region only, three of which are shown in Fig 5.15.

The onset of excitation clearly corresponds to an increase in the sample conductivity through absorption. The data can be considered in three parts; the amount of excitation, its time dependent component and its behaviour at the cessation of illumination.

Increases in the wavelength results in a dramatic decrease in the photocurrent above 850nm. This is clearly linked to the decreasing probability for optical absorption. At a wavelength of 1050nm, 0.37eV below E\(_g\), thermal broadening of the band edges, 25meV, is insufficient to account for charge carrier generation.
In the excitation region the photocurrent possesses a time dependent component similar to that seen for the dark current, section 5.2. The same mechanism is thought to be involved for both cases as the sample temperature is the same in both cases.

The most striking observation concerns the current change at the cessation of illumination. For the shorter wavelength photons the sharper decrease is followed by a more gradual decrease to the dark current value prior to excitation. Increases in wavelength bring about a faster decrease towards the dark current value. At 900nm this is almost instantaneous to the dark current value. Further increases in the photon wavelength result in a rapid decrease in current to values below that prior to excitation. This is quite a surprising result as effectively optical excitation can increase the sample resistivity. The lowest value for the post excitation current was for the 1050nm photon where a current 26% below that of the dark current was attained. Increases in photon wavelength above 1050nm gave rise to smaller differences in the minimum value the dark current at cessation.

This might indicate that a mechanism exists whereby the sample resistivity could be increased through optical doping. Such a technique could be used to improve the
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spectroscopic performance by further reducing the component of the spectroscopic resolution due to shot noise. This result will be explained in chapter seven and reveals that this is not the case.

5.5.3 Thermally Stimulated Current

Thermally Stimulated Current measurement or TSC came to the fore as a possible technique to provide evidence for defect levels within CZT [16,37,38]. The theory of this technique was established in chapter 2. The technique involves the cooling of a sample to LN\(_2\) or LHe temperatures before filling the defect levels using optical absorption. These trapped carriers are then unable to de-trap due to the low temperatures. The sample temperature is then increased and the traps begin to empty starting with the shallowest first. A change in the observed current, which if measured simultaneous to the temperature can reveal the number of separate trap levels and their depth. Our experimental set-up here is not sufficiently sophisticated to allow the identification of trap depth, but is merely intended to conclusively prove the existence of defect levels within the material.

The crystal was orientated in the configuration of Fig 5.6 allowing illumination to be carried out through one of the passivated surfaces. Prior to illumination the crystal was cooled to 77K. The 850nm infrared semiconductor laser in continuous wave mode provided illumination for thirty minutes. The use of super-bandgap radiation would result in nearly 100% of this radiation being absorbed in the passivated surface and would not fill the bulk material traps, but recombine at the surface. The external E-Field was not applied during illumination, as it would deplete the region around the contacts, an area of considerable interest for defect levels [22].

At the cessation of illumination the cryostat was covered with an Al cover to remove room light simultaneous to the temperature being increased. The ramp rate was approximately 2Ksec\(^{-1}\). Current measurements were recorded by the HPPA by integrating the charge for 320ms. The current as a function of temperature is shown in Fig 5.16.
Thermally stimulated current

This figure consists of several large peaks corresponding to rapid changes in the sample conductivity linked to the detrapping of charge carriers due to increasing temperature. The result reveals conclusively that the CZT detector possesses a large number of defect energy levels. The low temperature (<140K) hump is believed to be the tail of a lower trap depth than we are currently not able to examine.

The two major peaks are centred around 180K and 280K with several changes in the gradient of each indicating the presence of different levels of lower concentration superimposed on the large signals of more abundant energy levels. These two major defect levels will be related to the other electronic properties and the spectroscopic characteristics in chapter seven. The two peak temperatures will prove interesting when looking at the change in photocurrent as a function of temperature.

Multiplying the peak current due to each defect level by 20 can approximate the depth of the energy level [26]. In this case 180K and 280K give rise to values of 0.3eV and 0.47eV respectively. Szeles et al [38] using TSC measurements and a second technique called TEES found two activation energies of 0.14eV and 0.46eV dominating the conductivity at low and high temperature respectively. In their case the lower activation energy was attributed to V\textsubscript{Cd}-Al\textsubscript{Cd} that are formed by the capture of vacancies.
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\( V_{\text{Cd},V_{\text{Zn}}} \) at \( \text{Al}_{\text{Cd}} \) atoms during annealing. The higher activation energy level was attributed to the double acceptor level of Cd (Zn) vacancies.

5.5.4 Summary

In this section three experiments have been used to provide evidence for the existence of defect levels within the bandgap of a CZT radiation detector.

Transmission and reflection measurements made at a wavelength of 850nm allowed the refractive index and absorption coefficient to be measured as 2.9 and 0.9cm\(^{-1}\) respectively. There is no published data for the refractive index \( n(\lambda) \) for the \( \text{Cd}_{1-x}\text{Zn}_x\text{Te} \) system although a separate piece of work revealed a similar value for \( n(\lambda=844\text{nm}) \) of 3. The attenuation coefficient is a combination of optical scattering and absorption within the material. This scattering/absorption has been shown to vary across the CZT boule [39].

The photoresponse indicated the change in photocurrent with wavelength, the variation with time of the current and critically the ability for the current to fall to levels below the dark current prior to excitation. The change in photocurrent was linked to the previous photocurrent data versus wavelength curve. Time dependence of photocurrent is believed to be linked to the dark current variation seen for changes in E-Field, section 5.2. Readings below the dark current for the high wavelengths is a more subtle indicator for the existence of defect levels. This is fully explained in chapter seven.

Lastly, the TSC measurements yielded a number of dramatic increases in the integrated current as a function of increasing temperature. The two dominant levels indicate levels that are active in the 180K and 280K region. This measurement showed conclusive proof for the existence of defect levels in the bandgap of a CZT radiation detector.

It is unfortunate in these experiments that a more complicated arrangement that could yield more accurate data such as defined energy levels and their concentration was not possible. It would now be timely to investigate the effects of these energy levels on the charge carrier properties for a radiation detector.
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5.6 Carrier Transport Properties

Following the interaction of X-ray photons in a CZT detector a high concentration of electron-hole pairs are produced. These are then swept from the detector by the applied electric field. Whilst in transit the defect energy levels may cause trapping-detrapping and recombination phenomena to occur. This will affect the spectroscopic performance of any semiconductor detector, giving rise to low energy tails to spectra or decreased peak height.

To build a model of the radiation detector the effect of these levels within the bandgap on the carrier transport properties is now highly relevant. In this section the changes in photocurrent as a function of interaction location, photon flux and temperature are studied. This will study the effect of carrier transport properties, probability of extrinsic absorption and defect phenomena.

5.6.1 Photocurrent versus Position

In chapter four the spectroscopic performance was found to deteriorate rapidly as the point of interaction was increased from the cathode. In this experiment we wish to compare this with the change in photocurrent as a function of position. The ratio of the charge carrier mobilities ($\mu_e/\mu_h$) in CZT is approximately 10. The hole component of the dark current will then fall more sharply with distance from the cathode than the electron component from the anode. The induced photocurrent should then be greatest in the region of the cathode.

The crystal was maintained at 300K in the cryostat. Photoexcitation was carried out by the monochromator with the E-Field applied and the current continuously recorded by the HPPA. The intensity of illumination, less than 10mW, is sufficiently small not to perturbate the E-field. The E-Field was maintained for one hour prior to measurements being recorded. The dark current was 0.94nA. The experiment involved continuous current measurements for three minutes, the middle minute of which excitation was carried out. Each current measurement integrated the collected charge for 640ms.

The position of interaction for a wavelength of 1050nm on the crystal surface was varied with the lateral micro-positioners. Three positions were tried; one central and the other two 1mm towards either electrode, denoted by the closest electrode. The current
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was recorded for a time of three minutes. During the second minute excitation was carried out. The three measurements are shown in Fig 5.17.

As expected the excitation clearly corresponds to an increase in the conductivity that has a position dependent component. The photocurrent was seen to decrease from the cathode to the anode. In addition the photocurrent exhibits the same time dependence with the cessation of illumination leading to sub dark currents of equal size. Neither of these characteristics has a time dependent component.

This experiment indicates that the degradation in spectroscopic performance with distance to the cathode can be illustrated by the decrease in photocurrent.

5.6.2 Photocurrent versus Light Intensity

In section 5.5 the defect energy levels found through TSC measurements were related to the extrinsic absorption observed by the photocurrent response experiment. The size of the photocurrent is dependent on the absorption coefficient, which is itself dependent on the number of absorption centres. If the number of defect centres available to contribute in extrinsic absorption is decreased then the photocurrent may also be
decreased. In this experiment the photon flux provided by a laser incident on a CZT detector is varied and photocurrent recorded.

The crystal was maintained at 300K in the cryostat and orientated in the side irradiation mode of Fig 5.18. A 1mW 850nm infrared semiconductor laser in continuous wave mode incident on the surface provided excitation. The intensity of incident radiation was varied using neutral density filters of known optical opaqueness. The E-Field of 400Vcm$^{-1}$ was applied and the current continuously recorded by the HPPA. The E-Field was maintained for one hour prior to measurements being recorded. The dark current was 0.94nA.

The experiment involved altering the photon flux followed by a delay time in which the photocurrent was continuously recorded. To ensure accurate measurements the delay time was sufficient to allow the current to attain a stable equilibrium. At this point 101 current measurements were taken with an integration time of 640ms each. The average was then taken of these and the data possessed a standard error of less than 1\%.

The photon intensity was varied upwards from the highest neutral density filter of 4. The experimental set-up is shown in Fig 5.18.

![Laser spot illumination of the CZT crystal](image)

The recorded photocurrent divided by the incident power is shown in Fig 5.19 for incident powers up to 0.01mW and in Fig 5.20 this is expanded up to 1mW full power. This y-axis variable is a more interesting quantity than the simple photocurrent as it
provides an indicator for the amount of generated current per incident photon. In these measurements the dark current of 0.94nA has been removed.

In Fig 5.19 the generated current per incident photon is seen to fall with increased photon flux. The rate of change of the data decreased with incident power. In Fig 5.20, which extrapolates this curve to 1mW (x100), the data continues the trend towards an unknown limiting value. The change in induced current per incident photon continues to fall.

![Fig 5.19](image)

Photocurrent divided by input power versus input power below 0.01mW

This data suggests that as the optical photon flux is increased the concentration of absorbing centres decreases due to prior absorption. The absorption component of the attenuation coefficient found in section 5.5.1 is dependent on the photon intensity. The role of defect levels in this process is discussed fully in chapter seven.
5.6.3 Photocurrent versus Temperature

In chapter four the spectroscopic performance was found to depend very heavily on the sample temperature. The complete loss of spectra was seen for temperatures below 280K. The TSC measurement indicated the existence of a defect level at 280K. In this experiment we wish to compare this with the change in photocurrent as a function of temperature. This is done at a fixed photon intensity and E-Field using the optical cryostat.

The crystal was held in the cryostat and orientated in the side irradiation mode of Fig 5.18. The cryostat was then evacuated. A 1mW 850nm infrared semiconductor laser in continuous wave mode incident on the surface provided excitation. The E-Field of 400Vcm$^{-1}$ was applied and the current continuously recorded by the HPPA. The E-Field was maintained for one hour prior to measurements being recorded at each temperature. This ensured thermal equilibrium across the sample and that a sufficient hold time was allowed to prevent the photocurrent variation with time, sections 5.5.2 and 5.6.1. The temperature was checked using the thermocouple.
The experiment involved altering the temperature from 300K downwards. At each step 101 current measurements were taken with an integration time of 640ms each. The dark current was subtracted from the attained photocurrent values. The average was then taken of these and the data again possessed a standard error of less than 1%. The recorded photocurrent as a function of temperature is shown in Fig 5.21.

The data indicates a very sharp fall in the generated photocurrent with decreasing temperature. From 300K to 80K the photocurrent falls by nearly four orders of magnitude. The data can be divided up into two linear regions. The first that is termed high temperature is from 140K to 300K and the second, low temperature, is from 80K to 140K. At 140K a change in the gradient is observed, becoming less steep. The two regions have been approximated using a line of best fit for comparison. The correlation coefficient for the high and low readings was 0.9972 and 0.9965 respectively.

Clearly the temperature effects on the collected current is very severe. In this situation the generated charge must become trapped by defects as usual. At depressed temperatures the rate of thermal detrapping must be considerably reduced and this results in a loss of signal due to recombination. This will be expanded upon in chapter seven.
Chapter 5: Electronic and Optical Measurements of a CZT Radiation Detector

The two regions to the data indicate that two defects may be in play. This agrees with the TSC measurement very well which indicated the presence of defects centred at 180K and 280K.

This result is very interesting when compared with the loss of spectra from $^{241}$Am at reduced temperatures, section 4.4. Johnson et al [20] reported the loss in $^{241}$Am spectra for temperatures of 260K and below. This phenomena was attributed to either defect trapping properties that are effecting the carrier transport properties [20]. A second explanation was suggested by James et al [40], where the internal field distribution is temperature dependent.

A comparison was made with the temperature dependence of electron and hole charge collection on E-Field due to LED illumination [20]. The maximum collected electron charge has a maximum at about $-20^\circ$C, which is agreement with the pulse height analysis investigations. The hole signal was maximum between 0 and $-20^\circ$C and decreased by about an order of magnitude at $-60^\circ$C. This large reduction in hole current is most likely attributed to deep hole trap in the bulk of the material.

5.6.4 Summary

In this section three experiments have been performed to examine the effects of interaction position, photon intensity and temperature on the measured photocurrent.

The variation of interaction position revealed that the integrated current was greatly increased as the interaction position was brought closer to the cathode. This is clearly related to the discrepancy in the values for the electron and hole mobilities in CZT, $\mu_e/\mu_h = 10$. In addition the decrease in photocurrent with time and the lowering of the detector resistivity at the cessation of illumination have been shown not to depend on the position.

The photocurrent variation with photon intensity at 850nm revealed that extrinsic absorption is intensity dependent. The photocurrent per photon reduced as the incident power was increased, but the photocurrent increased with increasing power.

The photocurrent was found to fall drastically at reduced temperatures. A fact that is clearly related to the loss in radiation spectra at suppressed temperatures. The loss was attributed to generated photons becoming trapped in the defect levels. At room temperature it is sufficiently likely that the thermal detrapping mechanism will allow
these carriers to escape. At depressed temperatures this probability falls off exponentially as the carriers are trapped and the defects become recombination centres. Thus a loss in signal is observed.

5.7 Discussion

In this chapter the electro-optic properties of a CZT radiation detector have been investigated in relation to its resistivity, contact barrier, bandgap, defect levels and carrier transport properties.

The detector resistivity was seen to depend on time following a change in E-Field, dependent on E-Field direction and to possess a hysteresis effect with the E-Field. Further the resistivity was seen to be non-linear with low values for the E-Field.

The non-linearity in this region was studied in more detail and found to relate to the formation of two schottky contacts at the Au/CZT interface. These contact barriers were not of the same height and this gave rise to the change in resistivity with E-Field direction. Non-linear IV behaviour has been linked previously with detectors of best performance. Photovoltaic measurements also indicated a contact barrier at the electrode region. This current was found to extend throughout the detector.

The bandgap was investigated using four methods. Three of these; Arrhenius plot, PL and PR yielded a bandgap of 1.57eV with varying accuracy. Photocurrent measurements were complicated by the presence of a passivated layer on the CZT surface. The transmission measurement that was performed never exceeded 40%.

The presence of defect levels within the detector were investigated using sub-bandgap radiation, photocurrent response and thermally stimulated current measurements. The optical constants of refractive index and attenuation coefficient were found for 850nm photons. The attenuation coefficient is believed to consist of components due to absorption and scattering within the bulk. The photocurrent response indicated that at the cessation of illumination with high wavelengths the dark current fell to levels below the pre-illumination value. The TSC current measurements indicated dramatic increases in the current at 180K and 280K due to thermal excitation from defect levels.
The carrier transport properties were investigated using the photocurrent as a function of illumination position, photon intensity and detector temperature. Movement of the illumination away from the cathode recorded a dramatic decrease in the recorded current. Increasing photon intensity indicated that the photocurrent due to each photon attained a saturation limit. If the detector was cooled then the photocurrent for the same incident beam would also decrease.

The work in this chapter provides some very fundamental investigations for the semiconducting nature of the CZT radiation detector. It is now necessary to consolidate this work by performing some structural investigations of a similar CZT detector.
6.1 Introduction

The experiments in chapter 5 examined the Electro-Optic properties of a working or cleaved CZT radiation detector. The results have revealed the presence of defect levels and have hinted at the way in which these influence the spectroscopic capabilities.

In this chapter, the structural and compositional properties of the detector are examined to complement the previously attained data. This will reveal any obvious factors, not yet considered, that can be correlated with the previous results. There is limited available literature concerning the structural properties of CZT detectors and this work aims to develop this area [1-7].

Direct measurement of the zinc concentration is a principal concern in this chapter. For Cd$_{1-x}$Zn$_x$Te crystals grown from the melt, the mole fraction of Zn has been shown to vary with respect to the sample position in the boule [8,9]. Changes in the composition along a boule have important consequences for spectroscopy applications. The variation in Zn leads to a variation in the bandgap and the number of photogenerated electron-hole pairs per incident gamma ray. In addition the leakage current is much higher in regions having a lower Zn concentration.

The employed techniques are Optical Microscopy, SEM, PIXE and XRD.

6.2 Optical Microscopy

To complement later measurements that were done with PIXE, an optical image of the sample was required. Upon viewing the crystal surface under diffuse light a band of material with a different reflection characteristic was observed. A film camera coupled to the microscope captured the image with a magnification of x10, Fig 6.1. The sample dimensions are 6mm wide by 2mm deep.
The image shows a continuous band of material that runs from back left to front right across the cleaved surface with almost parallel sides. At the right edge the band turns gradually 90° anticlockwise towards the rear before disappearing. The dark areas either side of the band that represent the majority of the material appear to be of the same colouration and texture. The change in reflection across this material must correspond to a change in the refractive index due to variations in the composition or crystal orientation. These two issues will now be discussed.

The refractive index of Cd$_{1-x}$Zn$_x$Te varies as a function of $x$ between CdTe and ZnTe [10]. Changes in the composition at one point will then manifest itself through the boule due to the change in the lattice constant. The amount of difference is dependent on the zinc fraction, Eqn[1.1].

The crystal structure of CZT is isotropic so that the refractive index does not depend on the crystal orientation unless a surface treatment is undertaken [11]. An example of this is the etching of Al with a NaOH solution giving rise to a patterned surface as the etching rate depends on the direction of the crystal in that region.

To establish which of these was the contributing factor the sample was placed into a variable pressure Hitachi S3200 SEM machine. A change in composition will be
revealed using either secondary or backscattered electron detection. The attained image using both techniques did not reveal the existence of a band of material to match that seen optically. Instead both techniques indicated a uniform surface. Further, EDX and the more accurate Wavelength Dispersive X-ray Analysis (WDX) did not show any change in the material composition across the sample width. Composition was then ruled out as the cause.

Unfortunately the sample was too small to allow an XRD measurement to be recorded at different regions of the sample. Future measurements could be best done using electron diffraction [12]. If this could be shown as a change in the crystal direction then the band arises through damage during the cleaving process. More precisely, material hardness is dependent on the orientation in which it is cleaved. In this case, during cleaving the light band material will have cleaved with a different amount of damage to the whole. This induces a change in the surface roughness and optically as a change in the reflectivity. The light band material would indicate a region of optical smoothness corresponding to an orientation of increased hardness over the remainder.

Such a material property of a cleaved CZT detector has not been previously reported. However, Fiederle et al [1] presented optical images of cross sections of a CZT boule. They described the crystalline quality of HPB CZT as poor because the material is polycrystalline with large grains and twins. Our own cross section of a CZT boule also possessed a network of changing optical reflections. It is then likely that these are incorporated in the fabricated detector.

### 6.3 Scanning Electron Microscope (SEM)

A sample was cleaved from a defective crystal with an area of approximately 15mm², to produce a fresh surface free of gross contamination and obvious defects. The exposed surface was free of extraneous features and mirror-like with the grey lustre typical of this material. Steps in the crystal surface were visible as lines indicating the change in reflection of light at these points.

The sample was placed onto a conductive carbon film with cleaved surface uppermost. The use of silver dag to prevent charge-up from the electron beam was found
to be unnecessary. So good was the crystal on the micron scale that imperfections such as steps in the crystal surface were used for focusing, due to its uniform appearance at the micron scale. An image of two steps in the crystal surface is shown in Fig 6.2.

The increased brightness at the edges indicates the step direction as the secondary fluorescence yield is improved in this region. The detector is positioned to the left of the image so that the step up can be determined to be from left to right across the picture. The top left therefore corresponds to the lower plane with two steps up to the bottom right plane. The width of the intermediate step is approximately 1µm wide.

The regions away from the steps are clearly very uniform and no definition is possible for focussing. The use of an automated EDX detector with the secondary X-ray emission from the sample allows for elemental analysis of the sample.

![SEM microprobe of a cleaved CdZnTe surface](image)

The observed composition and the experimental errors were found to be

\[
\text{Cd} = 45.8 \pm 1.1\%, \quad \text{Te} = 47.5 \pm 1.2\%, \quad \text{Zn} 6.7 \pm 0.9\%
\]

The error arises because the cleaved surface could not be perfectly orientated to the incident electron beam direction. Although the amount of Te is not exactly 50% the
data is close to what is expected. Using Eqn[1.3] for the bandgap dependence on Zn fraction x yields a bandgap of 1.59±0.01eV.

The EDX spectrum is shown in Fig 6.3. The resolution of the peaks is 62eV or 2% in the largest Cd peak at 3.2keV. The relative similarity of Cd and Te mean that there is some degree of peak overlap. The zinc k- X-ray =9keV is visible.

![EDX spectrum from a CdZnTe crystal](image)

No other elements apart from carbon are seen. This may result from subsequent handling after cleaving. The carbon then arises due to dust or grease from the atmosphere or contamination from the sample chamber. The latter belief based on the fact that carbon was also seen for the SEM data attained in chapter 9 on CdTe thin film material. Alternatively, the carbon may arise from the growth process.

The melting temperature of Cd$_{1-x}$Zn$_x$Te is comparable to or exceeds the softening point of quartz, the usual material for ampoules in this technique [13]. The growth of CZT using HPB in sealed quartz ampoules leads to incorporation of significant amounts of carbon and other impurities [14]. These have been shown to be detrimental to the
crystallinity of the material [9] and to carrier lifetimes in the fabricated detectors [15]. In practice, high purity graphite components are encased in a large steel shell designed to withstand internal pressures of over 100 atmospheres [16]. This could also lead to the C signal in the EDX spectra.

Oxygen as a shallow acceptor reduces detector performance and resistivity, but carbon does not [1]. It was also reported by Rudolph et al [17] that the use of a carbon crucible may help to compensate metal impurities. Franc et al [3] also carried out mapping of a CZT boule cross-section and found no identifiable precipitates.

6.4 Proton Induced X-ray Emission (PIXE)

The irradiation of a material surface with charged particles ($e^-, p, \alpha$) can amongst other things give rise to Bremsstrahlung and characteristic X-rays[18]. The quantification analysis of the X-ray spectra enables the composition to be evaluated.

In PIXE, as opposed to SEM, protons are used in the place of electrons. The component of the X-ray spectra due to Bremsstrahlung is reduced as protons are decelerated more slowly than the electrons due to their larger mass. This leads to an increase in the observed spectral resolution. PIXE has been previously used to characterise the homogeneity of CZT detectors [4], the presence of heavy element contaminants in CdTe detectors [19,20] and for the identification of elements in Sb-doped electrodeposited CdTe films [6].

A proton microprobe in Lisbon, Portugal was used for these investigations. A second piece of CZT was cleaved from the same crystal used for the SEM measurements. The incident protons have an energy of 2MeV with a beam diameter of 1μm and the X-ray spectra was recorded using a Si(Li) detector [21]. The PIXE spectra recorded over an area of 2mm$^2$ is shown in Fig 6.4.
The spectra indicates the presence of a large number of peaks due to the Cd, Te and Zn in the crystal. The principal L-edge peaks from both Cd and Te are seen without overlap at 3.1keV and 3.8keV respectively. Both the Cd and Te escape peaks at 1.5keV and 2.9keV are observed. A pile-up peak at 6.4keV is due to simultaneous collection of two Cd 3.2keV X-ray photons. In addition the K X-ray peaks from Zn are also observed. A repeat scan recorded the same peak positions and relative intensity. The k-lines for Cd and Te at approximately 25keV to 30keV were relatively small and are not shown here.

An automated scanning system and the ability of the detector to differentiate between the principal Cd and Te L-lines at 3.1keV and 3.8keV respectively allows spatial mapping of the constituents using these lines only. The Cd and Te concentration over an area of 2mm² is shown in Fig 6.5 where the yellow points correspond to an increase in concentration and the blue points to a decrease. The images comprise 256 pixels both horizontally and vertically so that the spatial resolution is ≈ 8μm.
The black borders to both images correspond to the crystal edge. On both images the concentration of both Cd and Te is seen to increase in the bottom left corner. The increase corresponds to a change of approximately 20% in both cases [21]. The decrease is not due to a change in the stoichiometry, but the loss of detection efficiency as this corresponds to a sloped region that faces away from the detector, Fig 6.1.
Chapter 6: Structural Measurements of a CZT Radiation Detector

The recorded images in Fig 6.6 are for a selected region of 750\(\mu\)m\(^2\) over both the high and low concentration regions. In the Cd image the concentration distribution is as that recorded above whereas the Te image shows the presence of a highly concentrated region of Te of approximately 20\(\mu\)m across, marked by a circle. The presence of Te concentrations has been discussed previously [5,9,22-24]. They arise from the growth process where the Te forms precipitates in the crystal bulk.

The corresponding Cd plot does support the increase in Te concentration by showing a darkened region of low Cd concentration. This may be due to the resolution of the detector itself. Previous work has identified that the CZT detector contains a large number of Te precipitates [5,9,22-24]. Their presence may give rise to optical scattering due to a change in the refractive index at the Te/CZT boundary.

Infrared microscopy has been used previously to identify numerous inclusions and precipitates in CZT crystals [5,9,22-24]. The presence of Te precipitates appears to be variable although there is strong evidence indicating that they occur at grain boundaries [5]. Hermon et al [4] used PIXE previously to study the homogeneity of CZT detectors. Similar to this work they were able to produce concentration maps, but in their case used the Zn/(Cd+Te) ratio. They determined the composition of their samples to be Cd_{0.71}Zn_{0.23}Te_{1.06} indicating an excess of 6% Te. The use of spatial mapping in PIXE is a very useful tool to facilitate further developments in CZT detectors.

6.5 X-ray Diffraction (XRD)

The X-ray diffraction measurement requires the use of a large sample. A redundant 10x10x3mm detector was thus used. The X-ray diffraction measurements were recorded on a Philips PW 1051 diffractometer using Cu K\(\alpha\) (\(\lambda=1.54\)\(\AA\)) radiation. The energy of this radiation is \(\approx8\)keV. The obtained diffraction pattern is shown in Fig 6.7.

The pattern clearly indicates the existence of eight definable peaks superimposed on the background. The observed peaks are due to the CZT detector alone. The peaks were dominated by the 38.7° signal. This is clearly the dominant growth direction.
The assignment of the peaks was done in the following way. The orientations that give rise to constructive interference in hexagonal structures such as CdTe or ZnTe are well documented [25]. The zinc concentration is known to be approximately 10%. By substituting this value into Eqn[1.1] the value of the lattice constant, a, can be found. The values for the lattice spacing for each orientation can then be established using Eqn[1.2]. The angles for constructive interference can then be computed using the well known Bragg equation where the diffracted X-rays emerge at twice the Bragg angle \( \theta_B \),

\[
n\lambda = 2d \sin \theta_B
\]

where \( \lambda \) is the X-ray wavelength of 1.54Å, \( n \) the diffraction order and \( d \) the interplane spacing corresponding to this crystal direction, Eqn[1.2]. Comparison with standard tables allowed the correct identification of peaks. The angle, count, corresponding value for \( d \), relative intensity and the assigned peak are shown in Fig 6.8.

The XRD pattern corresponds to the existence of CZT in the hexagonal closed packed structure. All the peaks bar one were assigned to crystal directions in CZT where the Zn concentration was approximately 10%. The crystal structure is then dominated by the (220) direction which is the growth direction for this crystal. The unknown peak does
Chapter 6: Structural Measurements of a CZT Radiation Detector

not correspond to any intensity angle that can arise from cubic phase CZT. The PIXE measurements indicated the presence of Te precipitates, but there are no interplane spacings in room temperature hexagonal Te matrix that corresponds to this angle. The closest value found is that for the (200) plane in ZnTe [25]. However, the SEM measurements of stoichiometry do not agree that this is present.

### Table 6.8

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<th>Peak No</th>
<th>Angle</th>
<th>Counts</th>
<th>(d(\AA))</th>
<th>Relative I</th>
<th>Assigned</th>
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<td>3.206</td>
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<td>(200)</td>
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</tr>
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<td>2.338</td>
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<td>(220)</td>
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<td>668</td>
<td>1.174</td>
<td>7</td>
<td>(440)</td>
</tr>
</tbody>
</table>

Fig 6.8

X-ray diffraction data for a CZT radiation detector

The crystal structure of CZT has been studied using XRD elsewhere [3,4,26-28]. Additionally, Fiederle et al [1] showed that the HPB CZT boule was polycrystalline with large grains. Franc et al [3] found that the crystals grew in the (111) or (100) orientations with (111) being the dominant orientation. A deviation of less than 3° was also reported for the (111) plane. Hermon et al [4] used XRD to show that deviations in the axial direction of the boule were on the order of 1-2% over a large area, \(\approx 90\%\). Butler et al [26] measured (111) orientations from \(\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}\) and \(\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}\) crystals grown by the HPB technique.

### 6.6 Discussion

In this chapter, four experiments have been performed examining the structural properties of the CZT radiation detector. Optical microscopy identified changes in visual appearance of a cleaved surface, SEM examined the microscale surface topography, EDX and PIXE established the composition of a separate cleaved surface and XRD analysed the structural properties.

In optical microscopy, the contrasting region with different reflection properties was found not to be due to a change in the composition between these two regions using...
secondary and backscattered electrons, EDX and WDX. The change was thought due to a change in the orientation, which could not be established here. Further work using an electron diffractometer is required.

In SEM, the topography was found to be uniform with steps in the surface caused by the employed cleaving method. The use of a silver dag was found to be unnecessary due to the excellent charge transport properties for this material. The composition yielded a Zn concentration of 7%.

The use of PIXE proved very interesting for future work. The equipment used allows the spatial mapping of an area of a detector. The detection system is able to differentiate between closely space X-ray energies to measure the spatial composition. This is particularly useful for CdTe. This revealed a largely uniform surface with some inclusions due to Te precipitates. These have been observed elsewhere [22] and may give rise to optical scattering in the bulk material.

In XRD, the CZT detector was found to consist of several orientations. The dominant of these was the (200) orientation. The existence of multiple crystal orientations within one material compliments the optical microscopy data very well. This only suggested a change in reflection due to a change in orientation. Again future investigations with electron diffraction will prove useful.

Structurally the CZT detector is composed of multiple crystal orientations and contains Te precipitates, but still works well as a radiation detector. This is not a traditional semiconductor detector. In chapter seven the results of both chapters five and six are brought together to give an overview of the CZT material. This enables the development of an explanation for the observed spectroscopic behaviour.
7.1 Introduction

In this chapter the experimental results from the preceding two chapters are consolidated to develop a more detailed understanding of the HPB grown CZT material. The experimental results are divided into two components that affect the carrier transport properties in different ways. These are defect levels in the bulk material and the formation of a contact barrier at the Au/CZT interface. As a result of this the spectroscopic properties, observed in chapter 4, are discussed to yield a model for radiation detection using CZT. A conclusion discusses the progress that has been made in understanding CZT radiation detectors.

7.2 Defect Levels

The contribution of defect levels within the CZT detector to carrier transport is categorised into three cases based on the observed changes in detector resistivity. These cases are the non-illuminated, illuminated and temperature dependent properties. They are discussed in turn.

7.2.1 Non-Illuminated Resistivity Dependence at Room Temperature

In this sub-section the resistivity behaviour of the non-illuminated detector at RT, attributable to defect levels, is discussed. The discussed results are the time dependent resistivity and the hysteresis effect seen in section 5.2.

7.2.1.1 Time Dependent Resistivity

The application of an E-Field to the CZT detector was accompanied by an increasing detector resistivity with time, i.e. dI/dT<0. This was most apparent at 300K.
By considering the presence of a single defect level, for ease of explanation, a mechanism exists to account for this variation. In Fig 7.1 a single occupied donor level of energy $E_d$ below the conduction band is shown, possessing equal probabilities for de-trapping and recombination of trapped carriers.

![Diagram of De-trapping and Recombination from a Donor Level](image)

Fig 7.1

Recombination and de-trapping from a donor level at $E_d$ below the conduction band

In Fig 7.1 at a constant E-Field, carrier equilibrium is attained where the rates of trapping, de-trapping and recombination at the donor level are constant. A change in the E-Field leads to a change in the rates of each of these processes. If the E-Field is increased then the rate of trapping falls as carriers attain a greater carrier velocity, Eqn[2.10], and are swept from the medium in a shorter time. If the E-Field is decreased, the carriers attain a lower carrier velocity and the rate of trapping is increased.

In this example the E-Field is applied to a semiconductor that previously had no externally applied E-Field. In the absence of an external E-Field the concentration of the occupied donor levels is a maximum. The addition of the E-Field then requires a reduction in the number of occupied defect levels, this is done through thermal de-trapping or recombination. The probability of de-trapping is exponentially dependent on the sample temperature and at low temperatures is very small so de-trapping is negligible and at high temperatures is sufficiently high for the concentration of occupied defect levels to be very small. At intermediate temperatures the rate of de-trapping is such that carrier equilibrium occurs over an extended time frame.

In this instance a defect level, donor or acceptor of sufficient depth, exists within the CZT material to allow only the slow escape of trapped carriers. The rate of de-trapping of these carriers decreases as the new equilibrium is approached leading to the exponential like time dependent current.
Chapter 7: Carrier Behaviour in a CZT X- and γ-Radiation Detector

7.2.1.2 Hysteresis Effect at Room Temperature

By varying the E-Field in a loop the recorded current was observed to differ depending on the direction of change of the E-Field, Fig 5.3. The experimental data is repeated in Fig 7.2, where the arrow direction indicates the direction of E-Field change. In the increasing E-Field direction the detector dark current was higher than for the decreasing direction, for both initial E-Fields of 0Vcm\(^{-1}\) and 400Vcm\(^{-1}\). The size of the hysteresis loop was found to increase for increased rates of change of E-Field. The direction of the E-Field across the detector influenced the resistivity as a whole and not the size of the hysteresis loop.

![Image of hysteresis loop](image)

**Fig 7.2**
Hysteresis phenomena in CZT, see Fig (5.3)

Recalling that the de-trapping of carriers over time controlled the attainment of a constant current at 300K, a similar argument is now described. Principally, the application of high E-Field leads to a reduction in the concentration of occupied defect levels. At the highest E-Field of 400Vcm\(^{-1}\) the concentration of occupied defect levels is at a minimum.

In the increasing E-Field direction the concentration of occupied defect levels decreases as free carriers are more likely to be swept from the detector prior to trapping. For each increasing E-Field step the concentration of occupied defect levels must decrease through de-trapping or recombination processes. At 300K this has been shown to depend strongly on time.

In the decreasing E-Field direction the number of occupied defect levels increases as free carrier are now less likely to be swept from the detector prior to trapping. For each
decreasing E-Field step the concentration of occupied defect levels must rise through absorption of free carriers.

This argument is illustrated in Figs 7.3 and 7.4 for the two scenarios where the E-Field starts at the minimum and maximum values respectively.

In Fig 7.3 the E-Field starts from 0V cm\(^{-1}\) and climbs (a) to the maximum (b) before returning (c) to the initial value. In the increasing direction (a) the rate of de-trapping is increased over the rate of trapping and the concentration of occupied defect levels decreases. At the maximum E-Field (b) the concentration of trapped carriers is a minimum. As the E-Field is reduced (c) the concentration of occupied defect levels is below the equilibrium value and free carriers are absorbed from the conduction band, reducing the recorded current.

In Fig 7.4 the E-Field starts from 400V cm\(^{-1}\) and descends (a) to 0V cm\(^{-1}\) (b) before returning (c) to the starting value. In the decreasing E-Field direction (a) the rate of trapping is increased over the rate of de-trapping and the concentration of occupied defect levels increases. At the minimum E-Field (b) the concentration of occupied defect levels
is a maximum. As the E-Field is increased, the rate of de-trapping is increased and the defect levels empty, yielding excess current.

7.2.2 Illuminated Resistivity Dependence at Room Temperature

In this sub-section the experimental observations of the illuminated detector at room temperature that can be attributed to defect levels are discussed. The discussed phenomena are the resistivity dependence on photon wavelength and intensity, and the detector response to illumination. Additionally, the optical constants attained for sub-bandgap radiation are included.

7.2.2.1 Photon Wavelength

The photocurrent variation with incident wavelength indicated extrinsic absorption up to 1050nm (1.2eV), limited by the end stop of the monochromator only. In addition, the transmission curve for the crystal using a spectrophotometer indicated that the optical transmission never exceeded 40%. The involved defect level then lies less than 1.2eV from either the conduction or valence band, ignoring the contribution of thermal broadening to the band edges, =25meV at 300K.

The observed peak at 816nm corresponded to the attenuation coefficient of this radiation being the reciprocal of the detector thickness \[1\], or \(2\text{cm}^{-1}\). This compares well with the value of \(0.9\text{cm}^{-1}\) for 850nm radiation that was also established, section 5.5.1. The decrease in attenuation clearly indicates a general trend in decreasing absorption with increasing wavelength.

7.2.2.2 Photon Intensity

The photocurrent per mW of illumination power, at 850nm, as a function of illumination power was found to be sub-linear, Fig 7.5. The photocurrent per mW of illumination power began to saturate at increased illumination intensities. The decrease in generated photocurrent per mW with increasing intensity indicates a decrease in the number of absorbing centres with increasing photon flux.

Under illumination, the concentration of trapped carriers is decreased from the non-illuminated case through extrinsic absorption. At low intensities the change in the concentration of occupied defect levels, and therefore absorption centres, is relatively unchanged from the non-illuminated case. As the illumination intensity is increased the
concentration of trapped carriers is reduced appreciably. The probability for extrinsic absorption and the generated photocurrent due to each photon are reduced.

![Illustration](image)

**Fig 7.5**
Illustration of the change in photocurrent per incident mW versus incident power in mW, see Fig 5.19

A further observation can be made. One method for determining the mobility and lifetime products in CZT involves the use of a laser in pulse wave mode at a certain point from the electrode [2-4]. If the illumination is sufficiently intense to alter the concentration of occupied defect levels the carrier lifetime will be disturbed due to an increase in the probability of trapping, prior to collection at the electrodes.

### 7.2.2.3 Photocurrent Response

The final observation concerns the photocurrent response to incident illumination. An illustration of the photocurrent response to 1 minute illumination with 1050nm photons is shown in Fig 7.6. The response can be grouped into four sections. In (a) the dark current is stable prior to illumination. In (b) at the onset of illumination a sharp increase in current is seen due to extrinsic absorption through defect levels within the bulk material. This has a time dependent component (c). In (d) at the cessation of illumination the recorded current falls to levels below that of (a) before rising to the same value over 20 minutes. A route exists whereby the collected charge at the electrode is temporarily reduced following illumination with sub-bandgap photons.
A possible mechanism for this is depicted in Fig 7.7. Prior to illumination (a) the number of occupied defect levels is constant. If the crystal is illuminated (b) then trapped carriers can be excited into the conduction or valence band through extrinsic absorption, thus lowering the concentration of occupied defect levels. Further irradiation (c) is then less likely to generate a photocurrent for two reasons. Firstly, the decrease in the concentration of occupied defect levels lowers the probability for extrinsic absorption to occur. Secondly, the increase in probability of trapping of generated carriers due to an increase in the concentration of vacant defect levels. At the cessation of illumination (d) the concentration of occupied traps is below that of the pre-illumination region. The detector will then re-establish the correct concentration of occupied defect levels by trapping free carriers from the conduction or valence band. Free carriers are then more likely to undergo trapping prior to collection at the electrodes leading to a reduction in the recorded current until the rates of trapping, de-trapping and recombination are the same as that prior to illumination (a).
At shorter wavelengths the minimum value for the post illumination current was seen to increase. This is believed to relate to the 1050nm photon being more likely to give rise to extrinsic absorption over the photon energy of 850nm. For a deep defect the optical cross section, $S_d$, is related to defect level of energy $E_d$ by [5],

$$S_d(h\nu) \propto (h\nu - E_d)^{1/2} / (h\nu)^3$$  \[7.1\]

which rises rapidly for $h\nu > E_d$ and shows a relatively broad maximum for $h\nu = 2E_d$. The variation of $S_d$ versus the photon energy, $h\nu$, divided by the trap depth, $E_d$, is shown in Fig 7.8.

In Fig 7.8 no absorption is seen for photon energies less than the depth of the trap, climbing to a maximum when the photon energy is twice the depth of the trap, i.e. $h\nu = 2E_d$. Increasing the photon energy further results in a slower decrease in absorption leading to the relatively broad maximum. If a photon wavelength of 1050nm ($h\nu = 1.2\text{eV}$) corresponds to the maximum absorption cross section, a value of $E_d$ of approximately 0.6eV is surmised.

7.2.3 Resistivity Dependence on Temperature

In this sub-section the resistivity dependence on temperature, attributable to defect levels, are discussed. This includes the resistivity variations recorded for the non- and illuminated detector as a function of temperature. The relevant observations are the
7.2.3.1 Resistivity Variation with Time and Temperature

The rate of change of the resistivity with time following a change in the E-Field was seen to depend on the detector temperature, Fig 5.1. This has been described in terms of the presence of defect levels within the material. The attainment of equilibrium was found to be faster at temperatures of 280K and 320K than 300K. In Fig 7.9 a single donor level $E_d$ below the conduction band is shown at three temperatures with arrows indicating the relative changes in the de-trapping and recombination probabilities.

The three temperatures correspond to (a) recombination dominant (low T), (b) recombination and de-trapping are equal (intermediate T) and (c) de-trapping dominant (high T). The change in dominant processes is due largely to the variation in thermally excited de-trapping due to its exponential dependence on the sample temperature [6].

![Diagram of resistivity variation with time and temperature](image)

**Fig 7.9**
Dominant trapping parameters as a function of temperature for an electron trap $E_d$
(a) Low T (b) Intermediate T (c) High T

The attainment of equilibrium was faster at temperatures above and below 300K. The current variation can be explained if the temperatures of 280K, 300K and 320K correspond to the low, intermediate and high temperature regions of Fig 7.9 respectively.

In the low temperature region of 280K the probability of being thermally de-trapped is sufficiently small that recombination processes dominate. The concentration of trapped carriers at this temperature varies only slightly with applied E-field strength as the traps are effectively frozen out. The attainment of equilibrium is then quick when an E-Field is applied to the detector.

In the high temperature region of 320K the rate of de-trapping is sufficiently high to now dominate over recombination processes. Carriers are then able to rapidly...

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resistivity with time, the hysteresis effect, Arrhenius plot, photocurrent versus wavelength and the thermally stimulated current measurement.
compensate for changes in the carrier concentration in the conduction band. In this case the current equilibrium is established quickly following the application of the E-Field.

At 300K recombination and de-trapping are equally probable. The rate of de-trapping is only sufficient to allow the slow escape of trapped carriers. The attainment of carrier concentration equilibrium is then slower at 300K than at temperatures above and below this.

This variation in the relative rates of recombination and de-trapping are well known for semiconductors with known defect levels. Indeed in the more advanced technique of PICTS [7,8] the phenomena is used to provide evidence for the depth of these traps and their density.

7.2.3.2 Hysteresis Dependence on Temperature

The size of the hysteresis loop, observed when varying the E-Field, was seen to also possess a dependence on temperature and was found to be a maximum at 300K. The similarity with the resistivity versus time measurements indicates that the same mechanism is involved here.

At the temperature of 320K the attainment of carrier equilibrium was faster because the rate of de-trapping was higher and the material adjusted easily to changes in the E-Field. As a result, in the increasing E-Field direction the change in the trapped carrier concentration decreases more quickly than at 300K. In the decreasing E-Field direction there is a far greater number of free carriers in the conduction and valence bands, so that the required increase in the concentration of occupied defect levels is easily made.

At 280K the attainment of carrier equilibrium was equally rapid as the rate of de-trapping is much reduced and no change in the concentration of trapped carriers is recorded, i.e. the trap is frozen out. In the increasing and decreasing E-Field directions minimal changes in the trapped carrier concentration are seen, so that the size of the hysteresis loop decreases.

However at 300K the trapped carriers are sufficiently probable to de-trap, but not sufficiently likely that the equilibrium value is established at each E-Field strength. In the decreasing direction the change in trapped carrier concentration, and therefore the change in current, is a maximum.
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7.2.3.3 Arrhenius Plot versus Temperature

The variation of the detector resistivity with temperature was used in the range of 300K to 380K to establish a value for the detector bandgap. A value of 1.57±0.02eV was established and found to agree well with those values attained using PL and PR of 1.57±0.02eV and 1.57±0.01eV respectively. In this temperature region the change in current was found to follow very closely (correlation coefficient of 0.996) the theoretical predictions based on the temperature dependence of band to band thermal excitation in an intrinsic semiconductor, Eqn[2.13].

However, below 290K the recorded current values were found to deviate suddenly and strongly from the theoretical predictions. The nature of the change gave rise to a current larger than theoretically expected. In this section an explanation is provided for this.

The existence of at least one defect level within the material has been confirmed through our previous descriptions. In this case we need to examine more closely the role of these defect levels to the total detector current. In an extrinsic semiconductor the total current density, $I_{\text{Tot}}$, is the sum of that due to the intrinsic band to band transition, $I_{\text{Int}}$, and that due to the de-trapping of charge carriers from a defect level, $I_{\text{Ext}}$, Eqn[7.2].

$$I_{\text{Tot}} = I_{\text{Int}} + I_{\text{Ext}}$$

The value for $I_{\text{Int}}$ is dependent on the number of charge carriers and their mobilities, Eqn[2.11]. The number of charge carriers is dominated by the exponential term $[-E_g/2kT]$, Eqn[2.12].

In the range of the Arrhenius measurement the current was dominated by the intrinsic component leading to the excellent correspondence with that of an intrinsic material. At reduced temperatures this is no longer true and the extrinsic component now plays a larger part in determining $I_{\text{Tot}}$. This is illustrated in Fig 7.10.

In Fig 7.10 the intrinsic current and the total current are near identical at temperatures above 300K. As the temperature decreases below this, deviations between the two increase due to the exponential decrease of the intrinsic current and the relatively unchanging value of the extrinsic current in this temperature region. This leads to deviations from the theoretical predictions.
7.2.3.4 Photocurrent versus Temperature

A further variation in the resistivity as a function of temperature was seen when the detector was illuminated with a 1mW 850nm semiconductor laser. The photocurrent for this continuous wave illumination fell dramatically with temperature. In a defect free semiconductor the dark current is exponentially dependent on the temperature, but the photocurrent is not.

It has been seen that defect levels move from de-trapping to recombination dominated at reduced temperatures. Under IR illumination, carriers are generated in the conduction and valence bands through extrinsic absorption. This is shown in Fig 7.11 at low, intermediate and high temperatures.

In the low temperature regime (a) excited carriers if trapped are more likely to recombine than thermally de-trap to the conduction band. At intermediate temperatures (b) photoexcitation is accompanied by a reduced probability for re-trapping and subsequent recombination. At high temperatures (c) photoexcitation is also accompanied by a large probability for thermal de-trapping and so any trapped carriers are quickly de-trapped and recombination is considerably reduced. This relates very easily to the loss of spectroscopic capabilities at reduced temperatures.
7.2.3.4 Thermally Stimulated Current

The last experimental observation concerning the change in resistivity with temperature relates to the thermally stimulated current measurements that were undertaken. In this case the detector was optically doped at 77K using 850nm photons to fill the defect levels within the material. As the temperature is increased the trapped carriers are thermally excited into the conduction or valence band giving an increase in the conductivity of the sample.

This gave rise to two major peaks centred around 180K and 280K with several changes in the gradient of each indicating the presence of different levels of lower concentration superimposed on the larger signals of more abundant energy levels. Multiplying the peak current due to each defect level by 20 can approximate the depth of the energy level [9]. In this case values of 0.3eV and 0.47eV respectively are obtained.

7.3 Contact Barrier Properties

In this section the narrow range IV measurement is used to examine the Au/CZT contact barrier. Previous work has comprehensively studied this property [2] and our results concur with those and a review of that work is made to avoid repetition [2]. The photovoltaic effect at the electrodes also indicates the existence of a contact barrier, but is not able to provide further information and its discussion is therefore unnecessary.

7.3.1 Review

The previous work [2] established that the bulk of the CZT detector is intrinsic as a result of material purity or from compensatory doping. The fermi level is held precisely
half way between the conduction and valence bands. The bandgap is 1.55eV with \( E_f \) sitting 0.78eV below the conduction band.

Both contacts are Schottky barriers with heights of 0.79eV. Between the Au contacts and intrinsic CZT there is a thin 10-20\( \mu \)m layer of p-doped CZT. The concentration of acceptor levels in this region, \( N_a \), is approximately \( 10^{10} \text{cm}^{-3} \). This is sufficient to pull the fermi level down in this region by 0.2eV. Alignment of the fermi level then increases the barrier from 0.79eV to 1eV reducing the thermionic current by a factor of 3000.

7.3.2 Narrow Range IV Measurement

The narrow range IV measurement recorded a non-linear relationship between the applied E-Field and the recorded leakage current, Fig 7.12. The relationship presented a S-shaped curve that is indicative of that due to a blocking contact at the Au/CZT interfaces. The general nature of the IV profile is one of increasing resistance with E-Field. This is illustrated in Fig 7.12.

The recorded variation was not symmetric about the y-axis, which is attributed to the variation in contact barrier height of 0.99eV and 1.02eV. Although this difference appears small, substitution of these values into Eqn[2.22] yields a variation in the thermionic emission current of a factor of 5, accounting for the variation in detector resistivity with E-Field direction.
Knowing the barrier heights of 0.99eV and 1.02eV it is now possible to derive the resistivity of the bulk CZT material itself. This means the contribution of the thermionic current density must be subtracted from the total current density, Eqn[2.23].

\[ J = A^* T^3 \exp \left( \frac{-\phi_n}{kT} \right) + \frac{V}{\rho d} \]  \[2.23\]

The total current density \( J \) is \( 2.7 \times 10^{-9}\text{Acm}^{-2} \) and \( 2.5 \times 10^{-9}\text{Acm}^{-2} \) for the contact barriers of 0.99eV and 1.02eV respectively at 300K. Substitution of these values into Eqn[2.23] at a temperature of 300K yields values for the bulk resistivity of \( 1.6\pm0.05\times10^{11}\text{\Omega cm} \) and \( 1.7\pm0.05\times10^{11}\text{\Omega cm} \). The contact barrier height is then very important in determining the resistivity of the detector. The mean resistivity at 300K can be given as \( 1.65\pm0.02\times10^{11}\text{\Omega cm} \) and using the reciprocal of Eqn[2.9] which related the conductivity of the detector to the concentration of each charge carrier and their respective mobilities we obtain,

\[ \rho = \frac{1}{ne\mu_e + p\mu_p} \]  \[7.2\]

where \( \mu_e \) and \( \mu_p \) have the values \( 1000\text{cm}^2/\text{Vs} \) and \( 100\text{cm}^2/\text{Vs} \) respectively at 300K [10]. If the material is intrinsic, i.e. \( n=p \) then the concentration of either charge carrier is \( 3.44\pm0.04\times10^4\text{cm}^{-3} \) at 300K. In contrast the concentration of free carriers in intrinsic Si at RT is \( 10^{10}\text{cm}^{-3} \) [11].

The contact barrier increase is due to the formation of Au acceptor levels through diffusion at elevated temperatures. If this process could be better understood further reductions in the detector leakage currents could be made.

7.4 Electronic Structure of a CZT Detector

The homogeneity of the CZT bulk material determined by the EDX and PIXE measurements is largely uniform with the bulk material being compensated [2,12]. Resultant variations in the bandgap leading to a change in the w-value and the number of radiation induced EHPs per keV are not possible [13]. The bandgap of the material is \( 1.57\pm0.01\text{eV} \) with the fermi level pinned half way between the valence and conduction bands, indicating a zinc concentration of \( 9.7\pm1.6\% \). In XRD the crystal was seen to
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consist of several grain orientations, principally in the (220) direction, which can be compared to the optical microscopy image of the cleaved surface, indicating a change in the refractive index. Measurements using energy and wavelength dispersive X-ray analysis (EDX & WDX), backscattered electrons and secondary electrons showed that this change in refractive index is not due to a change in composition. Infrared images of a CZT detector, which possessed a double peak for every photopeak, indicated that a large grain boundary divided the detector in two [2]. The detector then behaved as two detectors in parallel. Avoidance of grain boundaries in the growth process is therefore absolutely essential.

The use of stoichiometry mapping, with PIXE, indicated the existence of a single Te precipitate approximately 20μm across. Firstly, the decrease in photocurrent with increasing photon wavelength did not correspond to a proportionate rise in the optical transmission. The photocurrent and transmission at 840nm and 1050nm were 4nA, 20% and 0.5nA, 35% respectively. Secondly, the photovoltaic measurement, Fig 5.7, found a measurable current throughout the detector thickness, although of course the sign of the current changed close to the halfway point. The role of Te precipitates in the bulk material to variations in optical transmission is seen in Fig 7.13.

Incident photons from the left may undergo reflection from the air/CZT interface, absorption in the bulk through defect levels or valence band to conduction band transitions, scattering from Te precipitates or be transmitted. Scattering from Te precipitates is more apparent for sub-bandgap radiation, which will have a longer mean free path in the material than super-bandgap optical photons. Scattered photons can escape the detector in a direction different to the incident beam, reducing the observed
transmission, without giving rise to a photocurrent. The optical attenuation consists of components due to intrinsic or extrinsic absorption or scattering from the Te precipitates.

Infra-red imaging of HPB grown CZT has taken place elsewhere and has also revealed the presence of black inclusions that have unanimously been agreed to be Te precipitates [2,14-18].

Solid Te has a bandgap of 0.33eV [14], so the electrical resistivity of the Te-rich precipitates will be several orders of magnitude lower than the surrounding CZT matrix. Consequently, the higher leakage currents that have been found along grain boundaries may be due to the high density of conducting Te inclusions [14]. Also, at the wavelengths used, solid Te will be highly absorbing acting as a dead region for optical transmission.

Because these regions of high leakage must be avoided in the fabrication of large-volume CZT spectrometers, it would be useful to remove them without adversely altering the electrical properties of the surrounding CZT crystal. Removal of the Te precipitates can be accomplished by annealing in a Cd vapour. Unfortunately this leads to generation of dislocations as Cd interstitials react with Te to form CdTe [15].

In the contact region, the diffusion of Au from the electrode leads to the raising of the contact barrier at the interface. This is key to the use of CZT radiation detectors as it reduces the thermionic emission current density by a factor of ≈3000. The gold diffusion is not repeatable at either electrode, leading to asymmetry in the detector conductivity. The Au forms two acceptor levels in this region, a shallow one at 80meV and a deeper one at 0.28eV [19].

The role of defect levels within the bulk material in determining the charge carrier properties has already been discussed. From the thermally stimulated current measurements defect levels at approximately 0.3eV and 0.47eV were seen. The first of these is believed to be the deeper Au acceptor level at the contact and the latter due to the Cd(Zn) vacancies which are known to manifest themselves abundantly in CZT [2]. The deviation in current with reduced temperatures from theoretical predictions is almost certainly due to the extrinsic current generated at the contact region dominating the bulk current. The electronic structure for the detector is shown in Fig 7.14.
The experimental investigations carried out in chapters 5 and 6 have now been consolidated to produce a more fundamental understanding of the CZT detector. It has been shown that defect levels, contact barrier, Te precipitates amongst other influence the electronic properties of the CZT detector. It is now necessary to use this understanding of the CZT electronic structure to develop a model for the spectroscopic behaviour of chapter 4.

7.5 Radiation Detection in CZT

In this section, the electronic properties of the CZT detector, determined by the defect levels, contact barriers etc, are used as a basis for developing a model for the observed spectroscopic performance. This section is divided into three parts corresponding to the different aspects of the spectroscopic performance that were studied. These were; room temperature performance with $^{241}$Am and $^{57}$Co, variable temperature and interaction position with $^{241}$Am only.

7.5.1 Room Temperature Spectroscopy of $^{241}$Am and $^{57}$Co Sources

7.5.1.1 $^{241}$Am Source

In the case of $^{241}$Am the detector was found to give a recordable photopeak for the 59.5keV line for E-Fields as low as 400Vcm$^{-1}$ with cathodic irradiation. Due to its high Z and high density the mean free path for 60keV photons in Cd$_{0.8}$Zn$_{0.2}$Te is only 280μm.
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[20]. The hole transit time, where \( \mu_h=100 V^{-1}s^{-1}cm^2 \), for an applied E-Field of 400V/cm is 0.7\( \mu \)s, outside of the 0.5\( \mu \)s shaping time. The proportion of radiation interacting within a distance of the cathode corresponding to a hole transit time of 0.5\( \mu \)s is \( \approx 20\% \). These values clearly correspond to the improvements in spectra for increasing E-Field.

Increasing the E-Field allowed the 23.4keV \( \gamma \)-ray, Np L\( \alpha,\beta \) X-rays and the Cd and Te escape peaks to be resolved due to improvements in the resolution, peak to valley ratio and the charge collection efficiency. Increasing the E-Field strength to 1kV/cm\(^{-1} \) reduces the hole transit time for an interaction depth of 280\( \mu \)m to 0.28\( \mu \)s. The point corresponding to a transit time of 0.5\( \mu \)s at 1kV/cm\(^{-1} \) is 500\( \mu \)m from the cathode. At this depth 85\% of the incident radiation has been photoelectrically absorbed.

Clearly in the case of \(^{241}\)Am radiation the spectroscopic characteristics are reasonably predictable and complex explanations are unnecessary. A discussion of the more subtle changes that occur in the detector is though appropriate. Increasing the E-Field affects the carrier mobility-lifetime product in two ways. Firstly, carriers attain a higher velocity, spending less time in the vicinity of traps and recombination centres so that the lifetime increases. However, opposing this, increased E-Fields lead to a decrease in the concentration of occupied defect levels, increasing the probability of carrier trapping. The net effect is one of increased lifetime, but the varying trapping probability component will tend to cause the true lifetime to deviate from theoretical predictions. This is important when changes in the charge collection efficiency with applied field are used to determine the carrier-lifetime product [21]. The postulated change in carrier velocity as a function of E-Field is shown in Fig 7.15 for the two cases of carrier trapping and without. The carrier velocities for both material tends towards a saturation value, but the extrinsic material is limited by the varying concentration of occupied defect levels to values below the intrinsic material. At high E-Field strengths when the probability for trapping is reduced and at low temperatures when the defect levels are nearly fully occupied, Fig 5.1, the carrier velocity tends towards that of the intrinsic material. In CZT this contrasting behaviour will be most apparent at room temperature for the hole carriers due to the large number of acceptor levels that exist in the bulk, Cd(Zn), and at the electrode, Au.
In Fig 7.15 the carrier velocity is reduced for the defect containing material over the defect free material. This introduces a new variable to the establishment of the carrier velocity dependence on applied E-Field. The contribution of the charge trapping to the overall carrier mobility, \( \mu_{e,h} \), can be expressed as \( \Delta \mu_{e,h} \). The change in the carrier velocity with E-Field, Eqn[2.10], is then more appropriately written as

\[
v_{e,h} = [\mu_{e,h} - \Delta \mu_{e,h} (E,T)]E
\]

where the component \( \Delta \mu_{e,h} \) depends on the concentration of trapping centres and is therefore a function of the applied E-field and the sample temperature.

Investigations were also carried out using anodic irradiation of the detector, which recorded no spectra, other than low energy noise. This is due to the poorer hole transport properties allowing the carrier to become trapped in the \( \approx 5 \text{mm} \) distance to the cathode. In this event sufficient trapping and recombination occurs to render the signal unrecognisable.

7.5.1.2 \(^{57}\text{Co} \) Source

The higher energy of the \(^{57}\text{Co} \) 122keV photon to the 59.5keV \(^{241}\text{Am} \) photon required a higher minimum E-Field of 800Vcm\(^{-1} \) to attain a recordable spectrum. At this E-Field the best performance was attained with a shaping time of 1\( \mu \)s followed by the 2\( \mu \)s and 0.5\( \mu \)s times respectively. The mean free path of a 122keV photon, 0.15cm, is approximately five times that of the 59.5keV photon.
Interaction at this point for holes, with an applied E-Field of $800\text{Vcm}^{-1}$, leads to a hole transit time of $1.9\mu\text{s}$, inside the $2\mu\text{s}$ shaping time. The proportion of radiation interacting within a distance of the cathode corresponding to a hole transit time of $0.5\mu\text{s}$ is $\approx7\%$. Clearly the attainment of a signal for these higher E-Fields corresponds to the observed behaviour very well.

In the higher energy radiation scenario a greater component of the induced signal will undergo carrier trapping prior to collection at the electrodes. The change in the FWHM with increasing E-Field was predominantly due to improvements in the low energy side indicating an improvement in the charge transport properties. As the E-Field is increased, carriers are swept more quickly from the detector and the probability of detrapping is subsequently reduced. The transport of carriers for the two cases of low and high E-Field is illustrated in Fig 7.16.

![Fig 7.16](image)

Signal collection and pulse shape for low (a & b) and high (c & d) E-Fields

In the low E-Field region (a) carriers may become trapped prior to collection. The trapped carrier may undergo recombination or subsequently de-trap. Recombination results in a reduced signal and detrapping leads to increased noise. The resultant spectra (b) therefore possesses a large FWHM and reduced peak channel number, peak1, indicative of inferior charge collection efficiency. In the high E-Field region (c) carriers can traverse the crystal entirety with minimal trapping occurring. In this case the recorded spectra is more symmetric with improved resolution and the peak channel number, peak 2 is higher than peak 1. For all E-Field values those signals that display minimal trapping will generally have travelled less of a distance in the detector.

If a hole does become trapped both de-trapping and recombination can degrade the integrated signal leading to a low energy tail. In the case of de-trapping this depends on whether these carriers arrive at the electrode within the shaping time. The processes
that a trapped hole may undergo are illustrated in Fig 7.17 for an acceptor level $E_a$ above the valence band. In Fig 7.17 the recombination's due to (a) pair recombination between a nearby donor and acceptor level and (b) recombination between a free electron and a trapped hole are shown.

![Fig 7.17](image)

**Fig 7.17**

Trapping and recombination of a hole prior to collection (a) pair recombination between a nearby donor and acceptor (b) recombination between a free electron and a trapped hole

Earlier measurements indicated that a deep acceptor level lies in the CZT detector $0.47eV$ above the valence band. This defect level is almost certainly the factor limiting the charge collection efficiency and the associated energy resolution for this radiation. The acceptor levels that are known to exist at the electrodes are not thought to be the most important factor here as they are limited to a distance of $20\mu m$'s from the electrode.

### 7.5.1.3 Miscellaneous Experiments

In the miscellaneous experiments, polarisation of the detector under prolonged E-Field application was not found to be a problem at 300K. Given the problems that were encountered with the CdTe detector polarisation twenty years ago [22-27] work has also been carried out on the count rates of CZT detectors with time. Both Butler et al [28] and Lund et al [29] showed no signs of polarisation of CZT detectors in a week of continuous E-Field application.

The spectra recorded at 300K in five minute intervals following the application of an E-Field showed improvements in peak channel number and peak height between the first two only. An increase in the charge collection efficiency is then surmised. It is believed that the Au acceptor levels that exist at either Au/CZT interface are responsible for this change. As the defect levels are emptied the E-Field is able to penetrate into the detector bulk to a greater distance. Charge carriers then feel a stronger E-Field at the point of generation with a subsequent decrease in the carrier collection time and charge
trapping in the bulk. If the concentration of occupied defect levels falls at the Au/CZT interface the increase in E-Field penetration must be sufficient to overcome this.

The change in resistivity with E-Field direction did not alter the energy resolution for the 59.5keV $^{241}$Am photopeak. However, the diffusion of the Au electrode into the bulk material is not easily controlled and raises concerns about repeatability. It is possible to foresee a situation in which the Au diffusion from one electrode is poor, yielding a detector in which effective operation is achieved in one E-Field direction only.

7.5.2 Spectroscopic Temperature Dependence

In this sub-section the temperature dependent spectroscopic capabilities are discussed. The temperature dependence was established with time at 200K and as a function of temperature from 280K to 360K. They are discussed in turn.

7.5.2.1 Spectroscopic Capabilities at 200K

The detector was cooled to 200K and the radiation spectra recorded at five minute intervals following the application of a 1kVcm$^{-1}$ E-Field. The spectra quality was seen to fall dramatically with time, less than 10 minutes.

Let us first examine the role of a recombination centre in a material in Fig 7.18, where an acceptor level lies at energy $E_a$ above the valence band. At 200K the defect level due to the Cd(Zn) vacancy at 0.47eV will behave as a recombination centre as thermal de-trapping is negligible. Trapped carriers are then permanently lost from the signal pulse. However, these traps should be mostly occupied at this temperature so that little change in the spectra will be seen with time. Indeed, the addition of radiation induced charge carriers will increase the concentration of occupied defect levels, thus lowering the probability for trapping to occur.

![Fig 7.18](image.png)

Free carrier recombination or de-trapping through an acceptor level
A second explanation can be found from the existence of Au induced deep defect levels at the Au/CZT interface. In this case a region of ≈20μm from either contact contains a large number of acceptor levels due to Au diffusion. Under non-radiation conditions the occupancy of these defect levels will attain equilibrium. The addition of a source of radiation will increase the number of free carriers. On route to the electrode it is conceivable that they become trapped in the Au defect levels. In this case they may be heavily concentrated in this region. This is shown in Fig 7.19 for a hole captured at an imperfection in a detector with two non-ohmic contacts [30].

![Fig 7.19](image)

Trapping of a hole at an imperfection with non-ohmic contacts

In this case the detector polarises, the trapped charge cancels the applied E-Field through its space charge, limiting the E-Field penetration of the material. In this case the E-Field in the detector bulk is considerably reduced and generated EHPs in this region then only feel a very small E-Field. Reductions in the carrier velocity and therefore the probability of signal collection ensue leading to degradation in the collected signal.

### 7.5.2.2 Americium Spectra versus Temperature

In this measurement the radiation spectra from an $^{241}$Am source were recorded as a function of the detector temperature. The results indicated that the recorded spectra were reasonably similar in the range of 280K to 360K. Below this temperature, a rapid deterioration in the attained spectra through the size of the photopeak and the peak channel, which is indicative of the charge collection efficiency, decreased rapidly. It is possible that both the polarisation at the defect levels and the trapping of charge carriers within the bulk material are responsible for this.
In the first case the defect level observed at 0.47eV is linked to the Cd(Zn) vacancy in the bulk material which will be frozen out below 280K. Additionally, the two acceptor levels that Au forms in CdTe are at 0.08eV and 0.262eV above the valence band [2]. The deeper of these is almost certainly the likely candidate for a polarisation effect at the Au/CZT interface. As the temperature is lowered the probability of occupation will increase in the electrode region resulting in detector polarisation. The change in E-Field distribution in the detector with temperature is illustrated in Fig 7.20.

![E-Field distribution in CZT detector as a function of temperature](image)

The top part of Fig 7.20 shows the ideal situation in a radiation detector where the E-Field ($\varepsilon_i$) is uniform across the detector at V/x. In the second case the detector has become polarised following carrier trapping at the electrode region. The effect of these trapped carriers is to shield the remainder of the detector from the applied E-Field. In this region the potential drop with distance is more rapid leading to a larger E-Field. The abrupt E-Field variation shown is an approximation to the actual curve that will be seen due to the variation of Au concentration with depth.
If we assume that 50% of the E-Field is dropped at either contact for a 500V potential difference then the applied E-Field in the contact region, $E_2$, is approximately $100\text{kV cm}^{-1}$. This is a considerable field and may explain why CZT radiation detectors are still able to operate at reduced temperatures for the $^{55}\text{Fe}$ radiation [31,32]. This source emits a 5.9keV photon that has a 90% probability for photoelectric absorption within 7$\mu$m of the CZT surface. In addition the polarisation behaviour will be less severe for radiation sources of lower activity due to the reduced number of free carriers that result reducing the concentration of occupied defect levels.

### 7.5.3 Positional Dependence

In this experiment the point of interaction of $^{241}\text{Am}$ radiation was varied using a brass collimator between the two opposing electrodes. The centroid channel number for the 59.5keV photopeak and the energy resolution were greatest when irradiation was closest to the cathode. Deterioration in the spectra was clearly seen with increasing distance from the cathode. It was not possible to record a spectra when irradiation was more than 2.5mm from the cathode.

The theory predicts an optimal distance between the electrodes when the charge transit times are equal. Due to the disparity, factor of 10, in the mobilities for electrons and holes this point is less than 500$\mu$m from the cathode. It was not possible with the experimental arrangement and the $^{241}\text{Am}$ source currently available to us to resolve this effect clearly. The experimental results are shown in Fig 7.21. The best performance is clearly achieved with irradiation close to the cathode. A region of best performance exists within 500$\mu$m of the cathode indicating a strong dependence on the hole transport properties.
Reductions in the peak channel number clearly correspond to a loss in the charge collection efficiency for the 59.5keV $^{241}\text{Am}$ photon. A dramatic increase in the FWHM is believed to be related to the effect of charge trapping of the generated hole carriers prior to collection at the cathode. This has previously been discussed and is not repeated. By increasing the distance of interaction from the cathode several important effects are at play. Firstly, the increased path length for signal carriers will proportionally increase the probability for trapping to occur. Secondly, the E-Field in this region is reduced lowering the carrier velocities and further degrading the signal.

For low energy photons side irradiation offers no discernible advantages over the traditional cathode irradiation as the density of charge carriers is limited to a region very close to the cathode. For higher energy radiation, a possible advantage exists. In electrode irradiation the exponential absorption law governs the distribution of charge carriers so that carriers are generated throughout the detection medium, Fig 7.22. If the high energy photons were of sufficient flux and collimating was possible, the density of generated carriers could be confined to a region of close proximity to the cathode. This would overcome difficulties that are currently seen in fabricating large volume detectors, greater than 1cm$^3$, and considerably reduce the effects of carrier trapping. Both these factors will considerably improve the efficiency of the detection medium.
In Fig 7.22 the distribution of generated charge carriers for each irradiation configuration are shown in an arbitrary detection medium. The width of the path in the material serves as an indicator of the number of EHPs generated in the region. The proximity of generated carriers to the electrodes is clearly more desirable for the case of side irradiation.

7.6 Conclusion

In this chapter the experiments undertaken in chapters 5 and 6 have been discussed with reference to known properties of the CZT detector. The result of this is the model for the CZT radiation detector. Using this model the spectroscopic behaviour seen in chapter 4 was discussed. This allowed a more detailed understanding for this material and how it differs from the more traditional Si and Ge radiation detectors.

The detection of 60keV radiation was excellent at room temperature, but fell significantly for the 122keV photon as a result of the increased penetration allowing for longer transit time, increased charge trapping and the interaction in a region of lower E-Field. At reduced temperatures the detector was seen to polarise due to charge trapping at the Au/CZT interface, effectively reducing the E-Field in the detector bulk to zero [33].

The variation of the interaction position with inter-electrode distance confirmed the best performance was within 500μm of the cathode and the use of side irradiation for detection of higher energy irradiation was discussed.
The CZT detection medium has been seen to perform well for the photon energies below 122keV, a good indicator for its use as a X-ray detection medium. In the next two chapters the fabrication of this material for a flat panel imaging system, using electrodeposition is discussed.
Chapter Eight: Electrodeposition of Thin Film CdTe.

8.1 Introduction

Having assessed the viability of CZT radiation detectors it is now appropriate to turn our attention to the somewhat challenging task of thin film growth of CdZnTe. To considerably reduce the difficulty associated with growing this material, growth is considered only for CdTe. In this case only binary deposition is important and the problems that arise from the incorporation of zinc in ternary deposition are removed.

CdTe is a material currently used for solar cell applications as a result of two important optical characteristics. Firstly, its bandgap of 1.45eV is ideally matched to the solar spectrum which facilitates its efficient utilisation. Secondly, the direct mode of the optical transition from the valence to conduction band results in a large absorption coefficient [1] and in turn permits the use of thin layers (1-2μm) of active material.

This use has driven considerable research into the growth of thin film CdTe using a large number of techniques. In this chapter we investigate the cathodic electrodeposition of CdTe films under potentiostatic, constant deposition potential, conditions. The choice of available growth processes as a fabrication route is discussed, leading to the choice of electrodeposition and in particular cathodic electrodeposition as the preferred option. The theoretical background of electrodeposition and its application to CdTe is described concisely for readers that have only a limited knowledge of electrochemistry. Next the experimental arrangement is explained including justification for the choice and preparation of a suitable substrate material. Characterisation of the growth process is then presented with preliminary results from grown films. A discussion is included at the end to relate the current status of our own growth process.
8.2 Choice of Growth Process

Thin films of CdTe for use in solar cells have been fabricated by a number of different techniques such as close-spaced vapour transport (CSVT) [2-5], metalorganic chemical vapour deposition (MOCVD) [6], molecular beam epitaxy (MBE) [6,7], sintering [8,9], screen printing [10,11], electrodeposition [12-13] and vacuum evaporation [14,15] etc. Each of these techniques have both advantages and disadvantages involving cost, repeatability, substrate temperatures which need to be minimised and film size (area & thickness). Among these, electrodeposition is the most attractive method [16] for large scale use because of several key advantages: (i) minimal material cost because the film can be deposited on to the desired area of the substrate only, (ii) relatively cheap equipment, (iii) the same solution can be used for extended periods of time, about 8-9 months [17], (iv) the method is reproducible as the deposition parameters are easily controlled (v) it is a low temperature process allowing the use of inexpensive substrates such as metallised or conductive oxide coated glass [18] (vi) the toxic materials are in an aqueous medium from which clean up is readily accomplished. Further the technique can be easily extended to larger areas allowing the technique to be studied and perfected on the small scale before enlargement to the required area.

Previous work [19] has also shown that electrodeposited films had fewer impurities as revealed by SIMS than had crystalline CdTe purchased as 99.999% pure from commercial suppliers.

Most CdTe co-deposition processes make use of an aqueous solution containing cadmium sulphate, tellurium dioxide and sulphuric acid as the electrolyte [12,13,20]. Due to the possibility of unexpected effects caused by hydrogen evolution during electrodeposition from aqueous solutions, non-aqueous solutions for CdTe deposition have also been developed. Darkowski et al [21] reported the use of propylene carbonate electrolyte containing tri-n-butylphosphine telluride, cadmium perchlorate, lithium perchlorate and tri-fluoromethane. Dimethylformamide saturated with tellurium and containing CdCl₂ and KI has also been used as an electrolyte for CdTe deposition [22]. Skyllas-Kazacos [23] used alkaline solutions and investigated CdTe electrodeposition from tellurocyanide (KTeCN) and CdCl₂. Pandey et al [24] have obtained CdTe films from ethylene glycol electrolytes containing TeCl₄ and CdCl₂. The above electrolytes
were utilised in cathodic deposition. On the other hand, Rajeshwar et al [25] have investigated the anodic electrosynthesis of CdTe thin films. They reported that CdTe films were obtained on a cadmium anode from an alkaline electrolyte containing \( \text{Te}^2^- \) species. As an electroless bath, Bhattacharya et al [26] have used 10% sulphuric acid solution containing \( \text{TeO}_2 \) and cadmium acetate. Buckley [27] has studied CdTe thin film deposition from an electroless bath containing ammonia solution, \( \text{CdCl}_2 \), \( \text{TeO}_2 \), triethanolamine and hydrate hydrazine.

Thin film CdTe is usually cathodically electrodeposited from an aqueous electrolyte containing \( \text{Cd}^{2+} \) ions and \( \text{HTeO}_2^- \) ions. In comparison to those deposits from aqueous systems, non-aqueous deposits can have significant differences in morphology and grain size [28]. However, the ease of use and low cost of aqueous systems have given these a key advantage over non-aqueous electrolytes.

Either cathodic or anodic methods may be employed in aqueous media - the former involving the co-deposition of higher valence metal and chalcogenide ions (e.g. \( \text{Cd}^{2+} \) and \( \text{HTeO}_2^+ \)) and the latter based on the corrosion of the metal in a chalcogenide environment. The anodic process may be represented, rather simplistically, by Eqns[8.1 & 8.2] [29].

\[
\begin{align*}
\text{Cd}^0 & \rightarrow \text{Cd}^{2+} + 2e^- & [8.1] \\
\text{Cd}^{2+} + \text{Te}^{2-} & \rightarrow \text{CdTe} & [8.2]
\end{align*}
\]

Generally, more precise control of the film stoichiometry is obtained with the cathodic approach [12,26,30]. In this chapter we investigate the use of cathodic electrodeposition of CdTe films under potentiostatic conditions [31].

### 8.3 Fundamentals of Electrodeposition

In this section the theory of electrodeposition is explained in such a way that the non-electrochemist may fully grasp the required concepts. The reader is referred to other, more detailed texts for in-depth discussions of this topic [32-34]. Electrochemistry is defined as the study of chemical properties and reactions involving ions in solution [35].
8.3.1 Electrochemical Cells

The device used to study reactions electrically is called an electrochemical cell. Such a cell consists of two electronic conductors dipped into an electrolyte (an ionic conductor), which may be a solution, a liquid, or a solid. An electrochemical cell that produces electricity as a result of the spontaneous reaction occurring inside it is called a galvanic cell. The commercially available nickel cadmium dry cells are examples of galvanic cells as they produce electricity as a result of the spontaneous chemical reaction between the substances built into them at manufacture. An electrochemical cell in which a non-spontaneous reaction is driven by an external source of direct current is called an electrolytic cell.

In its simplest form the electroplating or electrodeposition bath consists of an electrolyte containing metal ions, an electrode or substrate upon which deposition is desired, and a counter electrode. When a current flows through the electrolyte, the cations and anions move toward the cathode and anode respectively, and may deposit upon the electrodes after undergoing a charge transfer reaction, Fig 8.1.

Suppose Cu is to be electrodeposited. Then the electrodeposition bath could contain a Cu salt such as copper sulphate \( \text{CuSO}_4 \). The Cu\(^{2+} \) ions deposit on the cathode, and a copper coating is obtained.

In the analysis of electrochemical reactions it is important to note that it may be considered in terms of electron loss from one species and electron gain by another. Thus any electrochemical reaction can be expressed in terms of the relevant half-reactions. For
example, consider an electrochemical cell involving both the oxidation of zinc and the reduction of copper. These two components form the overall electrochemical reaction, but can be written in terms of two half reactions.

\[
\text{Zn(s)} \rightarrow \text{Zn}^{2+} (aq) + 2e^- \quad [8.3]
\]

\[
\text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu(s)} \quad [8.4]
\]

Half reactions are conceptual reactions showing the loss and gain of electrons: the reactions do not actually occur by one species releasing an electron and then another accepting it; electron transfer involves a more complicated reaction in which the electron is never free. The electrons in these conceptual reactions are regarded as being in transit and are not ascribed a state.

It is common practice to write all half reactions as reductions; so the zinc oxidation half reaction is reversed and expressed as a reduction.

\[
\text{Zn}^{2+} (aq) + 2e^- \rightarrow \text{Zn(s)} \quad [8.5]
\]

Now the overall reaction is the difference of the two reduction half-reactions. The electrons from the zinc reaction travel through the external circuit and reduce the Cu\(^{2+}\) in solution at the other electrode. The electrode where oxidation occurs is called the anode; the electrode where reduction occurs is called the cathode, Fig 8.1.

Each electrode in a cell makes a characteristic contribution to the overall cell potential. Although it is not possible to measure the contribution of a single electrode, one electrode can be assigned a value zero and the others assigned values on that basis. The specially selected electrode in the standard hydrogen electrode (SHE).

\[
\text{Pt} \mid \text{H}_2(g) \mid \text{H}^+(aq) \quad [8.6]
\]

\[E^o = 0 \text{ at all temperatures}\]

The standard potential for a half reaction is then measured against the SHE. The standard cell potentials for Cd and Te are -0.403V and +0.551V respectively.

**8.3.2 The Cell Potential and the Nernst equation**

So long as the reaction in the cell is not at equilibrium, electrons are made to travel around the external circuit. The work that a given transfer of electrons can do depends on the potential difference between the two electrodes. This potential difference
is called the cell potential and is measured in volts. It is known that the maximum amount of electrical work $W'$, that a system, the cell, can do is given by the value of $\Delta G$.

However maximum work is only achieved when the cell is connected to an external source of potential difference that opposes and exactly matches the potential difference generated by the cell.

When the reaction takes place, $\nu NA$ electrons are transferred from the reducing agent to the oxidising agent per mole of reaction events. Therefore the charge transferred between the electrodes is $\nu NA \times (-e)$, or $-\nu F$. The electrical work $W'$ done when this charge travels from the anode to the cathode is equal to the product of the charge and the potential difference $E$:

$$W' = -\nu FE \quad [8.7]$$

Which given the conditions outlined above we can equate the electrical work to the reaction Gibbs energy

$$\Delta, G = -\nu FE \quad [8.8]$$

the constant $F$ is Faraday's constant, and is the magnitude of electric charge per mole of electrons

$$F = eN_A = 96,485\text{Cmol}^{-1} \quad [8.9]$$

It has been seen that the reaction Gibbs energy varies with the composition of the reaction mixture and that

$$\Delta, G^\circ = \Delta, G^\circ + RT\ln Q \quad [8.10]$$

In this expression, $\Delta, G^\circ$ is the standard reaction Gibbs energy and $Q$ is the reaction quotient for the cell reaction. We can express the Gibbs energy in terms of the cell potential by dividing through by $-\nu F$ and using Eqn[8.8] which gives

$$E = E^\circ - \frac{RT}{\nu F} \ln Q \quad [8.11]$$

In this expression $E^\circ$ is the standard cell potential

$$E^\circ = \frac{\Delta, G^\circ}{\nu F} \quad [8.12]$$
Chapter 8: Electrodeposition of Thin Film CdTe

Eqn[8.11], which expresses the cell potential in terms of the composition is called the Nernst equation. Because $RT/F = 25.7\text{mV}$ at $25^\circ\text{C}$, a practical form of the Nernst equation at this temperature is

$$E = E^\circ - \frac{25.7\text{mV}}{v} \ln Q$$

[8.13]

Hence for a reaction in which $v=1$, if $Q$ is increased by a factor of 10 then the cell potential becomes more negative by 59.2mV.

**8.3.3 Electrodeposition of Tellurium**

Tellurium electrodeposition can be carried out in an aqueous medium, in an acidic or alkaline pH range. Let us suppose that we have an acidic aqueous solution of TeO$_2$ that generates HTeO$_2^+$ ions in the electrolyte. The cathodic electrodeposition of tellurium occurs through the reaction

$$\text{Te} + 2\text{H}_2\text{O} \rightarrow \text{HTeO}_2^+ + 3\text{H}^+ + 4\text{e}^-$$

[8.14]

The equilibrium potential of tellurium can be written using the Nernst equation as [32]

$$E_{re} = E^\circ_{re} + \frac{RT}{4F} \ln \frac{a_{\text{HTeO}_2^+}}{a_{\text{Te}}} + \frac{3RT}{4F} \ln a_{\text{H}^+},$$

$$= E^\circ_{re} + 0.0148 \ln \frac{a_{\text{HTeO}_2^+}}{a_{\text{Te}}} - 0.0443\text{pH}$$

[8.15] [8.16]

The standard potential, $E^\circ_{re}$, for the above reaction is +0.551V (v s SHE). Thus tellurium deposition at the cathode can take place at potentials that are more negative than $E^\circ_{re}$ (i.e., <0.551V). The actual value of the deposition potential of tellurium will be decided by the activity (concentration) of HTeO$_2^+$ and the pH of the bath.

**8.4 Electrodeposition of CdTe**

The first article on the electrodeposition of II-VI compound semiconductors was published in 1975 [36]. This article described the electrodeposition of ZnSe from two kinds of molten salts. After this publication, articles on the electrodeposition of CdSe [37], CdS [38], Bi$_2$S$_3$ [38], CdTe [12], CdS$_x$Se$_y$ [39] and CuInSe$_2$ [40] appeared in succession.
The basis of all research on cathodic electrodeposition of CdTe from aqueous solutions is the work of Panicker et al [12] in 1978. They showed that Cd\textsuperscript{II} and Te\textsuperscript{IV} can be reduced simultaneously from aqueous solutions to grow CdTe:

\[ \text{Cd}^{2+} + \text{HTeO}_2^+ + 3\text{H}^+ + 6\text{e}^- \rightarrow \text{CdTe} + 2\text{H}_2\text{O} \quad \text{[8.17]} \]

The aqueous electroplating solutions used, consist typically of millimolar TeO\textsubscript{2} and an excess of Cd\textsuperscript{2+} salt, and are adjusted to a pH<3. Those authors also showed that p-type and n-type deposits could be created through suitable control of the deposition potential.

Their work and subsequent work by other groups [18,20,41-43] has shown that appropriate choices for the Te\textsuperscript{IV} and Cd\textsuperscript{II} concentrations and the deposition potential enable growth of near stoichiometric CdTe. Since then, the literature has grown extensively concerning the electrodeposition of CdTe and its characterisation. The success of this technique has been rationalised on the basis of thermodynamic and kinetic arguments [20], but more recently it has also been recognised that the nature of the substrate exerts considerable influence on the quality of the electrodeposited film [18].

### 8.4.1 Growth Mechanism

All previous CdTe electrodeposition studies have resulted in polycrystalline deposits. There are four primary reasons for the formation of polycrystalline deposits: nucleation and growth kinetics in the co-deposition of a compound semiconductor; the absence of an ordered substrate structure; lattice match between substrate and deposit; and substrate, solvent, reactant and electrolyte contamination [44].

The electrochemistry of Te has been extensively reviewed [45]. It is clear from the literature that, depending on the pH and deposition potential, tellurium may exist in one of a number of oxidation states in solution ranging from +6 to −2 [20].

Tellurium dioxide, TeO\textsubscript{2}, is the most widely used Te compound for CdTe electrodeposition, and is only slightly soluble in aqueous solutions [46-50]. In acidic solutions pH<2, the soluble species is the telluryl ion, HTeO\textsubscript{2}\textsuperscript{+}. There is some debate as to the exact mechanism for reduction of HTeO\textsubscript{2}\textsuperscript{+} to Te(0). Evidence has suggested that the reduction occurs by a two step mechanism [20,51].

\[ \text{HTeO}_2^+ + 5\text{H}^+ + 6\text{e}^- \rightarrow \text{H}_2\text{Te} + 2\text{H}_2\text{O} \quad \text{[8.18]} \]
Although the first step is a 6-electron process, for high concentrations of HTeO\textsuperscript{2+}, the net reaction yields a 4-electron reduction per deposited Te(0). This mechanism parallels one previously suggested for the reduction of Se(IV) [52,53]. Other evidence indicates that the mechanism involved is a simple 4-electron reduction of Te(IV) to Te(0) [54,55].

\[ HTeO_2^+ + 3H^+ + 4e^- \rightarrow Te + 2H_2O \] \[ 8.20 \]

It is generally agreed nevertheless, that for potentials more negative than \(-0.36\)V (vs.SHE), a second mechanism for Te(0) deposition can occur [20,54].

\[ Te + 2H^+ + 2e^- \rightarrow H_2Te \] \[ 8.21 \]

\[ HTeO_2^+ + 2H_2Te \rightarrow 3Te + 2H_2O + H^+ \] \[ 8.22 \]

The detailed mechanism to explain the electrodeposition of CdTe from an aqueous electrolyte is then not fully understood. However, in general terms the overall deposition process may be represented by two steps [56].

a) Tellurium reduction

\[ HTeO_2^+ + 3H^+ + 4e^- \rightarrow Te + 2H_2O \] \[ 8.23 \]

b) The deposited tellurium reacts rapidly with the Cd\textsuperscript{2+} ions in solution (due to the large free energy of compound formation for CdTe).

\[ Te + Cd^{2+} + 2e^- \rightarrow CdTe \] \[ 8.24 \]

The low solubility of TeO\textsubscript{2} leads to a low solution concentration of HTeO\textsubscript{2}+, such that the kinetics of the overall process is mass transport controlled by the HTeO\textsubscript{2}+ availability. Hence the current density during deposition of CdTe is proportional to the concentration of HTeO\textsubscript{2}+ ions and the stirring rate (i.e. degree of agitation) [57].

### 8.4.2 Underpotential Deposition

The electrochemistry of Cd has been extensively reviewed [58]. Various polycrystalline [59-61] and single crystal [62-65] substrates have been used to characterise the underpotential deposition of Cd. Cadmium underpotential deposition or UPD appears to be relatively straightforward, although there is some evidence that Cd\textsuperscript{2+} may absorb prior to UPD [41]. Reports of the alloy formation with Au [59], Ag [61,63] and Cu [64,65] electrodes have also been published.
Chapter 8: Electrodeposition of Thin Film CdTe

The conditions to be met to achieve cathodic deposition of compounds have been analysed in [13]. The key factor here is the extent to which the deposition potential of the less noble element (i.e., Cd in this case) is shifted relative to that of the noble species (i.e., Te in this case) by the free energy gained from compound formation. For CdTe, the difference in standard potentials (0.954V) is greater than \( (G_{\text{CdTe}}^{298}/2F) \) (\( G_{\text{CdTe}} \) = free energy of formation of CdTe) such that Cd remains the potential determining species throughout the stability range of the compound [12,13].

Electrodeposition of thin films of CdTe of good stoichiometry is achieved by using UPD as the means to achieve surface chemistry limited growth. The phenomenon of UPD is well-documented and reviewed [66,67]. It involves the deposition of one element on a second element at a potential prior to (under) that required for deposition of the first element on itself. Classically UPD involves deposition of the less noble metal (Cd) on a more noble metal (Te) [66-68]. The driving force for UPD, is the formation of a compound, which is energetically favoured relative to the bulk elements with a stoichiometry defined by the surface chemistry of the substrate.

The situation of UPD is represented in Fig 8.2. In this direction hexagonally stacked planes of Cd and Te alternate and the growth direction is in the \(<111>\) direction.

In Fig 8.2(a) only Te is initially capable of depositing on the substrate surface. In (b) Cd deposition is now possible prior to deposition upon itself, which is energetically forbidden (c). In (d) the second layer of Te can now deposit. Most commonly the first step is thought to involve the \( 4e^- \) reduction of \( \text{HTeO}_2^+ \) to Te, Eqn[8.25], which shows the reaction and the standard electrode potential for this reaction.

\[
\text{HTeO}_2^+ + 3\text{H}^+ + 4e^- \rightarrow \text{Te} + 2\text{H}_2\text{O}
\]  
[8.25]
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\[
E^\circ_{\text{Te}} = 0.551 \text{V vs SHE}
\]

This reaction is followed by Cd deposition and reaction to form CdTe. For Cd the relevant electrochemical reaction and standard potential is [12].

\[
Cd(s) = Cd^{2+} + 2e^{-} \quad \text{[8.26]}
\]

\[
E^\circ_{\text{Cd}} = -0.403 \text{V vs SHE}
\]

The deposition of Cd and Te in the ratio of 1:1 is carried out as follows. The potential is applied at a value more positive than that required to deposit the less noble species, in this case Cd (-0.403V). This leads to a reduction in the concentration of the more noble element Te, at the interface. The energy required to deposit Cd is achieved through the large free energy associated with the formation of CdTe from Cd and Te.

The free energy of formation of CdTe, \(G_{\text{CdTe}}\), is as large as 98.4kJmol\(^{-1}\). CdTe can therefore be grown from the standard value of the CdTe/Cd boundary, \(-0.403\text{V vs SHE}\) to the CdTe/Te boundary of \(-0.403 + G_{\text{CdTe}}/2F = 0.143\text{V vs SHE}\) where \(F\) is the faraday constant.

\[
E^\circ_{\text{Te}} = 0.551 \text{V} + 0.143 \text{V} = 0 \text{V} \quad E^\circ_{\text{Cd}} = -0.403 \text{V}
\]

Fig 8.3
Illustration of CdTe growth region due to UPD

On the left hand side of Fig 8.3, a region of Te only deposition is observed. Decreasing the potential, moving to the right, leads to the interface that exists when it becomes energetically possible for Cd UPD to occur. At which point Cd growth is initiated and the films are expected to be n-type due to an excess of tellurium. At the CdTe/Cd interface Cd deposition now becomes possible and the film may become p-type due to an excess of Cd. Below \(-0.403\text{V}\) a large increase in the deposition current is observed due to the large \(Cd^{2+}\) concentration now being able to deposit on itself and no longer limited by the deposited Te. Classically the deposition occurs in the region just above the Cd deposition potential, within 100mV. In this instance the films are of near perfect stoichiometry with optimal structural and electrical properties.
8.4.3 Review of Previous Results

Classically aqueous electroplating solutions for CdTe consist typically of millimolar TeO₂ and an excess of Cd²⁺ salt, and are adjusted to a pH<3. In this instance the experimental variables are limited to the deposition potential, the concentration of the two chemicals (in this case TeO₂ and CdSO₄), electrolyte temperature and electrolyte agitation. The effect of the electrolyte pH is considered in section 8.5.2.

Principally most investigations of the effect of the growth parameters have focused on the change in structural properties of deposited films with deposition potential [31,69-73]. Many authors have shown that CdTe films possess increasing crystallinity through XRD measurements principally in the <111> direction at decreased potentials. Valvoda [73] and Guo et al [69] identified a transition from p- to n-type behaviour with decreasing potential at approximately 40mV versus CdRE, cadmium reference electrode, (-0.403V). In the case of even higher deposition potentials than those for p-type behaviour the film was found to be highly amorphous. Bonilla et al [31] in 1991 also showed similar results, but also reported the presence of minor CdTe peaks due to the (220) and (311) crystal directions. They also confirmed a lattice constant of 6.6Å and at potentials +500mV v s CdRE the peaks were due solely to the presence of elemental tellurium only. They also showed that as the deposition potential decreased not only did the peaks due to tellurium inclusions disappear but that the FWHM did not appreciably change indicating a constant crystal size. In addition Kampmann et al [70] have investigated the change in optical transmission as a function of the deposition potential. They found that films deposited at +5mV above the CdRe showed higher optical transmission than those deposited at +65mV. The onset of transmission near the bandgap was more abrupt in the former case despite the extrapolated bandgap being identical for both cases. Similar results have been reported by Ou et al [74]. These results were felt to be consistent with the improvement in crystallinity deduced from the XRD spectra. At lower deposition potentials conditions for the Cd UPD are at their most favourable and Te is least likely to be able to deposit upon itself.

In the case of TeO₂ concentration several authors [72-73] have reported similar results. In both cases deposits carried out in a solution of higher TeO₂ concentration were less crystalline or amorphous. Valvoda [73] concluded that the TeO₂ concentration also
affected the crystal growth direction being weakly \(<110>\) in the amorphous region and predominantly \(<111>\) in the low \(\text{TeO}_2\) concentration regime. This is clearly related to the proposed mechanism for \(\text{CdTe}\) growth in which a slowly developed layer of \(\text{Te}\) is quickly covered with \(\text{Cd}\) from the electrolyte.

Results have consistently shown that films deposited in the high temperature regime have improved crystallinity \([12,73]\). Valvoda varied the temperature of deposition from ambient to 90°C. In this case they reported that deposits prepared below 60°C were largely amorphous, but those deposited close to 90°C were increasingly crystalline. Panicker \([12]\) in his groundbreaking article also showed that at 90°C alternative crystal directions to the dominant \(<111>\) were seen in the \(<220>, <311>, <002>\) and \(<400>\) directions in decreasing size. At higher temperatures the rate of \(\text{Cd}\) deposition is more likely to prevent \(\text{Te}\) inclusions according to the model whilst also helping to break those bonds that are too weak to be due to \(\text{CdTe}\).

The agitation of the electrolyte has not been extensively investigated although the model would predict increased deposition currents for increased stirring of the electrolyte. In this case the rate of \(\text{HTeO}_2^+\) renewal at the electrode-electrolyte interface is much increased. Danaher et al \([20]\) discussed the kinetics of \(\text{CdTe}\) electrodeposition by varying the agitation of the electrolyte. Here, a linear increase in the deposition current was reported versus the stirring rate.

### 8.5 Experimental Arrangements and Methods

The entire apparatus for cathodic electrodeposition of \(\text{CdTe}\) resides in a perspex glove box through which a filtered \(\text{N}_2\) flow is constantly maintained. The amount of oxygen in the glove box is monitored to be approximately 4%. The glove box resides in a clean room environment reducing the risk of electrolyte contamination and dust forming on the films. The glove box is at an over-pressure with respect to the clean room. A custom made potentiostat was used to apply the deposition potential. The circuit diagram for this instrument is included in appendix A.

#### 8.5.1 Electrodeposition Bath

The electrodeposition bath is a standard three-electrode cell with a 0.25mm \(\text{Pt}\) (Sigma-Aldrich 99.99%) foil counter electrode, \(\text{Cd}\) reference electrode and metal coated
glass as the working electrode, Fig 8.4. Previous work has concluded that baths made of teflon introduce fewer impurities into the solution than pyrex which is more commonly used as the containment vessel. Five optical windows allow the growth of the films to be viewed using a camera and small VDU. Prior to the introduction of any electrolytes, the bath was cleaned by refluxing trichloroethylene for several hours before washing in deionised water. The temperature of the electrolyte is monitored using a Pt resistance thermometer that is covered by a thin teflon sleeve to prevent contamination. The entire bath is positioned upon a heater mat with a sealing compound ensuring good thermal contact. A custom-made temperature controller allows the bath temperature to be varied in the range ambient to 95°C with an accuracy of ±0.5°C. The bath has a lid to prevent evaporation of the electrolyte that would otherwise disturb the ion concentrations.

The reference electrode was of our own design. Previous work has identified a perfectly distinguishable source of contamination emanating from the utilised reference electrode. The saturated calomel electrode (SCE) is used most frequently, as it has a constant, well-reproducible potential $E_{SCE} = +0.2422\, \text{V vs SHE}$ [75]. It consists of 0.1 mol KCl in contact with HgCl (calomel) and Hg. This commonly used electrode pours KCl into the electrolyte at an approximate rate of 5 mM/h which is, without any doubt an important source of contamination [71].

In this case a glass pipette shortened to a length of 8 cm was adapted for the task. The pipette was filled with an aqueous solution of pH 2 CdSO$_4$ to a concentration of 1 mol cm$^{-3}$. A permeable membrane prevents the solution draining into the electrolyte while maintaining electrical connection to the other electrodes. A Cd wire (Sigma-Aldrich 99.999%) of diameter 1 mm completed the electrode. The electrode was tested against a copper solution and the observed potential difference of the electrode was as theoretically predicted from standard tables [76] as 0.74 V vs SHE. The working electrode was our metal coated glass mounted in a teflon holder with contact made through a pressure pad.

The electrolyte was continuously stirred using a 7.5 cm long teflon coated magnetic rod, the action of which introduces fresh electrolyte to the surface of the substrate. Further agitation was achieved with a N$_2$ supply of 0.2 l min$^{-1}$ to the electrolyte.
This N₂ purge was carried out for twelve hours to purge the electrolyte of dissolved oxygen prior to the insertion of a substrate.

8.5.2 Electrolyte Preparation

Since aqueous solutions can be handled easily, most of the research on CdTe deposition has been done using aqueous solutions containing TeO₂, CdSO₄ and H₂SO₄. Water A.C.S reagent (σ≤2.0x10⁻⁶Ω⁻¹cm⁻¹) was introduced into the cleaned deposition tank to a depth of approximately 6cm. The volume of electrolyte is then approximately 1.0litre.

In acidic media, TeO₂ is protonated and exists as HTeO₂⁺. The solubility of tellurium dioxide is very poor, and reported by Pourbaix [77] and Lyons [46]. According to Pourbaix, the solubility of TeO₂ in an acidic media is given by

\[
\log_{10}[Te] = -1.0 pH - 2.0 \quad [8.27]
\]

Lyons showed that Eqn[8.28] is more applicable to this process in the pH range 1.2 to 2.6.

\[
\log_{10}[Te] = -0.84 pH - 2.5 \quad [8.28]
\]
At pH1.9 Eqn[8.28] yields a concentration for HTeO$_2^+$ of $8.0 \times 10^{-5}$ mol dm$^{-3}$. In turn the number of HTeO$_2^+$ ions in the electrolyte is $4.8 \times 10^{19}$. This is alarmingly low as a 1µm film deposited over an area of 15cm$^2$ will contain $5.5 \times 10^{18}$ unit cells. Each of these unit cells will contain 4 Te atoms and so the film has approximately $2.2 \times 10^{19}$ Te atoms. A substantial amount compared to the concentration available in the electrolyte. Such consumption of the available protonated Te will lead to a change in the electrode potential but also will affect the film stoichiometry. It is therefore imperative that the concentration of HTeO$_2^+$ is held as constant as possible. The electrochemical potential for Te will be increased as the availability of HTeO$_2^+$ is decreased.

The limiting (mass transfer controlled) current density for electrodeposition is proportional to the bulk concentration of depositing species. As the solubility of CdSO$_4$ is much higher than that of TeO$_2$, the limiting current density for CdTe deposition depends on the TeO$_2$ concentration. In order to achieve productivity the concentration of TeO$_2$ should be maintained as high as possible. Although this can be achieved by the use of a low pH electrolyte, it has been reported [51] that deposits obtained from low pH electrolytes tend to include excess tellurium, which can result in poor electronic properties. Consequently, Lyons et al [46] have recommended an electrolyte in the pH range of 1.5 to 2.5.

To maintain a constant amount of protonated tellurium dioxide HTeO$_2^+$ concentration in the solution, TeO$_2$ in lump form was placed in the electrolyte to maintain the concentration during deposition. The TeO$_2$ was supplied in the powder form and converted to granules in a sealed quartz tube under heating. Placing these in a perforated teflon container within the electrolyte overcame the change in concentration with time during deposition.

The acidity of the solution was adjusted to pH 1.9 by adding concentrated sulphuric acid (Sigma-Aldrich >97.5%) saturated with TeO$_2$ (Sigma-Aldrich 99.9995%). Monitoring the electrolyte pH was achieved using a pH glass electrode connected to a calibrated Cole-Palmer 2500 series readout display. The CdSO$_4$ was added in the powdered form and no problems were encountered in achieving a concentration of 0.1mol/dm$^3$. At this concentration the value for $E$ from Eqn[8.13], at which electrodeposition of Cd becomes possible, is $-0.373$ mV vs SHE.
8.5.3 Choice of Substrate

The majority of the work carried out on CdTe electrodeposition has used metallic or CdS-coated glass as the substrate. Our eventual aim is CdTe growth directly onto the metal readout pixels of an active matrix array and a metal substrate is therefore preferred. However, metal foils compromise measurements of transmission through the growing film, which can be a useful diagnostic. Therefore, we grow films on metal-coated glass where the metal is thin enough (<40nm) to be transparent at visible wavelengths. Previous work using metallic substrates has utilised nickel [12,78-80], platinum [81,82], steel [71,78,83], titanium [18,23,30,71,79,80,84-87] and molybdenum [88,89]. The best results have been reported using Ti as the substrate material. In addition Ti is a strong reducing agent and the bond at the SiO<sub>2</sub>/Te interface is expected to be strong.

8.5.4 Substrate Preparation

Substrates were borosilicate glass with a thickness of 0.7mm and an area of 15cm<sup>2</sup>. Initial experiments with microscope glass had proved unsatisfactory as this “soda lime” glass exhibits inferior adhesion properties with a metallic film [90] and acts as a source of Na, contaminating the electrolyte.

The glass substrate was cut using a diamond scribe into rectangles 30mm x 60mm with glass fragments removed with distilled water, preventing abrasion of the surface. Ultrasonic cleaning in a 1:10 Decon to water solution for 1 hour and subsequent rinsing in distilled was used to remove surface grease.

The glass was then placed in a home-made reflux cleaning unit. The refluxer consists of a cylindrical pyrex 250ml crystallising basin with an aluminium cover through which tap water is pumped to cool the slide. The cleaning agent used in this case was Sigma-Aldrich Analar grade (99.9%) Isopropanol, IPA. The glass was cleaned in this way for 1 hour. A further wash in de-ionised water removed excess IPA. Water drop and breath tests on preliminary slides indicated the absence of dirt or imperfections on the surface. Drying with a Nitrogen gun allowed water to be quickly removed from the surface.

In the cleaning process the glass will have absorbed a small but finite amount of water. This will then outgas in the coating vacuum chamber, degrading the strength of the
metal to glass bond. Heating the glass slide at 180°C for 1 hour in a vacuum oven is sufficient to outgas the absorbed water and overcome this problem.

Metal deposition was carried out using an Edwards E306 thermal evaporation unit where a base pressure of 1E-5mbar was routinely achieved. Titanium wire (99.8% Advent) of diameter 0.25mm was used for evaporation. A Cressington mtm thickness monitor was able to record the thickness of the evaporated film. Outgassing of the Ti by heating was made prior to coating, which were typically 20nm to 30nm thick. Such a thickness is partially transparent, ~20%, to visible radiation allowing transmission measurements to be carried out on deposited CdTe. Following evaporation the substrate was allowed to cool for 1 hour before removal.

8.5.5 Deposition

Following venting of the coater the metallised glass was quickly transferred to the deposition tank. Standard growth conditions were used for all data presented here. In each case, the growth substrates were immersed in the electrolyte at the applied potential for 1hr. At the end of this period, the substrates were removed from the electrolyte and thoroughly rinsed with de-ionised water, dried with a nitrogen gun and placed in airtight containers.

The images in Fig 8.5 show the change in room light transmission that occurs during a 1hr deposition. Although the change is not as clear as might be hoped the variation in reflection from the back surface is more noticeable.
8.6 Characterisation of the Growth Process

Before characterising the grown films it is essential to record some basic properties of the growth process. This builds a good understanding for the technique and allows direct comparison with the theory. In this section the deposition current as a function of time and electrolyte agitation are discussed.

8.6.1 Deposition Current versus Time

The deposition current is dependent on the rate of growth due to the requirement of electrons at the surface at the electrode/electrolyte interface, Eqns[8.23 & 8.24]. It is a potential dependent variable as this determines the film composition and rate of growth.

The electrolyte temperature was maintained at 25°C with the stirring rate at 2revsec⁻¹. Nitrogen gas bubbling was used prior to substrate insertion to remove dissolved oxygen. This was ended at substrate insertion as it considerably alters the deposition current due to the large flow of fresh electrolyte over the electrode surface. The substrate was a glass slide covered with 40nm of evaporated titanium. The immersed growth area was 12cm².

A deposition voltage of +40mV v’s CdRe was used as this should grow stoichiometric CdTe. This potential corresponds to −363mV v s SHE and in this electrolyte where the Cd²⁺ concentration is 0.1molL⁻¹ is 10mV above that required to deposit pure Cd.

Following immersion into the electrolyte the deposition current, I_D, as a function of time was recorded, Fig 8.6. It was not possible to record the deposition current accurately within the first five minutes due to large fluctuation in the readings. After this
time $I_D$ was recorded at several intervals by monitoring the current for one minute and taking the average of the readings.

The data in Fig 8.6 clearly shows a dramatic change in the deposition current with time during deposition. This change was found to be repeatable. It is believed that there are several changes in the growth process that account for this. These are the initial Te layer, hydrogen formation in the initial stages and the plating out of electrolyte impurities.

The raw Ti surface on immersion will be covered by an initial layer of Te metal. This is due to the inability for Cd$^{2+}$ to deposit at these potentials without the large free energy gain associated with forming the Cd-Te lattice. Following the growth of this primary Te layer, Cd deposition becomes possible and co-deposition is observed. The excess concentration of Cd in the solution means that the deposition current should increase from this component.

The second mechanism is thought to involve the formation of hydrogen in the initial stages on the Ti surface. This mechanism has been credited previously with a drastic change in deposition current with time [46]. In support of this hypothesis it was
found that the current decrease with time did not occur when the film was removed from the bath and then re-inserted.

The third mechanism concerns the presence of impurities within the electrolyte, which will be quickly plated out of the deposition bath [12]. This may contribute to the fall-off in current with time. Impurities may result from the bath materials or the employed reagents.

Of these, the first would result in an increase in current and although likely, the time scales involved are far too small to be applicable to this location. The fall-off in current is found to be repeatable and this would rule out the third mechanism although this again will be present. The second mechanism is then the most likely as the dominant cause of change in $I_D$ with time.

8.6.2 Deposition Current versus Stirring Rate

In this experiment the rate of growth as measured through the deposition current $I_D$ is recorded as a function of the rotation rate of the magnetic stirrer.

The proposed mechanism for CdTe electrodeposition, relies on Te deposition upon the growth surface followed by reaction with the Cd$^{2+}$ ions in solution. This result is due to the large free energy gained forming the Cd-Te bond. The rate of growth and therefore $I_D$ is dependent on the availability of HTeO$_2^+$ at the growth surface. This assumes that the concentration of Cd$^{2+}$ in the solution is sufficiently high that this does not contribute a rate determining step and slowing the rate of growth. In our electrolyte the concentration of Cd$^{2+}$ and HTeO$_2^{2+}$ are 0.1mol/dm$^3$ and 8.0x10$^{-5}$mol/dm$^3$, Eqn[8.28], respectively.

Increasing the flow of electrolyte over the surface of the film by increasing the rate of rotation of the magnetic stirrer should then increase $I_D$ and therefore the rate of deposition. In a production environment this would be highly favourable due to increased throughput.

The experimental conditions of electrolyte temperature, nitrogen gas bubbling, substrate size, Ti thickness and deposition voltage were the same as the previous experiment. To avoid the change in deposition current that occurs during the film growth the experiment was not started until 40 minutes had elapsed following insertion. The
deposition current was recorded 1 minute later when it had stabilised at a new value. The recorded data is shown in Fig 8.7.

![Deposition current versus stirring rate](representative-diagram)

The data shows a linear change in the deposition current for revolution rates less than 1 \text{revs}^{-1}. This then tends towards a limiting value at increased rotation rates. This indicates that at lower rotation rates, $I_D$ is proportional to the amount of electrolyte flowing over the surface. Deposition in this region is mass flow controlled. At increased agitation the changes in $I_D$ reduce and the value tends towards a limiting value. Deposition in this region is limited by the concentration of HTeO$_2^+$ in the electrolyte.

Danaher [20] who used a rotating ring disk electrode observed a linear relationship between the deposition current and the rotation rate. In this case we assume that they would have seen the same limiting condition at increased rotation rates. Barker [57] predicted, but did not confirm experimentally a linear relationship between the deposition current and the stirring rate.

8.6.3 Summary

Two experiments have been performed to characterise the cathodic growth process of CdTe from an aqueous solution at room temperature. These investigated the
change in the deposition current as a function of deposition time and as a function of electrolyte agitation.

A decrease in the deposition current towards an equilibrium value was seen during the growth. This has been attributed to the formation of hydrogen in the initial stages, which became inhibited as the film thickness increased. Other contributing factors concern initial growth of a Te layer and the plating of impurities from the electrolyte.

When the rotation of the stirrer was varied the deposition current initially increased in proportion with the rotation before reaching a limiting value at very high rotation rates. This was attributed to the mass transfer of HTeO$_2^+$ in the solution at lower rates and its dependence on the Te concentration at higher rates.

Having developed a successful growth process that agrees with the findings of other authors it is now appropriate to investigate the properties of some grown films.

### 8.7 Preliminary Results

Successfully grown films were characterised in a number of ways. In this section the surface appearance on the micron scale is investigated with SEM and the composition investigated with EDX and PIXE.

For the SEM measurement a section of a film grown at +10mV vs CdRe was cleaved into an area of approximately 1cm$^2$. The surface of the film at a magnification of x500 is shown in Fig 8.8. The width of the image is approximately 200µm.

The image is one of an irregular surface with inconsistencies such as protrusions, scratches and pinholes. The pinholes show very clearly as regions of black below the surface of the electrodeposited film corresponding to the evaporated Ti layer. The largest of these is more than 10µm across. Such a pinhole would create an electrical short between the Ti layer and a top contact material. These pinholes could be seen by holding the film in front of an intense light source and observing the points of transmission.
It was decided to nevertheless record the film stoichiometry. This was done using EDX and PIXE. Samples of \( \approx 1 \text{cm}^2 \) were cleaved from films grown in the deposition potential range of \( +10 \text{mV} \) and \( -100 \text{mV} \) vs CdRe. The stoichiometry was found in the ratio of the Cd to Te present in the film. This is shown in Fig 8.9 for both techniques as a function of the deposition potential vs CdRe.

Both EDX and PIXE show a good degree of agreement in the Cd:Te ratio. At the lower deposition voltages the Cd:Te ratio is approximately 0.5 and this falls for both techniques at increasing deposition voltages.

Clearly this ratio is a long way from the ideal Cd:Te of 1 indicating that the Cd\(^{2+}\) concentration in the electrolyte is insufficient. In this case the Te metal is formed in the film due to reaction 8.23 but reaction 8.24 is not sufficiently fast to consume all Te and, therefore, free Te is left in the film.

The slight increase in the ratio at lower deposition potentials is due to it becoming easier for Cd to deposit upon both Te and itself. Here Eqn[8.20] is faster and less free Te metal remains.
8.8 Discussion

In this chapter investigations have been carried out into the cathodic electrodeposition of CdTe from an aqueous electrolyte. Consideration of the large number of possible growth processes for thin film CdTe has lead to the conclusion that cathodic electrodeposition is an appropriate choice for large area films of good quality at minimal expense. The fundamentals of electrochemistry have been introduced for the known electrochemist introducing the basic concepts behind this technique.

The background to the electrodeposition of CdTe has reviewed the large volume of literature available concerning the growth mechanism. The UPD of Cd$^{2+}$ on Te is critical to the growth of this binary semiconductor was introduced. A review of previous results found good agreement in the literature that this technique leads to good quality films that are reproducible.

The necessary experimental arrangement was discussed in depth. This included the teflon growth tank, electrolyte, choice of substrate and substrate preparation. This then lead to some images showing the change in film reflection as viewed by a camera during growth.
The cathodic electrodeposition growth of CdTe from an aqueous solution at room temperature was then characterised by studying the change in $I_D$ as a function of deposition time and electrolyte agitation. A decrease in the deposition current towards an equilibrium value was seen during the growth. This has been attributed to the formation of hydrogen in the initial stages, which became inhibited as the film thickness increased. Other contributing factors concern initial growth of a Te layer and the plating of impurities from the electrolyte.

When the rotation of the stirrer was varied the deposition current initially increased in proportion with the rotation rate, before reaching a limiting value at high rotation rates. This was attributed to the mass transfer of $\text{HTeO}_2^+$ in the solution at lower rates and its dependence on the Te concentration at higher rates.

Following this the surface appearance on the micron scale was characterised using SEM and the composition evaluated using EDX and PIXE. The surface micrograph indicated a poor surface with protrusions, scratches and pinholes. Compositional measurements using EDX and PIXE revealed good agreement between the two for the Cd:Te ratio as approximately 1:2 over the deposition range. This is someway from the ideal of 1:1 and is believed to be due to the concentration of Cd$^{2+}$ in the solution being insufficient.

A considerable amount of work has been employed in establishing a working CdTe electrodeposition rig based on a good theoretical understanding of the technique. Improvements in the technique must first focus on the adhesion and film properties before an investigation into attaining an ideal stoichiometry can be undertaken.

Unfortunately several constraints prevented continued work in this area. Firstly the glass-titanium bonding frequently failed so that peeling was observed off the glass leading to the observed poor adhesion. In retrospect the rotation rate may have been sufficient to lift the Ti layer from the glass. Lower rotation rates would have resulted in unfeasible deposition currents and rates of growth. It is fortunate though that a large supply of cathodic electrodeposited CdTe films was made available by BP Solar Inc. It is the experimental results obtained with these films that are presented in chapter nine.
Chapter 9: Studies of Electrodeposited CdTe Solar Cell Material

9.1 Introduction

In this chapter investigations are carried out on the CdTe thin films supplied by BP Solar Inc. Prior to experimental procedures the fabrication technique for the solar cell is described. Experimental studies focus on the structural properties of the films using X-ray diffraction (XRD), surface topography (SEM), stoichiometry (EDX) and bandgap through optical transmission measurements. A discussion considers the attained results for continued research into CdTe thin films and their implications for future work.

9.2 Fabrication Technique

BP Solar Inc has focused on the production of thin film solar cells based upon the sequential growth of the n-CdS/p-CdTe heterogeneous layer on SnO$_2$ coated glass. The SnO$_2$ coated glass has a resistivity of only 10$\Omega\cdot$cm$^{-1}$, allowing the electrodeposition potential to be easily applied with negligible resistance losses over the interface. The structure for the solar cell is shown in Fig 9.1 with the film thickness and semiconductor bandgaps. The growth process has been developed on an empirical basis for nearly ten years with changes in the procedure correlated against device performance. An outline of the growth process is now discussed.

Each tin oxide coated glass plate is first washed in an industrial plate washer using de-ionised water and dried with a dry air jet. A concentrated nitric acid wash is then used for 60sec to remove any metallic impurities before rinsing under a de-ionised water jet. The plates are moved to a sodium Gluconate and peroxide wash where they are
washed for 8 minutes in the Na gluconate/NaOH mixture at a minimum temperature of 50°C. This 25 litre aqueous solution consists of dissolved 300 g NaOH and 150 g Na gluconate. Washing is then carried out in de-ionised water for 1 min before being inserted in a hydrogen peroxide/acetic acid wash for 8 minutes. This second wash consists of 10 litres of 100 vol. hydrogen peroxide mixed with 500 ml glacial acetic acid.

<table>
<thead>
<tr>
<th>Top Contact</th>
</tr>
</thead>
</table>
| 2μm           | p-CdTe  
| 0.1μm         | n-CdS   
| 0.4-0.6μm     | SnO₂    
| 4mm           | Glass   
| Eg=1.46eV     | Eg=2.42eV  
| Eg=3.5eV    |  

Prior to the electrodeposition of CdTe, CdS is deposited using chemical bath deposition from an aqueous solution. Chemical bath deposition of the CdS layer [1] is preferable as the fabrication technique for this layer compared to vacuum evaporation [2,3], chemical vapour deposition [4], electrodeposition [5], spray pyrolysis [6]. The reason for this lies in the economy of the technique and the capability for large area deposition or multiple plate deposition leading to cheaper production costs. Experimental details for this process can be found in detail elsewhere [7,8].

Constituents of the deposition solution include CdO, ethylenediamine, ammonia and NaOH. The bath temperature is held at 75°C for fifteen minutes. Thiourea is then added to the solution simultaneous to the immersion of the plates in the bath. Upon removal, after 10 minutes, the plates are quickly rinsed in cold water. The dried CdS coated plate is then heat treated for 12 minutes at 410°C before again being allowed to cool slowly to room temperature.

The physical properties of CdS films deposited in this way are well known [7] and easily repeatable. Good adhesion to the tin oxide has been observed with adherence tests indicating strengths greater than 700 kgc㎡² limited only by the threshold for the epoxy
resin used [7]. Film thickness’ (<1000Å) are measured using a Dektak II A surface profiler with recorded fluctuations in the film thickness being ±10%.

For CdTe electrodeposition, an area of CdS is removed from the left and right edges of the plate to a distance of ≈2cm so that Cd wire strips can be taped to the edges of the plate. The potential is applied via these strips and the conductive nature of the SnO₂ ensures that the entire plate possesses a uniform deposition potential. The CdTe bath is computer controlled with the deposition potential continuously monitored and the deposition current for the entire growth cycle recorded. Deposition is typically carried out at elevated temperatures above 60°C for 6 hours as this has been found to yield dramatic improvements in the film crystallinity [9].

Upon removal, the plate is washed in de-ionised water and dried with a dry air gun. Following the electrodeposition of CdTe, the p-n heterojunction is formed by annealing the CdTe film at 450°C for 15 minutes. Further processing is then carried out to complete the solar cell. The solar cells produced in this way are 30x30cm in size with efficiencies reproducibly in the range of 8 to 10%. The pictures in Fig 9.2 show the appearance of the front, optically incident, and reverse, growth side, surfaces.

In the left-hand image the reflection from the film on the other side of the glass is smooth with a matt black appearance. So clear is the reflection that it is possible to make out the author and digital camera reflection towards the bottom of the image. In the growth side, Fig 9.2(b), the film appearance is one of a dull grey without the ability to observe a clearly reflected image. Clearly some difference arises in the growth process.
and a few suggestions are made here that may account for this change. Firstly, the CdTe at the start of deposition is grown on what should be a very smooth CdS layer. The CdS layer is very thin (<0.1μm) so that fluctuations in the surface are minimal and this promotes a good spectral reflection. Secondly, the contrast may result from a change in the stoichiometry during the growth process. Tellurium metal has a grey lustre and may account for the colouration. These ideas will be explored further in the experimental section.

9.3 Experimental Results

In this section the results of several experiments on the cleaved sections of completed CdTe/CdS solar cells are discussed. The above layers were characterised by selected techniques in order to monitor the bulk structure (XRD), surface topography (SEM), stoichiometry and homogeneity (EDX) and bandgap using optical transmission.

The observation of crystal orientations using XRD allows the crystal structure to be found and may identify sources of excessive contamination. The surface appearance allows the crystal size to be estimated visually while the stoichiometry can be used to identify any gross deviations from the ideal stoichiometry. Optical transmission measurements are very important for a solar cell material allowing the measurement of the optical efficiency and the bandgap. In the XRD and optical measurements a systematic approach is taken starting from the least complicated film to avoid complications that may arise from considering the whole four-layer system.

In all the measurements, cleaving of the 4mm thick semi-toughed glass was required. The pieces were carefully cut using a fine diamond scribe with a single scratch on the surface giving the best results for producing a well defined break with no shattering.

9.3.1 X-ray Diffraction Studies

The bulk structure of electrodeposited CdTe films has been reported previously [9-25]. Samples that represented each part of the growth process were made available to us. By performing a XRD study on each of the constituent films; SnO₂/glass, CdS/SnO₂/glass and CdTe/CdS/SnO₂/glass, it is possible to clearly identify which peaks correspond to which film. This is particularly useful considering that the final four layer
system was found to possess no less than fourteen peaks. Many of these peaks can be assigned to each film when considering the large range of possible crystal directions that can give rise to constructive interference. The glass plate in each case was split into square sections of approximately 1cm². The crystal structure for each of the film layers was evaluated using a Philips P505 Energy Dispersive X-ray Analysis Unit.

The XRD peak that was observed from the heat treated SnO₂ coated glass as a function of angle 2-theta is shown in Fig 9.3, where p# denotes the peak number. An XRD pattern from the raw SnO₂ coated glass was not taken as this may differ from the heat treated material in the solar cell. The diffraction pattern indicates the presence of a broad hump due to the amorphous glass with 8 peaks clearly visible superimposed on this due to the SnO₂ conductive layer [16]. No peaks were recorded for angle-20 greater than 80°.

![Fig 9.3](image)

XRD pattern for SnO₂ coated glass as a function of angle 2-theta

Each peak in this spectrum corresponds to either SnO₂ or SiO₂. The values for the (hkl) in both materials were obtained from a database [23]. The SnO₂ layers have been identified as those corresponding to the (100), (101), (200), (211), (220), (310) and (301) orientations with the dominant peak being the (200) plane. The SnO₂ layer was observed in the tetragonal phase with a=4.738Å and c=3.188Å [23]. One of the seven peaks, p2, does not correspond to any SnO₂ crystal orientation that could give rise to constructive
interference. It is possible that this corresponds to the (211) direction in SiO₂, where the interplane spacing, \( d=2.97\text{Å} \), is only 1% different from our experimentally attained value, 3.005Å. This has then been assigned to the glass substrate, which although largely amorphous clearly possess a certain degree of crystallinity. Such crystallinity may result from the glass toughening process in which it is heat treated.

The angle of intensity \( (\theta) \), counts, \( d(\text{Å}) \), relative intensity and assignation for the glass/SnO₂ spectra is shown in Fig 9.4. The quantity, \( d \), indicates the value \( d \) in Eqn[6.1] corresponding to the inter-plane distance required to give constructive interference at this angle in angstroms.

<table>
<thead>
<tr>
<th>Peak No</th>
<th>Angle</th>
<th>Counts</th>
<th>( d (\text{Å}) )</th>
<th>Rel I</th>
<th>Assigned</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.827</td>
<td>300</td>
<td>3.321</td>
<td>92</td>
<td>SnO₂ (100)</td>
</tr>
<tr>
<td>2</td>
<td>29.708</td>
<td>188</td>
<td>3.005</td>
<td>58</td>
<td>SiO₂ (211)</td>
</tr>
<tr>
<td>3</td>
<td>34.038</td>
<td>124</td>
<td>2.632</td>
<td>38</td>
<td>SnO₂ (101)</td>
</tr>
<tr>
<td>4</td>
<td>38.067</td>
<td>326</td>
<td>2.362</td>
<td>100</td>
<td>SnO₂ (200)</td>
</tr>
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<td>5</td>
<td>51.805</td>
<td>176</td>
<td>1.763</td>
<td>54</td>
<td>SnO₂ (211)</td>
</tr>
<tr>
<td>6</td>
<td>55.0</td>
<td>50</td>
<td>1.668</td>
<td>15</td>
<td>SnO₂ (220)</td>
</tr>
<tr>
<td>7</td>
<td>61.895</td>
<td>72</td>
<td>1.498</td>
<td>22</td>
<td>SnO₂ (310)</td>
</tr>
<tr>
<td>8</td>
<td>65.781</td>
<td>116</td>
<td>1.418</td>
<td>36</td>
<td>SnO₂ (301)</td>
</tr>
</tbody>
</table>

Fig 9.4
Diffraction data for SnO₂ coated glass with assigned peaks

The diffraction pattern attained from the annealed CdS layer is shown in Fig 9.5. As for the SnO₂ coated glass, no peaks were recorded for angle-\( \theta \) greater than 80°.

Comparison of Fig 9.3 and 9.5 reveals that only 1 additional peak was observed to those seen for the SnO₂ system. This may be due to the thinness of the CdS layer (only 0.1μm thick). This peak, p₃ at \( \theta=34° \), is somewhat of an enigma. This intensity peak does not correspond to any orientation in CdS, SnO₂ or glass that could give rise to constructive interference. This peak has been termed unknown. It is also possible that the peaks observed in this pattern consist of both SnO₂ and CdS contributions. For instance, p₁ here may also be CdS (002) (\( d=3.36\text{Å} \)) as well as SnO₂ (110) (\( d=3.35\text{Å} \)). This is again possible for p₆ where it may correspond to the CdS (112) orientation (\( d=1.76\text{Å} \)). This may explain why the relative intensities for these peaks are shifted in the CdS spectra to smaller angles (26.7°) as opposed to larger angles (38°) for the SnO₂ system.
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Fig 9.5
XRD pattern for CdS/SnO$_2$ coated glass as a function of angle-2-theta

The lack of a significant CdS peak is in stark contrast with the work of Das and Morris [13] and McGregor et al [16]. Here these authors found that the CdS layer formed, in both cases through electrodeposition, was clearly present in the hexagonal structure, a=4.136Å and c=6.713Å [23], with crystal directions of (100), (002), (101), (110), (103) [13 only] and (112) [16 only] observed. This may be a difference that results from the electrodeposition of CdS as opposed to the chemical bath deposition that may, through its nature, produce a largely amorphous layer. Electrodeposition relies on the material forming in a specific crystal direction. The peak intensity data for the CdS/SnO$_2$/glass structure with the assigned peaks is shown in Fig 9.6.

The XRD pattern attained with the triple layer structure of CdTe/CdS/SnO$_2$ is shown in Fig 9.7 with the log of counts against the angle-20. As before, no peaks were observed for 20 greater than 80°. Clearly the diffraction pattern is dominated by the contribution of the (111) plane for CdTe with some noticeable inclusions of Te that indicate some deviation from stoichiometry. Several of the peaks, p4-6 and p11-12 and p13 could be easily ascribed to SnO$_2$ and SiO$_2$. In these cases no significant gains in peak height were observed compared to previous results allowing their clear labelling.
Table 9.1

<table>
<thead>
<tr>
<th>Peak No</th>
<th>Angle</th>
<th>Counts</th>
<th>d (Å)</th>
<th>Rel I</th>
<th>Assigned</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.767</td>
<td>663</td>
<td>3.328</td>
<td>100</td>
<td>SnO$_2$ (100)/CdS (002)</td>
</tr>
<tr>
<td>2</td>
<td>29.715</td>
<td>238</td>
<td>3.004</td>
<td>36</td>
<td>SiO$_2$ (211)</td>
</tr>
<tr>
<td>3</td>
<td>31.899</td>
<td>190</td>
<td>2.803</td>
<td>29</td>
<td>Unknown</td>
</tr>
<tr>
<td>4</td>
<td>33.943</td>
<td>266</td>
<td>2.639</td>
<td>40</td>
<td>SnO$_2$ (101)</td>
</tr>
<tr>
<td>5</td>
<td>37.983</td>
<td>398</td>
<td>2.367</td>
<td>60</td>
<td>SnO$_2$ (200)</td>
</tr>
<tr>
<td>6</td>
<td>51.753</td>
<td>439</td>
<td>1.765</td>
<td>66</td>
<td>SnO$_2$ (211)/CdS (112)</td>
</tr>
<tr>
<td>7</td>
<td>54.756</td>
<td>100</td>
<td>1.675</td>
<td>15</td>
<td>SnO$_2$ (220)</td>
</tr>
<tr>
<td>8</td>
<td>61.805</td>
<td>124</td>
<td>1.5</td>
<td>19</td>
<td>SnO$_2$ (310)</td>
</tr>
<tr>
<td>9</td>
<td>65.765</td>
<td>193</td>
<td>1.419</td>
<td>29</td>
<td>SnO$_2$ (301)</td>
</tr>
</tbody>
</table>

The pattern confirms the presence of CdTe in the zinc blende configuration (a=6.28Å) [24] as opposed to the hexagonal (a=4.58Å and c=7.50Å) structure [11]. The position of the CdTe diffraction peaks at intensity 2θ=24°, 39.6°, 46.7°, 48.8° and 76° were identified as those corresponding to (111), (220), (311), (222) and the (333) or (511) orientations.

The positions and intensity of the diffraction peaks that can be ascribed to CdTe are in excellent agreement with the findings of previous authors. A review of the literature reveals that most authors have observed only the (111), (220) and (311) orientations in electrodeposited CdTe with XRD [12-21]. In all cases the (111) plane dominates by at least an order of magnitude over the other peak intensities. In addition a number of authors have observed further peaks. Panicker et al [17] and Llabres et al [15] reported the added existence of the (331) and (400) planes. McGregor et al [16], whose work aimed to identify all the observed peaks, reported only the additional (331) peak. The secondary reflections, n=2 in Eqn[6.1], that would result from the (111) plane at 2θ=56.2° are not seen. The agreement with the literature is rather convincing given the dominance of the (111) orientation and the other previously observed directions.
Rastogi and Balakrishnan [25] found the presence of the hexagonal (wurtzite) structure for CdTe in their films. The small peak seen at 21.6°, d=4.11Å, is close to the inter-plane spacing for the (100) orientation in hexagonal CdTe, d=3.98Å [25], and it has been ascribed as this. In addition, Llabres et al [15] have argued for the presence of the hexagonal form of CdTe giving rise to constructive interference at 51° (d=1.752) where the dimensions are a=4.58Å and c=7.50Å [11]. In our pattern it would be impossible to accurately record p11, d=1.767, as this given the presence of the SnO₂ (211) intensity peak from early results at this angle. However, the size of this peak does not appear to have increased noticeably from that in Fig 9.4 so that this can be considered negligible.

Fig 9.8 records the relevant peak information for the CdTe/CdS/SnO₂/glass system with the assigned peaks.
The presence of excess tellurium in the thin film is clearly seen due to peaks at intensity $2\theta=23.0^\circ$ and $38.0^\circ$, p2 and p7, that are due to coherent reflections from the Te (100) and (102) planes. The Te present was in the hexagonal configuration with $a=4.457\,\text{Å}$ and $c=5.929\,\text{Å}$ [23]. Excess Te has been indicated previously [11,12,14,15,18-21] and ascribed to the effect of an inappropriate deposition potential, i.e. too high. This favours Te deposition upon itself as opposed to the deposition of stoichiometric CdTe. Under these conditions the Te metal is formed in the film due to reaction 8.32 but reaction 8.33 is not sufficiently fast to consume all Te and, therefore, free Te was left in the film. At lower deposition potentials Eqn[8.33] is faster and less free Te metal remains. It has been shown that decreasing the deposition potential can remove this peak from the XRD pattern [15].

Most of those authors that reported the presence of metallic Te all confirmed the existence of the (101) direction ($2\theta=27.8^\circ$) [13,15,18-21] while some also observed additional peaks. Bhattacharya et al [11], Bonilla and Dalchielle [12], Llabres and Delmas [15], and Valvoda et al [21] also identified the (102) direction. The latter two works were particularly interesting as they identified a large number of peaks due to Te. Both observed the (101), (102), (110) and (201) orientations with Llabres additionally quoting (203) and (113) while Valvoda recorded the (100), (111), (003) and (002)
directions. We observed the (100) and (102) orientations, which fits well with the observations of these other authors.

The peaks, P8 and p10, were thought originally to belong to the Te (110), (200) and (201) directions respectively. However, the fit with CdTe (220), (311) and (222) planes is closer and the dominance of the CdTe (111) peak over the Te (100) peaks reinforces this argument.

9.3.2 SEM Measurements

The film morphology of electrodeposited CdTe films has been reported previously [10-12,15,17,22,26-30]. A second piece of CdTe/CdS/SnO₂/glass was cleaved from the same cell used for the XRD measurements into an area of approximately 1cm². The sample was attached to a sticky pad prior to insertion into a variable pressure Hitachi S3200N machine. The use of silver dag to form an electrical connection from the pad to CdTe layer was found to be unnecessary due to the high conductance of the SnO₂ layer. This prevented electrical charge up from the electron beam. The SEM image that was attained of the CdTe surface is shown in Fig 9.9 at a magnification of 5000x. The width of this image is equivalent to 22μm.

The image indicates a largely uniform surface consisting of mostly small nodular growth with several very large surface features. Each of these surface features consists of a number of clusters. The largest of these surface features is approximately 4μm across with each constituent cluster ranging from 0.2 to 1μm in diameter. The small nodular pattern was observed to cover nearly =100% of the film surface.

The SEM image shown in Fig 9.10 is a section from the centre of Fig 9.9 examining more closely the uniform area that constitutes most of the film. The magnification in this case was 20000x and the width of this image corresponds to =6μm. The region can be seen to consist of the nodular surface with the diameter of each nodule varying from 0.1μm to 0.7μm in the largest case.
Chapter 9: Studies of Electrodeposited CdTe Solar Cell Material

Fig 9.9
SEM micrograph of the CdTe surface

Fig 9.10
SEM image of the uniform film area
A literature review has revealed that the surface features observed here are seen elsewhere. Dennison [26] presented SEM micrographs that exhibited nodular, cauliflower-like, growths at the surface. In that case it is believed that this represents a film made up of columnar growths of CdTe, which terminate at the surface in the form of nodules. It was also reported that larger nodules appeared to break into smaller ones. Other authors have also found the electrodeposition of stoichiometric CdTe leads to nodular growth [11,12,17,22&29]. From the XRD pattern each of these columnar growths must be strongly orientated in the (111) direction.

The grain size for the nodules that we observed for the most part of 0.1μm to 0.7μm is in good agreement with the literature. Previously grain sizes have been reported as 0.6μm to 1μm [12], up to 4μm [15] and 0.4μm [22].

In addition Sugimoto and Peter [28] showed that optical illumination of the growing CdTe surface leads to a Te rich film. Illumination of a certain area of the film gave rise to Te rich deposits that formed in a dendritic, flower like, nature with a clear loss in the surface smoothness. Upon visual inspection with the naked eye the illuminated region corresponded to a dull spot on the highly reflective CdTe surface. Jackson et al [27] showed that carrying out the electrodeposition in the dark virtually eliminated the formation of excess Te. Residual excesses of Te may also be due to the deposition potential being too high as discussed in section 9.3.1.

The nodular growth observed applies to most of the films. Each nodule represents the top of a columnar growth, which is agreed on elsewhere [26]. The columnar structure is then only a general pattern, but columns may be terminated as others limit their growth or they themselves sub-divide. Columnar growth as a general rule is clearly favoured in this instance as the charge carriers generated following the interaction of an optical photon will traverse the solar cell along these crystals, with minimal grain boundaries.
As a final remark, efforts were made to reliably measure the stoichiometry of the CdTe film. The recorded EDX spectra that was obtained from the film is shown in Fig 9.11. The film indicated the almost exclusive presence of Cd and Te, with a minor contribution of carbon, possibly due to contamination from dust/grease or within the SEM machine. Measurements taken found that Cd and Te constituted the film entirety with the concentrations being within an order of magnitude of each other. However the surface roughness on the micron scale meant that the EDX measurements had very large errors of perhaps 50%. This questions those authors that have produced SEM image identical to ours before obtaining a near ideal Cd to Te stoichiometry [26,27].

Comparisons were made between the measurements taken on a large surface cluster and on the nodular background. Outside of the experimental error no variations could be seen between the two.
9.3.3 Optical Properties

Measurement of the optical properties of the CdTe/CdS heterogeneous junction solar cell is obviously important considering the intended application. In this section, the optical transmission for each of the component layers is evaluated allowing a more detailed understanding of this solar cell structure. If the transmission is measured for all the films it then becomes possible to determine the value of $E_g$ for electrodeposited CdTe.

The transmission coefficient for each system was measured using a computer controlled Camspec m350 double beam UV-IR Spectrophotometer in the wavelength range of 190nm to 1100nm. The spectrometer was calibrated to take into account differences in the photon flux between the reference and transmission beams.

It is desirable to accurately measure the optical characteristics for the glass and the SnO$_2$ layer separately. Techniques used to remove the SnO$_2$ layer included washing in fuming nitric acid or sulphuric acid with dissolved NaHSO$_4$ or in a neat solution of peroxide. Unfortunately, the SnO$_2$ layer did not separate from the glass. It is concluded that the contribution of the glass could be easily taken into account given the following assumptions. First, other than absorption in the UV part of the spectrum no absorption of optical photons will occur [31]. Second, the refractive index of glass is well known to be 1.45 [32] with negligible dispersion in the optical photon range.

Pieces of glass with areas of approximately 25cm$^2$ were cut from each of the SnO$_2$/glass, CdS/SnO$_2$/glass and CdTe/CdS/SnO$_2$/glass structures. The samples were orientated in the spectrophotometer as they would be for a solar cell with the light incident on the glass. In the case of the first two, these samples have been annealed and therefore their spectra are more relevant to the final structure. The transmission spectrum for each structure is shown in Fig 9.11. Slight sharp changes in the transmission data are due to the spectrophotometer altering the grating at certain wavelengths and are not related to material properties.
The full range from 190nm is not shown as all films indicated the 100% attenuation for photon wavelengths below 300nm. This was attributed to UV absorption in the glass and the SnO$_2$ layer. The bandgap of SnO$_2$ is 3.5eV [33], ($\lambda$=354nm), which will considerably attenuate the photon flux in this region through intrinsic, band to band transitions. The addition of the annealed CdS layer to the SnO$_2$ shows a similar wavelength for the onset of transmission with the values considerably reduced over the entire wavelength range. The final layer of CdTe shows no transmission for wavelengths lower than 750nm with a sharp increase from 800nm to 900nm before remaining stable just below 50% at higher wavelengths.

In the case of the binary structure, following the onset of transmission at 320nm a sharp rise is seen that peaks at 590nm (77%) before falling to 62% at 1100nm. It is not possible to derive the bandgap of the SnO$_2$ layer because of the contribution of the glass substrate to the absorption over the same wavelength range, although it does appear to be around 320nm to 400nm (3.88eV to 3.1eV). This agrees with the quoted value of 354nm (3.5eV) [33]. The decrease in optical transmission at higher wavelengths is not thought to be due to dispersion because of the negligible change in the refractive index over such a
small wavelength range being insufficient to account for this loss [32]. Absorption within the SnO₂ layer is the most likely cause [31].

The work of Ahmad-Bitar and Arafah [34] found that the SnO₂/glass structure gave rise to a sharp absorption edge at 400nm with oscillations in the recorded transmission up to 900nm. These oscillations, which were not observed in this instance, are well known to arise from the constructive-destructive interference of reflected photons. In this instance no such changes are seen and the contribution of interference to the transmission spectra can be considered negligible.

Returning to Fig 9.11, the CdS transmission curve has a similar onset to that already seen for the SnO₂/glass with a steady increase, some way below that observed for the binary system, up to 500nm. A more rapid rate of change is seen up to 600nm where a plateau is established up to 750nm at ~64%. Increasing wavelengths show reduced transmission, but the difference in the transmission between this structure and the previous one decreases. This convergence indicates that the loss is due primarily to the SnO₂ layer and not the CdS at these higher wavelengths.

This curve is consistent with the addition of a direct bandgap semiconductor with \( E_g = 2.4\text{eV} (=520\text{nm}) \) [24]. The film is sufficiently thin so that it is not able to absorb all super bandgap radiation through intrinsic band to band transitions. At the photon wavelength corresponding to the bandgap, \( \lambda = 520\text{nm} \), an increase in the transmission is observed as intrinsic absorption is reduced. The fresnel reflections at each of the interfaces in this triple layer structure air(n=1), SnO₂(n=1.5), CdS(n=2) mean that the maximum possible transmission is 76%. The maximum in the CdS spectrum is 65% at 700nm as a result of absorption in the SnO₂ and CdS layers.

Several authors have reported the optical properties of CdS as part of the CdS/CdTe solar cell. Ahmad-Bitar and Arafah [34] recorded oscillations in the transmission for wavelengths greater than 600nm. The bandgap of 2.4eV that was quoted did not include the effect of reflection losses. McGregor et al [16] who deposited their CdS using electrodeposition observed a sharper increase in the transmission curve between 480nm and 520nm. Conveniently, the bandgap of their CdS was quoted as 2.42eV (\( \lambda = 512\text{nm} \)) which is the textbook value [24]. Further, they did not take into account the reflection losses.
Before considering the optical transmission that was observed through the four layer structure, an interesting observation was made concerning the change in the CdS layer following the annealing process. This annealing, alters the colour of the film from an as grown bright yellow to a post annealing orange, Fig 9.12.

A sample was taken from the unannealed CdS for comparison. The optical transmission of both this and the annealed sample are shown in Fig 9.13. The transmission spectra correlates well with the observed optical properties. In the first instance a reduction in the optical transmission is seen over the entire wavelength range. However, the suppression is markedly less in the red region of the spectrum, \( \lambda = 650\text{nm} \), as opposed to the yellow region, \( \lambda = 570\text{nm} \), confirming what is seen visually.

What gives rise to this change in the colouration? The annealing process enhances the crystal structure of the film, leading to increased optical transmission due to improvements in the crystallinity. This lowers the chance of extrinsic absorption and sharpening of the band edge. As the opposite effect is observed with reduced transmission the cause must lie with the surface and not the internal structure.

The annealing is done in atmosphere and most likely leads to the formation of an oxide coating. Cadmium Oxide, \( \text{CdO} \), is the principal candidate. This is an oxide semiconductor with a bandgap of 2.3eV [33], \( \lambda = 540\text{nm} \) which lies in the region between 500nm to 600nm that sees the largest reduction in the optical transmission. The
oxide layer will be not more than a few atomic layers, \(a_{\text{CdO}}=4.69\,\text{Å} \) [33], thick, so that complete absorption of super-bandgap light does not occur. The CdS/CdTe junction is more correctly written as CdS/CdO/CdTe. McGregor et al [16] reported the sharpening of the absorption edge, but did not show the data to provide a direct comparison.

![Transmission of CdS/SnO\(_2\)/Glass structure before and after heat treatment at room temperature](image)

**Fig 9.13**

Transmission of CdS/SnO\(_2\)/Glass structure before and after heat treatment at room temperature

Let us return to the optical transmission that is seen for the four layer structure in Fig 9.11.

A dramatic change is seen in the transmission curve with the addition of the fourth CdTe layer. Total absorption is seen for wavelengths below 750nm with a constant gradient seen in the transmission up to 900nm. A region of little change is then seen for wavelengths up to 1100nm. A small dip in the transmission is seen at long wavelengths, this could be a result of constructive-destructive interference or absorption. Measurements at even longer wavelengths would be required to determine which of these is the true cause. The lack of interference oscillations in the sub-bandgap region from multiple reflections indicates the large thickness of these films, \(>2\,\mu\text{m}\).

The onset is clearly related to the bandgap of CdTe and it’s direct mode of transition. One route by which the semiconductor bandgap can be found from optical measurements is to graph the square of the attenuation coefficient against the photon
energy [35]. To establish the attenuation co-efficient for CdTe, the reflection and absorption losses that occur within the other layers must be found.

To evaluate the loss in the reflection that occurs at each interface the following procedure has been adopted. The air/glass/SnO$_2$/CdS/CdTe/air system possesses five changes in the refractive index for a transmitted optical photon. The refractive index, $n$, of each of these layers is 1, 1.45, 2.0 [33], 2.4 [36], $\approx$3.0 [37] and 1 again respectively. The CdTe refractive index is taken as 3 in this example, but a more accurate wavelength dependent value is used for the final procedure. Each boundary will result in the reflection of some of the incident light, Eqn[2.27]. In this scenario, the attenuation coefficient of each layer and the negligible components of secondary reflections are ignored.

The fresnel reflection that occurs is illustrated in Fig 9.14 for an incident intensity $I_0$. The percentage reflected is expressed as a percentage of that on the surface of each layer. The reflection magnitude from each layer is a percentage of the light incident on each interface and not $I_0$.

![Diagram](image)

Fig 9.14
Reflection at multiple interfaces and resultant theoretical transmission for Glass/SnO$_2$/CdS/CdTe.

From Eqn[2.21] the refractive index is required as a function of these wavelengths. Next, the refractive index for CdTe must be evaluated in the range of 750-850nm as this is the region of interest at the fundamental absorption edge. Fortunately the refractive index for cathodically electrodeposited thin film CdTe has been previously
evaluated in the region of 450 to 900nm [37]. The region of interest in this case can be modelled by the equation, where $\lambda$ is expressed in nanometers.

$$n = 3 \times 10^{-3} \lambda - 0.15$$  \[9.2\]

Next the transmission coefficient from the SnO$_2$/CdS/CdTe structure must be divided by the SnO$_2$/CdS component eliminating the losses that occur in the other layers. The difference in the reflection that occurs at the CdS/air interface (18%) and the CdTe/air interface (25%) was also taken into account.

In Fig 9.15 the attenuation coefficient squared versus the photon wavelength, from Eqn[2.21], is shown at the onset of optical transmission with the theoretical fit based on the chi squared parameter. From the statistical fit a bandgap of 1.46eV was derived. The correlation coefficient in this case was 0.99.

![Plot of the attenuation coefficient squared v's photon energy E (eV)](image)

A number of authors have reported the optical properties of electrodeposited CdTe on CdS, solar cells [16,30,34,37-43]. These authors, like us, made use of spectrophotometers to record the optical transmission versus photon wavelength. A number of these reported oscillations in the transmitted curve above 900nm (34,30,43). Two of these authors [34] and [30] both attained bandgaps of 1.52eV without taking into account the reflection losses or dispersion that occur. Even worse, McGregor et al [16]
directly used the transmission \( v ' s \lambda \) curve and quoted the bandgap as that corresponding to the peak transmission. Their bandgap of 1.40eV is not considered reliable. Dutta et al [38], Ou and Stafsudd [37], and Rakshani [43], who all accounted for the reflection losses derived bandgaps of 1.49eV, 1.46eV and 1.46eV respectively. Two of these [37], who also took into account the dispersion, and [43] are in agreement with our value. Kampmann [40], recorded a value of 1.49eV to 1.5eV with the band edge becoming sharper as the deposition potential was lowered towards the Cd/Cd\(^{2+}\) boundary. This is then clearly related to the simultaneous improvement in crystallinity that is observed [40,41]. Morris [42] found a value of 1.48±0.03eV also reported that the transmission above the band edge \((h\nu<1.48\text{eV})\) was only about 40% which was attributed to the presence of light scattering both within the film and at the CdTe/air interface.

### 9.4 Conclusion

In this chapter the physical properties of the thin film solar cell system of CdTe/CdS/SnO\(_2\)/SiO\(_2\) have been investigated. Measurements of the structural properties have been taken using XRD for the bulk structure, SEM for surface topography, EDX for the stoichiometry and homogeneity, and the optical properties of each component layer evaluated using optical transmission measurements.

The systematic approach employed in the XRD measurements allowed accurate labelling of many peaks in the more complicated systems. In the SnO\(_2\)/glass system the pattern consisted of seven peaks superimposed on a hump due to the amorphous nature of the glass substrate. Six peaks were attributed to the \((100), (101), (200), (211), (220), (310)\) and \((301)\) orientations for the tetragonal SnO\(_2\) structure. A seventh peak was attributed to the \((211)\) orientation in SiO\(_2\).

In the tertiary, CdS/SnO\(_2\)/glass, system all major peaks due to the SnO\(_2\) film were visible with only one further peak observed. This could not be attributed to an orientation in CdS, SnO\(_2\) or glass that could give rise to constructive interference. The lack of a sizeable CdS pattern is related to the comparative thinness of this layer, \(<1000\text{Å}\).

In the quarternary system, CdTe/CdS/SnO\(_2\)/glass, 14 peaks were recorded superimposed on the amorphous hump.
Six of these were assigned to CdTe, which was observed predominantly in the cubic zinc blende structure. The cubic CdTe orientations were the (111), (220), (311), (222) and the (333) or (511) with the (111) plane two orders of magnitude greater than the remainder. This relates very well to the theoretical growth mechanism that has been proposed and with the work of other authors who have observed the same dominance for the (111) plane over others. The CdTe layer was also believed to contain a very small contribution from the hexagonal wurtzite configuration.

Also observed in the patterns were two peaks corresponding to metallic Te in the (100) and (102) orientations. This has also been reported elsewhere [11,12,14,15,18-21]. This observation in the XRD clearly indicates a gross deviation in the stoichiometry for this material, which incidentally performs well as a solar converter.

Others authors have related this to a deposition potential that favours Te deposition although others believe that super bandgap optical photons may also affect the stoichiometry [28]. In this case it is felt that the deposition potential plays a more dominant role in determining the film stoichiometry. The increasing thickness of the film with time during deposition and the associated increase in resistance may reduce the overpotential applied to the solid/electrolyte surface.

The SEM image of the CdTe layer indicated a largely uniform topography consisting of clusters ranging in size from 0.2μm to 1.0μm. Additionally surface features up to 4μm across were seen. The subsequent EDX measurement of the stoichiometry at the surface was compromised due to the poor smoothness in the film. This contradicts many authors who have shown identical clusters at the surface before revealing the film stoichiometry derived from EDX was 50:50 [26,27]. It is my belief having performed these experiments that the EDX attained values can not be considered reliable.

The optical transmission measurements on the three component systems provided useful insights into this solar cell device. In the first case, SnO2/glass, a large proportion of the photons with a wavelength of <500nm were absorbed within the glass or SiO2 layer. The bandgap of the CdS layer could not be determined although this has been done with electrodeposited CdS [16]. Annealing of the CdS layer was found visually to alter the optical characteristics of the film, which was confirmed by the transmission measurements. This is believed to be due to the formation of a layer of CdO on the film
surface. These measurements allowed the bandgap for the CdTe layer to be confirmed as 1.46eV, which is excellent agreement with those quoted in the literature for electrodeposited CdTe [37,38,43].

These measurements have indicated that the CdTe film with a bandgap of 1.46eV has multiple crystal orientations, a film morphology comprised of columnar growths and a non-determined film composition that possesses metallic Te. Despite this, the CdTe/CdS solar cell attains solar efficiencies of ≈10%. The ability to grow this material over such large areas means that it is the primary choice for a future large area photoconductor.
Chapter 10: Conclusion

In this thesis investigations have been carried out into CZT X- and γ-radiation detectors and CdTe/CdS heterogeneous thin film solar cells. The work has furthered the research towards the goal of introducing a flat panel digital detector to replace conventional phosphor based systems in diagnostic imaging.

The spectroscopic capabilities for a CZT detector were characterised. The lack of basic experiments on these detectors has lead to a gap in the fundamental understanding. Further developments were best facilitated by undertaking measurements that are not ambiguous to interpret. The electrical, optical, electro-optical, structural, compositional and homogeneity properties were studied. Together with the spectroscopic capabilities, this indicates a more complicated system than Si or Ge detectors.

The HPB grown CZT material was found to consist of several grain orientations with Te precipitates present in the bulk. Electrically the material was found to be well compensated with a resistivity of $=10^{11} \Omega \text{cm}$ despite the presence of defect levels. The IV profile was asymmetric consisting of the bulk conductivity and thermionic emission over the contact barriers. The principal defect level in the bulk material is believed to be the acceptor Cd vacancy which sits at 0.46eV above the valence band [1]. At the contact region the diffusion of gold at the electrode increases the barrier height by 0.2eV and decreases the thermionic current by a factor of 3000. These results were related to the spectroscopic performance of the detector allowing a more detailed understanding for this material to be made.

The defect levels were found to control the bulk carrier transport properties. This was particularly important when the material was cooled to below 280K where the radiation induced signal disappeared as a result of polarisation at the electrodes.

In CZT a material exists that despite the material deficiencies is still able to operate as a room temperature radiation detector with sufficient resolution for spectroscopic applications. Consequently as a flat panel imaging photoconductor remains
the primary choice over other candidate materials given the lack of a large area, low cost, quick epitaxial growth technique. This is not to say that research in other materials is not useful, but that at present this is the case and further research may establish a better candidate.

The focus was then shifted towards the cathodic electrodeposition of CdTe under potentiostatic conditions. The choice of this technique was justified over other available options. The use of this technique in the photovoltaic industry gives a tremendous advantage for this work. The theoretical electrochemical process for depositing CdTe in the ratio of 1:1 and the experimental apparatus were described in detail. The growth process was characterised in terms of the change in deposition current with time and electrolyte agitation. The decrease with time is considered to be due to hydrogen evolution during the process and the increase in current with stirring rate was attributed to the increase in the availability of HTeO$_2^+$ at the electrode surface. This then tended towards a limiting value because of the finite concentration of HTeO$_2^+$ in the electrolyte.

The results of preliminary film stoichiometry using EDX and PIXE revealed a Cd:Te ratio of approximately 1:2 that decreased as the deposition potential was lowered towards the region of elemental Cd deposition. The film surface contained pinholes due to the poor adhesion of the Ti layer. As a result, further experiments were undertaken on commercially manufactured CdTe thin film using cathodic electrodeposition.

The structural properties using XRD, topography (SEM) and optical properties using a spectrophotometer of these films were evaluated. The XRD pattern confirmed the theoretical observation that Cd underpotential deposition lead to growth in the (111) direction. Contributions due to the (220), (311), (222) and (333) or (511) of zinc blende CdTe were also seen. A minor peak associated with the hexagonal wurtzite structure of CdTe was also seen. In addition the CdTe film was found to contain a substantial amount of metallic Te. This was credited to an inappropriate deposition potential of the action of super bandgap light on the growth surface.

The SEM image of the surface indicated that the growth was done along columns perpendicular to the growth surface. The film surface was not smooth on this scale, consisting of small nodular growths that correspond to the top of the columns. The with
of these was found to range from 0.2μm to 1.0μm. An attempt to measure the composition with EDX was found to be unsuccessful given the surface structure.

In a flat panel digital X-ray imager, generated charge carriers would travel along these columns with minimal probability of recombination occurring at grain boundaries. This is of considerable benefit considering the problems in temporal image blurring that may arise in fluoroscopy through the late attainment of trapped charge that then de-traps at a later time.

The optical transmission measurements indicated that the CdS/CdTe interface that constitutes the pn junction in this heterogeneous solar cell is more accurately written as CdS/CdO/CdTe. The CdO layer arises due to the thermal treatment given to the chemically bath deposited CdS layer. The addition of the CdTe layer showed no transmission below 750nm. Above this the transmission levelled out from 900nm to 1100nm at ≈40%. Having taken into account fresnel reflection from the other layers and the use of values for the refractive index for electrodeposited CdTe a bandgap of 1.46eV was evaluated.

The work in this thesis has used CdTe films of ≈2μm thickness. The X-ray stopping efficiencies in a flat panel system require a detector with a thickness of ≈500μm. Such a device would be of considerable benefit and would constitute a major technological advance.

How then does this leave CdTe and its ternary alloy CZT in the development of the next generation of X-ray imaging devices. Well, CZT has been found to be suitable as a radiation detection medium despite the physical deficiencies and electrodeposition offers the route for growing a large area film with minimal cost. A marriage of technology between X-ray detectors and their growth using electrodeposition is required to facilitate further work.
Appendix A
The custom made potentiostat circuit diagram
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Chapter 10: