Abstract

Semiconductor materials have a vast range of applications varying from basic electronic products to astronomy and their semiconducting properties can be altered through the growth of binary or ternary compound materials. CdZnTe and CdTe are prominent materials in radiation detector and photovoltaic solar cell applications. For radiation detectors, in the fabrication process, surface preparation (chemical polishing and passivation) and contact deposition are key to the detector performance. This thesis investigates the effect of these two processing steps on CdZnTe detectors through varying the passivation procedures and gold contact configurations. The surface composition, layer thickness and non-uniformity resulting from the passivation treatments have been investigated using X-ray Photoelectron Spectroscopy (XPS), Scanning Transmission Electron Microscopy (STEM), Energy Dispersive X-ray spectroscopy (EDX) and other materials characterisation techniques. The device electrical and spectroscopic responses were measured using the I-V characteristics and alpha spectroscopy respectively. Passivation using 30 % H₂O₂ and 5% NaClO treatments develops a very thin oxide layer of up to ~2 nm, while NH₄F/H₂O₂ and KOH+NH₄F/H₂O₂ treatments yield oxide layers of varying thickness (30 – 142 nm) and metal oxides comprising of Te₂/Te₃, CdO and ZnO. Devices were fabricated in metal-semiconductor (MS) and metal-insulator-semiconductor (MIS) configurations. The MIS configuration improves the mobility-lifetime product, partial charge collection and leakage current of a CdZnTe device. The MIS device barrier heights were calculated to be 0.83 ± 0.02 eV and 0.86 ± 0.02 eV for very thin and thick oxide layers respectively. For ultra-thin (0.5 μm CdTe layer in) CdTe/CdZnS solar cells, XPS and X-ray diffraction (XRD) were employed to study the effect of varying the CdCl₂ processing step. Increasing the degree of CdCl₂ activation and annealing treatment was found to increase sulphur diffusion into the CdTe layer (up to a concentration of ~ 2 at.%). Cell performance measurements showed that the increase in S concentration is directly related to the open-circuit voltage (V_{oc}), and increasing the degree of CdCl₂ treatment gives higher V_{oc} values.
Acknowledgement

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I would like to dedicate this thesis to all of my family members, especially to my parents Mr & Mrs Baber Shah, my (late) father-in-law Hafiz Sajjad Hussain, my husband Tariq Sajjad, my lovely son Arsalan and cute daughter Anayah, who kept me motivated throughout this period.

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1 Introduction

1.1 General introduction

Semiconductor materials and devices are being used extensively in a diverse range of applications from basic science and astronomy to commercial products and have become the foundation of many modern technologies. The growth of compound semiconductors, either binary or ternary, has made it possible to tailor the material properties according to a specified function of a device [1, 2]. The vast range of fields that use compound semiconductor devices include radiation technology, photovoltaic solar cells, electronics etc [3-5].

In radiation detector technology over the last few decades, there has been a continuously growing demand of high performance X-ray and gamma ray detector in many fields such as medical imaging, national security and environmental protection etc. [6]. A tremendous amount of research and development work is involved in fabricating radiation detectors especially semiconductor detectors of high yield that are portable, unbreakable, and workable in ambient environments.

The other important application of compound semiconductors devices is in the solar cell industry, as the demand of the renewable energy sources are increasing with the passage of time. Solar energy is one of the nature's free gifts as an alternative energy source. To convert this energy into electricity, many different materials are used in the manufacture of photovoltaic (PV) solar cells [7]. Installation of PV solar power stations has increased over the last few years; one of the example is shown in Figure 1-1. Intensive global research efforts are being made to achieve the high energy conversion efficiencies at a low raw material cost.
1.2 Background and context

In the fields of spectroscopy and imaging, after the discovery of different radiative processes, these processes have been used for various purposes in many fields. To maximise the impact of these new spectroscopic and imaging techniques, research has been undertaken to find materials that can detect high energy radiation with good resolution. As this technology has moved from the laboratory environment to commercial usage, the demand for more efficient, portable and room temperature operated detectors is rapidly increasing. As a result, detector technology moved from gas filled detectors to scintillators and then to semiconductor detectors for better energy resolution and high yield.

Single element semiconductors Ge and Si detectors require cryogenic cooling [9], making these unsuitable for commercial use. The binary semiconductor compounds such as gallium arsenide (GaAs), mercuric iodide (HgI$_2$) and cadmium telluride (CdTe) have been used as radiation detectors for a long time. CdTe is a group II-VI semiconductor compound formed of cadmium and tellurium. CdTe detectors exhibit high detection efficiency: photoelectric absorption is the main interaction process for up to 200 keV e.g. 1 cm thick detector can provide photoelectric efficiency higher than 90% at 140 keV [5]. However, it has some disadvantages that have hampered its usability, which include a high leakage current (low resistivity of $10^9$ $\Omega$-cm), its small size at a production level and polarization effects [10, 11]. Other work had observed that addition of transition metals to the II-VI semiconductor group can increase their semi-insulating properties. Research had shown that the addition of Zn to CdTe, giving the ternary compound cadmium zinc telluride (CdZnTe or CZT), reduces the free carrier concentration [12]. The addition of Zn also increases the material resistivity up
to \((10^{10} - 10^{13} \Omega \cdot \text{cm})\) and improves the structure quality of the crystal [13, 14], which made it possible to grow large size detectors with reduced noise levels. Figure 1-2 shows sectioned CZT crystal of different sizes. Using CZT, X-ray and gamma rays detectors are able to operate at room temperature with low leakage current, due to the wide band gap (1.5 eV - 2.2 eV) and the higher Z density which enhances the energy resolution of the detector [15].

![Sectioned CZT crystal of different sizes](image)

**Figure 1-2 Sectioned CZT crystal of different sizes [16].**

Although in radiation technology, the focus is shifted to CdZnTe, but CdTe is still a prominent material in thin film photovoltaic (PV) solar cells due to its high quantum efficiency and low production cost [17]. The direct band gap (1.5 eV) of CdTe has an excellent match to the solar spectrum for solar cell energy conversion. Additionally, high quantum efficiencies (the amount of charge carriers generated when a specific wavelength irradiates the cell) can be achieved from the ultraviolet region (\(\lambda \sim 10 \text{ nm}\)) to the band gap (\(\lambda \sim 825 \text{ nm}\)) due to a high absorption coefficient greater than 5 x 10^5/cm. CdTe absorbs energy (greater than its band gap) at shorter wavelengths than is possible with a silicon panel, making it suitable as an absorber layer material for thin film photovoltaic solar cells [18]. Cd is available in excess as it is isolated during the processing of other important industrial metals such as zinc; as a result its price has not risen as much in comparison to silicon in recent years [19]. It is reported that CdTe solar modules are most successful in thin film PV industry [20] and the efficiencies of these solar cells has improved in recent years. First solar, inc. has a world record in producing CdTe thin film solar cell of efficiency 20.5% in the laboratory and PV modules of efficiency 18.6% [21]. In a thin film PV solar cell, to form a p-n heterojunction: conventionally CdTe (absorber) layer is doped with an acceptor dopant to acts as p-type and n-type CdS is usually used as the window layer. The thickness of CdTe is kept in general between 2-10 µm, larger than the
absorption limit (1 µm), to avoid discontinuities and pinholes reaching down to the underlying window layer causing an electrical short from the back contact. Nevertheless, due to carrier recombination throughout the absorber layer and the uncertainty in the availability of Te resources, the trend is changing to ultra-thin (≤ 1 µm) CdTe absorber layers. A recent advancement is to develop ultra-thin heterojunction CdTe/CdZnS film PV cells that are cost effective due to the use of less material. [22, 23]. However, the reduction of absorber layer beyond the absorption limit degrades the cell performance caused by increase in recombination effects and in shunts [24]. To improve the efficiency, solar cells are processed by annealing and passivation treatment [25]. There is still need of more work to achieve high performance.

1.3 Scope and Objectives

Even though the development of CZT has much improved the radiation detector performance, it still experiences some limitations due to defects produced: (i) during its growth, cutting and slicing from the ingot; (ii) during surface polishing and (iii) through contacting with its electrodes. Research has revealed that the defects found in the detector material have an impact on the detector’s response [26-28]. Defects related to the surface of the material and the surface preparation for electrical contacts needed for device fabrication also affect the performance of the detector [29, 30].

The main aims and objectives of the research work presented in this thesis are:

- To establish the nature of macroscopic defects found within the CZT bulk and present at the surface
- To find a surface treatment that results in a low dark current for the CZT device. This work will investigate the effect of an initial bromine-in-methanol etching treatment and examine the oxide formed through the use of different passivation treatments using a range of materials characterisation techniques.
- To fabricate CZT based detectors in different configurations prepared using the most promising passivating processes and compare their electrical and spectroscopic performance.

During the PhD work, a collaboration was developed with the Centre for Solar Energy Research (CSER), Glyndwr University, Wales. This collaboration resulted in a substantial amount of materials characterisation work being undertaken on Metal Organic Chemical Vapour Deposition (MOCVD) grown ultra-thin CdZnS/CdTe based solar cells, hence similar in many respects to the main topic of the thesis, CdZnTe detectors. Consequently, it was decided to include the results of this work as a stand-alone chapter in the thesis. The aim of the solar cell work was:

- To examine the effect of varying the CdCl₂ post-treatment process parameters and to determine correlations between changes in the chemical composition/microstructure of the solar cell and its electrical/optical performance as a result of the treatment.
1.4 Overview of the thesis

After this brief introductory chapter, the remainder of the thesis is structured as follows.

- Chapter 2 is an overview of the CdZnTe radiation detector. It begins with a brief introduction of how the different radiation types interact with the material. It continues with CZT growth techniques, its crystal structure and material properties. The CZT detector operation and the parameters that affect performance are discussed. In the last section, a brief discussion of thin film CdZnS/CdTe solar cells is presented.

- Chapter 3 discusses the surface and bulk analysis techniques employed in the characterisation of CdZnTe material and ultra-thin film CdZnS/CdTe solar cells. This includes XPS and additional capabilities of XPS instruments, such as angle resolved XPS and Ar⁺ ion depth profiling. Aspects of other techniques employed: SEM/EDX, XRD are presented.

- Chapter 4 presents results on the characterisation of ultra-thin glass/ITO/CdZnS (240 nm)/CdTe (500 nm) solar cells and is a stand-alone chapter. Initially, the MOCVD solar cell growth technique and the effects of varying parameters during growth and post growth are described. Then, XPS and XRD characterisation results and the electrical/optical performance of these solar cells are presented. In light of these results, correlations between changes in the multilayer composition and structure and the performance of the PV solar cells are discussed.

- Chapter 5 to Chapter 7 are all related to the CdZnTe radiation detector. In Chapter 5, initial work undertaken to identify CZT defects found at the surface were examined employing SEM/EDX is presented. Then the effects of surface chemical etching using a bromine-in-methanol treatment and the thin oxide layer developed through an H₂O₂ passivation treatment are characterised by XPS depth profiling and angle resolved XPS.

- In Chapter 6, the composition and thickness of surface oxides formed using different passivating agents are compared using XPS depth profiling. This chapter includes a consideration of the Auger Parameter and the use of Wagner plots to assist in the understanding of the complex oxide compositions formed from the different passivation processes.

- Chapter 7 presents results on CZT fabricated detectors of two different configurations prepared using different passivation processes. The chemical composition and thickness of the different oxide layers of the detector are determined and the electrical and spectroscopic performance of the different detectors compared.

- Chapter 8 presents the main conclusions of the research and considers useful further work which could be undertaken.
2 Literature review

2.1 Introduction

To achieve optimal performance of the Cd$_{1-x}$Zn$_x$Te detectors, knowledge of their material properties, fabrication processes and detector output are required, as from growth to the fabrication process; each step can produce different types of defects. Growth defects can be inclusions, precipitates, voids, grain boundaries, etc., mishandling can result in stress in the crystal, dicing and slicing can produce a rough surface and chemical treatment of the surface can change its stoichiometry. In this chapter, first a brief overview of radiation types, the interaction of this radiation with the detector and requirements of a radiation detector are presented. Then, the CZT growth technique, the CZT crystal structure and material properties that are important for nuclear detectors are considered. The defects which can occur at different stages of the fabrication process are then explained. This is followed by a discussion on the use of CZT devices as radiation detectors and the spectra acquired due to the interaction between nuclear radiation and CdZnTe. As one chapter of this thesis is dedicated to collaborative work on ultra-thin CdTe/CdZnS solar cells, the final section of the literature review considers the properties of thin film CdTe/CdZnS solar cells.

2.2 Nuclear radiation

2.2.1 Types of nuclear radiation

Ionising radiation is the release of energy either in form of waves (photon) or high speed sub-atomic particles. The energy of the photons is proportional to their frequency, while the energy of the particles is related to their mass and speed in the non relativistic case. The ionising radiation can be
classified as *charged particles, uncharged particles* and *photons*. Charged particles include *alpha particles, beta particles, proton* and *fission fragments*. *Alpha particle* is consists of two protons and two neutrons within the nucleus, which is equivalent to the helium nucleus, *Beta particles* are of two types: negative charged beta and positive charged beta particle. A negatively charged beta particle is emitted from the nucleus, when a neutron converts into a proton, and is identical to electron but to distinguish it from orbiting electrons, these are called beta particles. A positively charged beta particle is emitted when a proton converts into a neutron in a nucleus. This emitted particle is identical to an electron except that it has positive charge, and is also known as positron. Uncharged particles refer to gamma rays, X-rays and neutrons [31]. Most of the radiation types are *directly ionising*, as after collision with a matter it ionises a number of atoms. These radiation types can be produced in a number of ways. Alpha, beta particles and/or gamma rays are produced by radioactive decay of an excited nucleus. Electrons are generated by different means, for example, by ionisation of an orbital electron as a conversion electron due to relaxation of the unstable nucleus, or when outer orbital electron (Auger electron) is emitted by de-excitation of an atom. X-rays are produced when an electron of higher energy orbital falls to lower energy orbital during the relaxation of an excited atom. X-rays have energies between 1 keV – 100 keV. Gamma rays have higher energy than X-rays i.e. 100 keV – 10 MeV.

### 2.2.2 Interaction of radiation with a detector

The interaction of radiation with matter depends on the type of the radiation (charged or uncharged), its energy, mass and also the composition of the interacting material. Charged particles such as alpha and beta (electron, positron) particles and protons may interact with the electrons of surrounding material via coulomb scattering or through nuclear reactions.

Since alpha particles are comparatively large (He nucleus), with 2 units of positive charge they have a strong interaction with a detector. They have short penetration depths and are absorbed in the material through ionisation or excitation of orbital electrons. Negatively charged beta particles are electrons that can either annihilate with positron or can interact with materials in two ways, either through ionisation and excitation, or emission of *Bremsstrahlung radiation*. The inelastic scattering of beta particles due to the interaction of its electric field with the orbital electrons of the detector results in excitation and ionisation of the atom. Whereas, *Bremsstrahlung radiation* is emitted when a high speed charged particle particularly electron undergoes a sharp acceleration or deceleration caused by nuclear scattering. Photons produced by this process have a continuous range of electromagnetic energies in the X-ray and gamma ray region [32].

X- and gamma rays interact with the surrounding material in a number of different ways. For radiation detection, three of them are important: the *photoelectric effect, Compton scattering* and *pair production*. The main concept revolves around the ejection of an orbital electron by an incident photon through an ionisation process. The ejected electron then moves typically in a different
direction from the incident photon, producing more ion pairs, in secondary ion processes.

*The Photoelectric effect* is typically an ‘ideal process’ for a radiation detector as all of the energy of the incident photon is transferred to an electron shown in Figure 2-1.

![Diagram of Photoelectric effect](image)

*Figure 2-1 Photoelectric effect, (a) the ejection of K-shell electron and (b) jumping of L-shell electron to fill the hole, adapted from [33].*

The kinetic energy of this photoelectron is the difference in energy between the incident photon energy and binding energy of the electron. This photoelectron will then interact with other atoms, producing electron-hole pairs in a semiconductor. The number of electron-hole pairs created depends on the energy of the incident photon. In *Compton scattering;* after the collision between the incident photon and outermost orbital electron (shown in Figure 2-2), some of the energy of the incident photon is used to knock out the electron. The incident photon is not totally absorbed, as ejection of the outer shell electron requires small amount of energy (compared to the inner shell electrons). The photon of reduced energy is scattered from its original direction after this collision and may further involve photoelectric absorption or Compton scattering. The emitted electron will generate electron-hole pairs [31].
Figure 2-2 Compton scattering process, adapted from [34].

Pair production typically occurs when a photon having energy of more than 1.02 MeV interacts with an atom’s nucleus. An electron-positron pair is created in this process as shown in Figure 2-3. The excess energy is transferred to the electron or positron as kinetic energy. The positron then interacts with another electron resulting in annihilation, producing two 0.511 MeV photons that interact with the material in the processes described above [35].

Figure 2-3 Pair production process, adapted from [36].
The interaction probability of X- and gamma rays depends on the atomic number \( Z \) of the material. For Compton scattering, it is directly proportional to \( Z \), for pair production it is \( Z^2 \), and for photoelectric effect, it is related to \( Z^n \) (4 < \( n < 5 \)) [6]. This shows that heavier elements are more capable of detecting X- and gamma rays than lighter elements. In order to get high spectral resolution, good detection efficiency, high sensitivity and functionality at room temperature, the semiconductor material used as a radiation detector should have (be)

- High density and high atomic number - as the photon-atomic cross-section increases between \( Z^4 \) and \( Z^5 \).
- Wide band gap (>1.3eV) - this is necessary for high resistivity (>10⁹Ω cm) and low leakage current that in turn minimizes the noise level for room temperature operation
- Homogenous - a single crystal is required for low trapping of charge carriers
- A good mobility-carrier lifetime product giving a high carrier drift length and maximizing charge collection
- Non-polarized – so as not to be affected by electric fields [37].

CdZnTe, has proven to be a material that can give optimum results at room temperature compared to other semiconductor materials. Table 2-1 summarise some important materials properties. CdZnTe is able to operate at room temperature with low leakage current, due to the wide band gap (1.5-2.2 eV) and the higher Z density which enhances the energy resolution of the detector.

**Table 2-1 Summary of some material properties [5].**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Atomic number ( Z )</th>
<th>Bandgap ( E_g ) (eV)</th>
<th>Resistivity at room temperature (Ω/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>14</td>
<td>1.12</td>
<td>~10⁷</td>
</tr>
<tr>
<td>Ge</td>
<td>32</td>
<td>0.67</td>
<td>50</td>
</tr>
<tr>
<td>GaAs</td>
<td>31/33</td>
<td>1.43</td>
<td>10⁹</td>
</tr>
<tr>
<td>CdTe</td>
<td>48/52</td>
<td>1.44</td>
<td>10⁹</td>
</tr>
<tr>
<td>Cd_{0.9}Zn_{0.1}Te</td>
<td>48/30/52</td>
<td>1.57</td>
<td>10⁻³</td>
</tr>
</tbody>
</table>

### 2.3 CZT crystal growth

Before discussing crystal growth techniques, it is important to understand the phase diagram (shown in Figure 2-4) of the CdTe-ZnTe pseudobinary section. The upper and lower curves represent liquidus (temperature above which material is completely liquid) and solidus (temperature below which material is completely solid) respectively. The region between them contains both of the phases. The end points of the curves correspond to the melting points of the two pure materials. The two compounds form a complete series of solid solutions over the entire range of concentrations. The
phase diagram shows that at the beginning of the cooling process, the amount of zinc will be higher in the first formed crystal than the melt content. [38].

![Phase diagram for CdTe-ZnTe pseudobinary section, representing liquidus (upper) and solidus (lower) curves. The dots are experimental points [38]. © 2001 Elsevier Science.](image)

CZT crystals are grown by different methods, but mainly using the Bridgman method [39-41]. This has been modified to give the low pressure Bridgman [42-44], high pressure Bridgman, vertical and horizontal Bridgman methods. Other methods include the travelling heater, vapour phase epitaxy and physical vapour deposition. These growth processes are aimed at obtaining a good yield at low cost [38].

The main principal of the vertical Bridgman method involves a quartz ampoule containing each element that moves into the furnace with a certain temperature profile to produce the melt and then slowly forming the single crystal, as shown in Figure 2-5.

The crystals are grown by the mechanical movement of either the ampoule or the furnace heater. Modern systems are computer controlled that shifts the temperature gradient electronically, without any mechanical movement of any part of the growth chamber [39, 45, 46]. The horizontal Bridgman method is named as such due to the horizontal position of the furnace. For volatile materials, usually a sealed ampoule is used. To reduce the loss of the volatile component, a high pressure inert gas is employed above the melt. This method is known as high pressure Bridgman method and minimises the loss of these materials, but cannot totally eliminate the loss. Among the elements employed for the growth of CZT, Cd has highest vapour pressure, which results in a Te enriched melt [47]. In the travelling heater method, the bottom of the ampoule contains the CZT seed crystal, then the Te-rich CZT alloy and on top, the polycrystalline CZT. The heater is adjusted in front of the ampoule such that it first melts the Te-rich CZT compound and moves up to melt the pollycrystalline CZT which
then dissolves in the molten zone as shown in Figure 2-6. Meanwhile, cooling begins at the interface of this molten zone and seed crystal that result in the formation of crystalline CZT on top of the seed [48].

![Figure 2-5 Illustration of the vertical Bridgman method [49], © Universität Bern.](image)

**Figure 2-5** Illustration of the vertical Bridgman method [49], © Universität Bern.

![Figure 2-6 Schematic of travelling heater method technique, adapted from [50].](image)

**Figure 2-6** Schematic of travelling heater method technique, adapted from [50].

## 2.4 CZT material properties

### 2.4.1 CZT structure

The Cd$_{1-x}$Zn$_x$Te crystal is usually modelled as a CdTe crystal, where the fraction x of the cadmium atoms have been randomly replaced by Zn atoms [38]. CdTe and ZnTe have a zinc blende structure with two face centre cubic (FCC) sub-lattices, one for the Te atoms and the other for Cd (or Zn), which are arranged in such a way that one FCC sub-lattice is penetrated diagonally into the other with
the distance of one quarter of a unit-cell body [51]. The CdZnTe atoms exhibit covalent bonding due to the zinc blende structure which results in sharing of the valence band electrons.

\[ a(x) = a_1 (1 - x) + a_2(x) \]

where \( a_1 \) and \( a_2 \) are the lattice constants of CdTe and ZnTe with values of 6.482 Å and 6.104 Å respectively. The average lattice constant can be measured experimentally by employing X-ray diffraction [38].

**2.4.2 Resistivity**

For good performance of the detector, one of the desired attributes of the material is high resistivity, as this property reduces the leakage current. \( \text{Cd}_{1-x}\text{Zn}_x\text{Te} \) is a direct-band gap semiconductor. Its band gap depends on the Zn fraction \( x \) and at room temperature the band gap varies between 1.5 eV (CdTe) and 2.2 eV (ZnTe) [55]. Thus, the resistivity can be increased by increasing the Zn fraction in CZT. It has been previously shown that an increase in zinc fraction \( x \) from 0 to 0.2 leads to an increase in the resistivity from \( 3 \times 10^9 \) to \( 2.5 \times 10^{11} \) Ω·cm by approximately two orders of magnitude which results in a decrease in the leakage current of the same order [56].
2.4.3 Fraction of zinc in Cd$_{1-x}$Zn$_x$Te

In addition to enhancing the resistivity, the addition of Zn to CdTe reduces the concentration of native defects such as Cd vacancies and Te interstitials. Muren chu et al. [57] showed that Cd$_{1-x}$Zn$_x$Te with Zn fraction of 0.1 grown using the vertical Bridgman method gives the optimal performance when compared to other Zn fractions, with $x = 0, 0.15$ and 0.20. Zinc has a high segregation constant of value 1.3 that results in a variation in the Zn concentration within the CZT crystal during growth from melt. The Zn fraction, $x$, slowly changes from the top to the bottom of the crystal [37], which affects the performance of the radiation detector. The region of low zinc will have lower band gap and higher leakage current and the number of electron-hole pairs generated by the incident radiation will vary depending on the band gap. The spectroscopic response is broader for a detector with a variable amount of Zn in the bulk compared to material with a uniform zinc distribution, if all other parameters are kept the same [37].

2.4.4 Mobility-lifetime product

To achieve a sharp and narrow photo peak, ideally the charge carrier’s mean free path should be larger than the thickness of the device [58]. This allows all the photogenerated carriers per incident radiation to move towards contacts which reduces the effect of incomplete charge collection on spectroscopic response [59]. A charge carrier’s mean free path is the product of its mobility, lifetime and electric field, which makes the mobility-lifetime product an important attribute of the detector’s performance. This can be determined by plotting the Hecht equation [60] that relates the photopeak centroid as a function of voltage bias. The carrier lifetime can be improved by enhancing the homogeneity and purity of the CZT material [37]. The reported values vary between $2 \times 10^{-2}$ and $5 \times 10^{-3}$ cm$^2$/V for electrons and $3 \times 10^{-5}$ - $8 \times 10^{-4}$ cm$^2$/V for holes [61-64].

2.4.5 Growth defects

The performance of the CZT detectors depends on the presence of different types of defects. Two types of defects are present in CZT: a) point defects and b) extended defects. Point defects (single level traps) are distributed within the material, whereas extended defects include grain boundaries, cracks, pipes, Te inclusions, Te precipitates and voids etc.

2.4.5.1 Te inclusions

Te inclusions and Te precipitates are distributed in the bulk in two different ways; the most common is decoration along grain and twin boundaries and the other is a dispersed distribution throughout the material [65]. During crystal growth, Te precipitates are formed due to the retrograde solidus and Te inclusions are formed when interfaces of crystallized CZT trap the Te liquid drop during crystal growth [66].
2.4.5.2 Zn inclusions

It has been found that due to a higher segregation constant, Zn segregates near the heel of the ingot during the crystal growth [37]. J. Zhu et al have suggested that the growth of Zn inclusions could be due to the segregation of Zn during the crystal growth [67].

2.5 CZT detector operation

In a CZT detector, the radiation is incident on the CZT crystal, which forms a sandwich between two metal electrodes. The radiation energy is transferred to an orbiting electron in the form of kinetic energy, which is then responsible for creating more electron-hole pairs in the crystal. Under an applied electric field, electrons and holes move to the respective electrodes which are connected to the external circuitry that amplify and shape the pulse current which can be seen on a display screen or oscilloscope. A schematic diagram of the detector is shown in Figure 2-8.

![Figure 2-8 Block diagram of CZT radiation detector.](image)

The smooth flow of charge to their respective electrodes depends on the physical properties, homogeneity, purity, and surface roughness of the CZT material as well as the physical properties of the interface between the surface and contact. The homogeneity and purity depends on the crystal growth technique. In the next section these parameters are discussed in detail.

2.6 Factors affecting CZT detector performance

2.6.1 Defects

Spectral broadening and peak shift result from the defects described above, but these effects can be corrected by different techniques. The defects which deteriorate the device performance are extended defects [53]. These act as trapping sites for the carrier charges that result in poor charge collection. Early research suggested that dispersed Te inclusions and Te precipitates have no significant effect on the performance of the CZT detectors [47] but later, with the development of more advanced techniques, it was revealed that they do degrade the detector’s performance [68].
2.6.2 Surface preparation

The importance of surface processes in device fabrication is due to the correlation between surface properties and charge generation, charge collection and drift length affecting the performance of the detector [69]. The pulse height spectrum of the detector depends on the dark current, which is related to surface preparation of the detector. Babalola [53] showed that a rough surface used as the cathode gives rise to a degraded photo peak response. The resistivity of the surface determines the optimum voltage for the device and this has a direct correlation with the surface processing. A high surface leakage current results from one or more of the following: a non-stoichiometric surface, surface roughness or dangling bonds, which in turn are all dependant on the quality of the mechanical and chemical polishing process [53]. To reduce crystal damage, scratches and roughness induced from cutting of the ingot, the first step in device fabrication is mechanical polishing of the crystal surface with silicon carbide paper and then with an alumina suspension of different sizes (3µm-0.01µm), depending on the roughness of the surface. The roughness is further reduced by chemical etching. When the material is dipped in the chemical etchant, the surface layer of material is etched away and a flat, smooth surface is left behind. The surface composition after this chemical treatment depends on the chemical solution employed. A chemical treatment using an acidic solution produces a Te-rich surface, while an alkaline solution etch gives a Cd-rich surface [70]. The most common ambient temperature etchant is 0.2-10% bromine in methanol (BM) in order to get a smooth surface. Özsan et al [71] found that the Cd/Te ratio at the surface was invariant after a 2 minute exposure in 0.2 and 1.0 % BM solution, but the graded Te layer increased in thickness as the BM concentration was increased. However, the enriched Te layer thickness was not quantified. The pH of the BM affects the composition of the surface. Aging of the BM solution increases its acidity, resulting in an enrichment of elemental Te at the surface. Rouse et al [29] found that once the Te layer reaches a thickness of approximately 2 nm, the layer thickness is then independent of the duration and acidity of the BM solution. Bensalah et al [72] have shown that variation in BM exposure affects the surface roughness and leakage current. The Te enrichment changes the stoichiometry of the surface and due to smaller band gap (~0.3 eV), increases the leakage current, deteriorating the radiation detector performance. To minimize the leakage current, the Te rich surface is passivated to develop an insulating oxide layer.

Different passivating agents a have been employed on the CZT surface. Özsan et al [71] showed that passivation of BM etched surfaces with 30 % H2O2 produces an oxide thickness which is dependent on BM concentration up to a BM concentration of 2 %. The oxide thickness dependence on exposure time of the passivating agent was only measured for a 0.2 %, BM concentration, but was found to be similar, for all exposure times [71]. Considering a number of authors work, the thickness of the H2O2 generated oxide is in the range of 1.6 - 4.5 nm, depending on the BM concentration employed and oxide thickness calculation method [71, 73, 74]. There are some other passivating agents that also have been used to produce oxide layers such as NH4F/10%H2O2, KOH+KCl, NaClO-
DI etc. The thickness and composition of the oxide layer formed depend on concentration, exposure duration and combination of the passivating agents [75-77]. For optimisation of the detector performance and in order to get a highly smooth surface, there is a need to investigate the concentration and exposure duration of etchant and passivating agent in detail, which is one of the main aims of this thesis.

2.6.3 Electrical contacts

An important part of device fabrication is the CZT electrical contact. Electrodes can be deposited in different configuration depending on the application of the detector. There are three common geometries shown in Figure 2-9, a) single planar detector; is easy to fabricate and is used in large volume detector, b) co-planar grid detector; is employed to generate good spectral resolution for high energy gamma rays, and c) pixellated detector; is used as portable high resolution imaging detector.

![Illustration of electrode geometries](image)

*Figure 2-9 Illustration of electrode geometries, a) single planar; b) co-planar grid and c) pixellated detectors.*

The contact also affects the performance of the detectors. A tremendous amount of research has been performed to analyze the effect of different contact materials (e.g. In, Au and Pt), different deposition techniques such as sputtering, evaporation and electroless deposition and the interfacial composition on the detector’s quality [29, 30, 78]. The interface between metal and semiconductor (MS) plays an important role in charge transport as a potential barrier is developed at this interface due to the difference in work functions of the metal and the semiconductor. The band structure at the interface of a MS, when the work function of the metal ($\Phi_M$) is higher than that of the semiconductor ($\Phi_S$) is illustrated in Figure 2-10. A Potential barrier developed as a result of band bending, once the thermal equilibrium is reached as shown in Figure 2-10(b).
Figure 2-10 Schematic diagram of energy band structure of metal-semiconductor interface ($\Phi_M > \Phi_S$), a) before and, b) after thermal equilibrium, adapted from [79].

According to the Schottky-Mott (S-M) theory, the barrier for electrons ($\phi_e$) and holes ($\phi_h$) can be expressed as [80, 81]

$$\phi_e = \Phi_M - \chi$$

$$\phi_h = E_g + \chi - \Phi_M$$

Where $\chi$ and $E_g$ are electron affinity and bandgap of the semiconductor respectively. There are many methods to find out the barrier height including current-voltage (I-V), capacitance-voltage (C-V) characteristics, valence band study of ultra-thin metal contact (~0.5 nm) employing synchrotron based X-ray photoelectron spectroscopy [82-85]. The most common technique to determine the Schottky barrier height (SBH) is measuring the I-V characteristics [86]. It is assumed that only those electrons can contribute to the current that have sufficient thermionic energies ($> kT/q$) to overcome the potential barrier height. The net current density ($J$) for the forward bias can be written as [87]

$$J = J_s \left[ exp \left( \frac{qV}{kT} \right) - 1 \right]$$

where $J_s$ is the saturation current density and is expressed as

$$J_s = A^* T^2 \exp \left( \frac{-q\phi_b}{kT} \right)$$

where $k$ is Boltzmann’s constant, $T$ is temperature, $q$ is electron charge, $A^*$ is Richardson’s constant dependant on effective mass ($m^*$) and is equal to 120 ($m^*/m$) with $m^* \approx 0.13 m$ and $J_s$ is the saturation current density which can be obtained by the straight line intercept of ln $J$ at V=0. Equation 2-5 can be rearrange to find the barrier height $\phi_b$ [85]
It is seen that surface preparation the of CZT alters the barrier height [83]. The electrode deposition method can also vary the interface of MS. One study showed that electroless deposition can decrease the leakage current while sputtering can improve the contact adhesion [88]. An Au electrode deposited by sputtering has a strong adhesion whilst electroless deposition gives it ohmicity [47, 78]. Detectors with In contacts have a low dark current when thermally treated but a thermal treatment above $300^\circ C$ has been shown to degrade the energy resolution [30]. A passivation treatment prior to contact deposition restricts the leakage current. However it is found that TeO$_2$ impedes the Pt inter-mixing with CZT when deposited by sputtering which then adversely affects the performance of the detector [29].

There is still a need for further studies on surface preparation, selection of material for the electrodes, variation in MS interface due to surface preparation and the deposition process to achieve optimal detector performance.

**2.7 Thin film Solar Cells**

Thin film photovoltaic solar cells are fabricated by sandwiching cadmium telluride with cadmium sulphide (or cadmium zinc sulphide) to form a p-n junction; deposited at the glass substrate as shown in Figure 2-11. This simplifies the manufacturing process and lowers the cost compared to silicon solar panels where multi steps are required to join two different types of doped silicon.

![Figure 2-11 Schematic diagram of the thin film CdTe solar cell.](image)

The glass substrate shields the device and the sunlight has to pass through it, to reach the solar cell, so the optical reflection from the glass is required to be negligible. Usually aluminosilicate glass is coated with transparent conducting oxide (TCO) that is used as front contact for the solar cell [89]. The thickness of the window layer is a compromise between being as thin to allow maximum light to penetrate through it and to be thick enough to screen the front contact and to form p-n junction with CdTe layer. The sunlight has to be absorbed in the CdTe layer, therefore its thickness is usually kept
above the absorption limit (∼1 µm) [90, 91].

A typical photoelectric I-V characteristic of a solar cell is shown in Figure 2-12. In this plot the maximum current is at zero applied voltage known as short circuit current (I_{SC}) and maximum voltage is reached when there is no current flowing through the cell, which is referred to as open circuit voltage (V_{OC}). The output power of the solar cell at these points is zero. Another key parameter in defining the performance of the solar cell is its fill factor (FF), which is the ratio of maximum power obtained from the solar cell to the product of I_{SC} and V_{OC}; it is illustrated by the ratio of area A to area B in Figure 2-12.

![Figure 2-12 Plot of current (black line) and power (blue line) verses voltage of a solar cell adapted from [92].](image)

Recent progress reported by First solar, inc. show that high conversion efficiencies can be achieved on a commercial scale, both for cells (20.5%) and modules (18.6%) [21]. To improve the efficiency further, instead of using CdTe, some researchers have tried ternary CdZnTe as the absorber layer, but this has resulted in decrease in efficiency [93, 94]. The thickness of CdTe is kept in general between 2-7 µm (larger than the absorption limit – as most of the photons are absorbed in the first µm) [90, 91] to avoid discontinuities and pinholes from penetrating down to the window layer causing shorting from the back contact [95, 96]. Although the CdTe PV industry has made very good progress, there are still some issues that hinder its usage worldwide and need to be addressed. Nevertheless, due to carrier recombination throughout the absorber layer and unlike Cd the uncertainty of availability of the Te resources [20, 91, 97], the trend is changing to the use of ultra-thin (∼1 µm) CdTe absorber layers. However, a drop in the open circuit voltage (V_{OC}), fill factor (FF) and photocurrent caused by an increase in defect density (pinholes and discontinuities) due to non-uniformity and reduced absorbing volume are limiting factors [22, 23]. To overcome the photocurrent loss, instead of using CdS as a window layer, a wider bandgap ternary material Cd_{1-x}Zn_{x}S is used to increase the
photocurrent generation and to give a better response in blue region of the solar spectrum compared to CdS [23, 24]. The appropriate amount of Zn in Cd$_{1-x}$Zn$_x$S for optimal performance of ultra-thin solar cells is still under investigation. In CdZnS/CdTe solar cells, another source of photocurrent loss is recombination at grain boundaries, as both materials have a polycrystalline structure. The grain size in both layers can be of the order of the layer thickness. To minimise this, following deposition of the CdTe layer, CdCl$_2$ is deposited on the surface, followed by annealing. This process acts to passivate the grain boundaries and improves the cell efficiency [25]. The optimal conditions of these processes are still unknown. Hence, more work is needed to understand the changes in the microstructure during processing, allowing improvements in the efficiency of ultra-thin CdTe solar cells to be made.

2.8 Concluding Remarks

In this chapter, the interaction of radiation with detector materials was introduced and important parameters regarding the performance of the radiation detector were described. A brief discussion on the current status of thin-film CdZnS/CdTe PV solar cell technology was also presented. In next chapter, the theory, capabilities and operation of the major characterisation techniques employed in this research work, XPS, XRD, and SEM/EDX will be described.
3 Experimental techniques

3.1 Introduction

To fully understand the device performance, the variation in processing parameters needs to be studied. For this purpose, the analysis of surface and bulk of the materials and devices at different stages of processing are undertaken by a range of characterisation techniques. In this chapter, the experimental techniques employed to characterize the surface and bulk of the specimens will be described. To understand the surface and bulk of a CdZnTe crystal and its interface with the gold contact, the characterisation techniques mainly employed were X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy, (SEM), and energy dispersive X-ray (EDX). For surface imaging and composition, SEM and EDX were used. The variation in crystal structure after passivation treatments was analysed by XRD. The main characterisation technique employed in this study was XPS. It was used to investigate surface chemistry and to calculate the thickness of the layers developed at the surface after different chemical processing (chemical etching and passivation) methods either by a non-destructive method i.e. Angle Resolve XPS (ARXPS) or a destructive method i.e. depth profiling by noble gas ions. In the later stages of the work, after device formation, XPS was also used to study the Au/CdZnTe interface. For ultra-thin CdZnS/CdTe solar cells; the analysis of compositional changes occurring due to variations in processing parameters was undertaken by XPS depth profiling and the resultant structural changes by XRD.

3.2 X-ray photoelectron spectroscopy

XPS has a long history in surface and interface science. It is widely used in different fields due to its ease of use for almost every type of material i.e. conductors (metal), semiconductors and insulators (polymers) that can sustain ultrahigh vacuum conditions. The other name of XPS is ESCA (electron spectroscopy for chemical analysis). This analytical technique has power to identify elements (and
their chemical state), except hydrogen and helium, at a concentration of 0.1 at % from the depth of ~ 3-10 nm [98].

The fundamental principles of XPS, its instrumentation, quantification and its additional functions such as ARXPS and depth profiling are described below.

### 3.2.1 Principal of XPS

When X-rays are incident on a material, different processes occur in the interaction volume between the X-ray photon and the electrons of a material (detailed in chapter 2); XPS is based on the photoelectric effect: i.e. photoemission occurs when an electron is ejected from a core level of an element. When soft X-rays of well-defined energy, $h\theta$, are incident on a surface of a specimen, all of the X-ray energy can be transferred to an electron in an atom, leading to photoemission. Part of this energy is used to remove a core level electron (binding energy, $E_B$) and the remaining energy is transferred as kinetic energy $E_K$, enabling the photoelectron to escape from the surface to the vacuum as shown in Figure 3-1(a). This is easily described employing the Einstein relation given below,

$$E_K = h\theta - E_B - W$$  \hspace{1cm} (3-1)

where $W$ represents the work function of the instrument and is typically about 4.5 eV.

![Figure 3-1 Illustration of a) the photoemission process and b) XPS induced Auger electron emission [99].](image)

There is another type of electron emission during the relaxation of the excited atom when an outer electron fills the hole by transferring its energy to a third electron of the same principal quantum number. This emitted electron is known as Auger electron shown in Figure 3-1(b). The energy of the photo-emitted electrons are determined through the electron spectrometer and a spectrum of electron intensity as a function of binding energy is produced known as X-ray induced photoelectron spectrum. The elements present in the specimen can be identified and quantified knowing the kinetic energy and
intensity of the detected photoelectrons.

3.2.2 XPS instrumentation

The Thermo Scientific Theta probe is an advanced XPS instrument featuring a micro-focussing monochromator X-ray source with spot size in the range between 15 and 400 µm which enables small area analysis with high sensitivity. AlKα of energy 1486.68 eV is used as the monochromatic X-ray source. The monochromatic beam is achieved by directing AlKα radiation onto a single crystal (commonly a quartz crystal is used), where diffraction of X-rays occurs according to the Bragg equation (more detail in the XRD section). The reasons for employing a monochromator source include a reduction of X-ray linewidth that results in high resolution, removal of unwanted satellite radiation, ease of focusing on a small spot and multi point analysis due to tuning the beam to a small size. The schematic of the instrument is shown in Figure 3-2.

![Schematic diagram of a small-spot XPS instrument](image)

*Figure 3-2 Schematic diagram of a small-spot XPS instrument [100]. Image © Thermo Fisher Scientific.*

To transfer the photoelectrons to the analyser, a Radian lens is employed, which has a large acceptance angle (60°) and its axis at 50° normal to the surface of the sample. These high energy photoelectrons must be retarded to produce better energy resolution, for this purpose lenses are used that also focus these photoelectrons into a hemispherical analyser (HSA). In the HSA, there are two hemispherical electrodes both at negative voltages with respect to ground potential; the outer electrode is more negative relative to the inner electrode. This potential difference provides field to the electrons that enter the HSA and can pass through it only if their kinetic energy is proportional to this potential difference (ΔV) and is given by the expression 3-2 [101]:

\[
\Delta V = \frac{1}{2} m \frac{v^2}{r}
\]
\[ E = k e \Delta V \]

where \( E \) is known as the pass energy, \( k \) is a spectrometer constant, \( e \) is the electron charge. The pass energy is a user defined parameter and remains constant throughout the acquisition of a spectrum. Higher pass energies (> 100 eV) enhance transmission of the electrons but compromise the energy resolution and are typically selected for the wide scan to identify peaks of the element present in a material, whilst for narrow scans of core-level peaks (used in quantification and for chemical state information), a lower pass energy (e.g. 20 eV) gives better resolution. The HSA is attached to a two-dimensional detector which collects spectroscopic and angular information together.

The specimen is analysed in a vacuum chamber under Ultra-high vacuum. For this purpose, a turbomolecular pump and rotary pumps are attached to the analysis chamber to attain a vacuum better than 5 x 10^{-10} mbar. An Ar^+ ion gun is used for depth profiling. A number of samples can be accommodated on an automated stage enabling unattended operation including depth profiling for optimum yield. The Avantage software is employed to set up the instrument parameters and process the data [102].

All the photoelectrons of binding energy less than the X-ray photon energy will appear in the spectrum that represents the electronic structure of the material under investigation. The measured binding energy of the electron is specific to an element and the associated chemical states of that element present at the surface [103].

Figure 3-3 shows a survey spectrum of pure tellurium. The elastically scattered, photo-emitted electrons produce XPS peaks and these directly reach the detector without losing energy, while inelastically scattered photo-emitted electrons contribute to the background of the spectrum as these lose part of their energy before reaching the detector. The part of the spectrum corresponding to very low binding energy is referred to as the valence band region. This part contains information about the electronic structure and orbital bonding of a material. An AlKα photon of energy 1486.68 eV can knock out the core level electrons up to the 3p shell of tellurium. Doublets comprising of two peaks of different intensities and width can be seen for the core level p and d shells, which is the result of spin-orbit coupling. Spin orbit splitting is more enhanced with increased binding energy. Quantification and determination of chemical state of a material is obtained through examining the core-level peaks. The photon induced Auger peak often also has a unique shape and position and is usually analysed to investigate the elemental identification and chemical changes that cannot be distinguished from studying the core level peaks. As the Auger process involves three electrons, a small variation in chemical environment is often observable. A useful parameter to analyse the chemical state, independent of any charging effect, is known as the modified Auger parameter and is the sum of the kinetic energy of the Auger peak and binding energy of core-level photopeak.
3.2.3 Quantification in XPS

Quantification of the XPS spectra can give very useful information on the surface and near surface region. The peak intensity (number of electrons emitted at a particular energy) depends on the concentration of the emitting atom in the specimen. For a homogeneous solid, the intensity is simplified as

\[ I = J \rho \sigma K \lambda \]  

3-3

where \( J \) is the photon flux, \( \rho \) represents concentration of the element in the specimen; \( \sigma \) represents the cross-section for photo-emitted electrons that is related to the element and the energy of the peak, \( K \) is an instrument related factor and \( \lambda \) is the electron attenuation length. Basic quantification can be performed with this equation but generally, experimentally measured sensitivity factors (\( F \)) are used, which include the effects of more features (e.g. characteristic losses) in addition to \( \sigma \), \( K \) and \( \lambda \) of equation 3-3. Usually, the intensity of the peak is calculated by integrating the area of the peak after subtracting the background. Once \( I \) is determined for the elements present in the sampling depth, the atomic percentage of the desired element is obtained by dividing the peak intensity by its sensitivity factor and manipulating it as a fraction of the addition of all normalized intensities (given that the photon flux has remained the same throughout the experiment) as given by equation 3-4 [103]:

\[ [A] \text{ atomic } \% = \left( \frac{I_A/F_A}{\sum(I/F)} \right) \times 100\% \]  

3-4

This method assumes the homogeneity of the specimen within the sampling volume, which is generally not the case. For a more accurate analysis and to investigate which overlayers are present, angular dependent XPS is employed.
3.2.4 Compositional depth profiling

Composition of the material as a function of depth can be found either non-destructively (without damaging the surface) employing the Beer-Lambert equation (equation 3-5 below) to manipulate the sampling depth, known as angle resolved XPS or destructively (in situ removal the material from the surface of the specimen) known as noble gas ion etching.

3.2.4.1 Angle Resolved XPS (ARXPS)

In the angle resolved XPS mode, the Thetaprobe acquires spectra in parallel over a 60° angular range without sample tilting, offering non-destructive depth analysis of ultra-thin films (< 10 nm). It can give information about chemical states present in the layer, stoichiometry, ordering, thickness and nature of the layers. The distribution of elements through the layer can be quantified. As the name suggests, the variation of emission angle of the photoelectrons plays an important role, and the depth of analysis changes with emission angle. Through collecting photoelectrons within the range of 20°-80°, in angle resolved mode, this range is usually divided into 16 parts. All of these angles are measured relative to the sample normal, so at higher angles, electrons are collected from deeper in the bulk of the material and at lower angles electrons from closer to the surface are collected. Consequently, as shown in Figure 3-4: increasing the emission angle with respect to the surface normal decreases the depth of analysis and the analysis becomes more surface sensitive.

![Figure 3-4 Schematic diagram showing the dependency of the XPS information depth on emission angle [100]. Image © Thermo Fisher Scientific.](image)

The depth distribution of the elements can then easily be found by examining the information collected at different angles. The thickness \( d \) of a thin overlayer can be found by manipulating this equation but is limited to \(-3\lambda\), when all the signal is collected normal to the surface (i.e. \( \theta = 0^\circ \)), which makes it necessary to know the value of \( \lambda \) at the kinetic energy of the required peak under
investigation. In the past, $\lambda$ was used to describe the inelastic mean free path (IMFP) and attenuation length (AL) interchangeably. Although both are related to each other, they are not the same quantities. IMFP is the basic property of the material in question and is defined as the average distance an electron travels between two consecutive inelastic events. It depends on the electron energy as $E^{0.5}$ in the range of interest and can be determined experimentally or calculated theoretically employing the Seah and Dench approximation [104] or TPP-2M equation of Powell and Penn [105], whilst the AL also takes into account elastic scattering between two consecutive inelastic events, which makes it a variable term unlike the IMFP. Cumpson and Seah [106] developed semi-empirical equations to estimate the AL for the electron energies between 50 and 2000 eV, with a standard uncertainty of 6%. The AL is an important parameter in the calculation of the thickness of the thin overlayer/film, as it is related to the attenuation of the electron energy in passing through one layer to another layer.

The equation of the intensity ($I$) of the photo-emitted electrons from a thin film/overlayer can be written as:

$$I = I_0 \left[1 - \exp\left(-\frac{d}{\lambda \cos \theta}\right)\right]$$

where $I_0$ is the intensity from an infinitely thick substrate, $d$ is depth of analysis and $\lambda$ is the photoelectron attenuation length.

These are the fundamental equations which are manipulated to find the thickness of the oxide overlayer in chapter 5. Generally, the variation in intensity of the XPS signal as function of angle is determined by acquiring spectra from a series of known emission angles to the surface normal. Modern multichannel detectors are common in hemispherical analysers that can simultaneously detect series of spectra at different angles. Larger emission angles particularly greater than $\sim 60^\circ$ are ignored during analysis due the fact that elastically scattered electrons originating deeper within material are emitted at large angles and can mislead the interpretation of the results.

3.2.4.2 Depth profiling by sputtering with noble gas ions

To assess the compositional changes and interfaces in the material from the depth greater than 10 nm, ion bombardment is used to progressively remove surface layers and analyse the bulk of the material. Figure 3-5 shows the experimental procedure to obtain a depth profile. First the native surface is analysed and then the surface is bombarded by noble gas ions for a specific period of time. The sputtered area is then analysed. This repetitive analyse-etch loop continues until the desired depth is reached.
Depth profiling is performed under high vacuum to avoid the adsorption of the residual gases from the vacuum to the highly reactive sputtered surface that acts as a gettering site for contamination. The most common ion guns attached to spectrometers use inert gas ions, most notably, Ar. Inside the ion gun, a heated filament produces electrons. Inert gas ions are formed after collision with these electrons. The kinetic energy of these positive ions depends on the applied voltage (0.5 – 5 k eV). The beam is focussed on to the specimen with a sputtering spot size ranging from 50 µm to 5 mm. The bottom of the crater created from the sputtering process is not usually flat due to the non uniform Gaussian cross-section of the current density profile of the beam. Hence, it is necessary to raster the ion beam. To obtain a good depth resolution, the analysed area should be five times smaller than the rastered (scanned) ion beam area. To obtain the depth of the crater, the etch rate must be known, which depends upon the chemical bonding of the material, the rastered area and the ion beam current. From this rate, the distribution of the elements as a function of depth into the bulk of sample can be obtained. In the depth profiling process, physical or instrumental effects broaden an abrupt interface. This broadening can be measured and is known as the depth resolution. Generally, the depth resolution is defined in terms of depth range $\Delta z$, which is the difference between the 84% to 16% concentration of the acquired profile for a sharp drop in the elemental concentration [103] as shown in Figure 3-6.

The depth resolution is affected by different factors. If the specimen surface is rough, this roughness could worsen during sputtering which ultimately affects the information gathered, due to several reasons, i) the rough surface may produce shadowing effects on some parts of the sample, ii) the roughness may change the angle of incidence between ion beam and the sample surface, and iii) in
compound samples, some elements may be sputtered more strongly than others by the ion beam, which could change the stoichiometry of the sample resulting in the change in the depth resolution. Another physical parameter that affects the depth resolution is *sputter yield*, which is the ratio of number of the atoms removed from the specimen per number of incident ions. The sputter yields of the elements present in a material can be different which leads to the composition of the surface layer being altered in a way that the surface is enriched with the element of low sputtering yield. This effect will produce an artefact in the profile due to changes in surface composition over the depth of 1-20 nm known as *preferential sputtering*. After a certain time/depth, a steady state is reached [98].

![Figure 3-6 Measurement of depth resolution. Adopted from [103].](image)

### 3.3 X-ray diffraction

X-ray diffraction is a well-established tool used in many fields of science for detailed structural and chemical composition analysis. It is very important in investigating the crystal structure due to the dependence of the physical properties of materials (electrical conductivity, magnetic and optical etc.) on the atomic arrangement in solids. Most materials are crystalline in nature i.e. they have a defined regular atomic structure. Crystals are made up of an array of unit cells in three dimensions, which have a specific arrangement which is repeated periodically. A unit cell has three physical dimensions known as *lattice parameters* that can vary in length depending on the type of cell e.g. cubic, hexagonal, etc. Different directions and planes can be defined in the crystal lattice. In the same set of parallel planes, the interplanar distance is known as the *d-spacing* that changes according to the nature of material. The relationship between the lattice parameters and the d-spacing depends on the type of the unit cell; for the simple cubic structure (where every dimension is of same length); the relationship
is given in equation 3-6:

\[ d_{hkl} = \frac{a_0}{\sqrt{h^2+k^2+l^2}} \]  

3-6

where \( d_{hkl} \) is the lattice (interplanar) spacing, \( a_0 \) is the lattice parameter and \( h, k \) and \( l \) are the reciprocal of the intercepts in three different dimensions (axes) respectively of a unit cell known as miller indices. Usually the d-spacing is in the range of ~0.3 nm. To determine the crystal structure, the incident beam is diffracted by the lattice planes which occur when the wavelength of the incident beam is comparable to the d-spacing. X-rays have a very short wavelength (0.1 to 0.5 nm), well in the range of the lattice spacing which makes them ideal for probing the atomic and molecular arrangement of most materials. X-ray diffraction involves the interference of waves. When two waves travelling in the same direction have the same wavelength and amplitude, they can either interfere constructively (when in phase) and superimpose to double the amplitude or destructively (when out of phase) to cancel each other out. Bragg represented this concept in terms of a reflection from the crystal planes. Consider an X-ray beam with an incident angle \( \theta \) and wavelength \( \lambda \) incident on a set of parallel planes (hkl) separated by the lattice spacing \( d_{hkl} \). The beam will scatter at the same angle, \( \theta \), as shown in Figure 3-7. The diffracted beam from the second plane will travel an extra distance of \( 2x \), equal to \( 2d_{hkl} \sin \theta \).

![Figure 3-7 Diffraction of an incident X-ray beam from the atomic planes of a crystalline material with a lattice plane spacing ‘d’. Redrawn from [108].](image)

According to Bragg’s law, for the diffracted maxima, this extra distance travelled must be an integer multiple \( (n) \) of the wavelength (i.e. both diffracted beams should be in phase), which is given below
\[ 2d_{hkl} \sin \theta = n \lambda \quad 3-7 \]

To find the \( d_{hkl} \), it can be rewritten as

\[ d_{hkl} = \frac{n \lambda}{2 \sin \theta} \quad 3-8 \]

Generally, the intensities of the diffracted peaks are plotted as a function of Bragg’s angle, \( 2\theta \), known as an XRD pattern, which is a characteristic of particular crystal structure and material. A large database of XRD patterns for the majority of the materials has been compiled and is frequently used to identify the crystal structures of compounds.

To enhance the beam intensity and angular resolution, generally, the optics of diffractometers are arranged in a manner that the sample and the detector are rotated in such a way that the sample is always at \( \theta \) and detector is always at \( 2\theta \) to the incident beam while keeping the incident X-ray beam fixed; this type of arrangement is referred to as the Bragg Brentano (\( \theta-2\theta \)) geometry as shown Figure 3-8. It corresponds to a parafocusing geometry in which the distance of the incident X-ray beam from the source to the sample (with the beam spreading out as it moves towards the sample) is the same as the distance between the sample and the point of refocus (at a receiving slit) on the diffracted beam side.

**Figure 3-8 Diagram of the Bragg-Brentano XRD geometry [109].**
The incident X-ray beam is generated inside the X-ray tube that consists of a cathode ray tube under high vacuum, in which a heated tungsten filament emits electrons that are accelerated towards the water-cooled metal target (usually copper) under the influence of high electric potential. Due to the interaction of these electrons with the target, the inner shell electrons are ejected and outer shell electrons fall down to fill the hole and emit the excess energy as X-rays. Monochromatic radiation is required for XRD. In the case of a copper target, the $K_\alpha$ line is selected and $K_\beta$ is removed using a nickel filter as shown in Figure 3-9.

![Figure 3-9 A diagram showing the X-ray spectrum of copper and the nickel filter allowing only the $K_\alpha$ peak of copper to pass through [110].](image)

These X-rays are then collimated through a series of slits (e.g. soller slits, divergence slit) prior to striking the specimen. The diffracted beam is also passed through a number of slits to limit the divergence and to refocus the beam before entering the detector.

### 3.3.1 Determination of crystallite size and structural variation.

One of the main uses of XRD is the estimation of the crystallite size. The average grain (crystallite) size can be calculated from the peak width, as sharp peaks arise from large crystallites and an increase in peak width indicates a reduction in the crystallite size. The average grain size is defined as the volume-weighted average length in the direction normal to the lattice planes, and is estimated employing the Scherrer formula [111]

$$
\sigma_{hkl} = \frac{0.9 \lambda}{B \cos \theta}
$$

where $\sigma_{hkl}$ represents the grain size in nm, $\lambda$ is the X-ray wavelength (0.154 nm for copper), $B$ is full width half maximum in radians and $\theta$ is the diffracted angle. Analysis of the crystallite size require careful interpretation as broadening of the peaks also depends on the variation in internal strain and crystallite refinement.

Structural distortion can be analysed by manipulating XRD data as the variation in d-spacing for a crystalline material due to change in any factor, e.g. chemical composition [112], residual stress, strain.
or thermal distortion can affect the X-ray pattern. According to Bragg’s law, in equation 3-8, the diffracted angle is inversely related to lattice spacing. So, changes in the lattice spacing can be identified from shifting of the peaks to higher or lower $2\theta$ values in the diffraction pattern.

### 3.3.2 Glancing Incidence XRD (GIXRD)

In conventional XRD, the X-ray penetration depth in the specimen increases (up to few hundred microns) with high incidence angles, depending on radiation density, which make it unsuitable for surface sensitive analysis, such as thin films and coated layers (with a thickness of a few nm); as most of the signal arises from the substrate or bulk of the material rather than the surface. To overcome this problem, an alternative optical arrangement is adopted to replace the Bragg-Brentano arrangement that can reduce interference from the substrate and increase the path length of the incident beam through the film in such a way that intensity of the diffracted beam from the layer can be enhanced. This technique is known as glancing incidence XRD (GIXRD).

The representation of GIXRD is shown in Figure 3-10. In this technique, the optics are arranged in a manner that the angle between incident beam and sample is kept small and fixed usually between 0.5 and 3 degrees and the diffracted pattern is collected by rotating the detector only. Incident and diffracted beams are made nearly parallel by the use of narrow slits on both sides or mirrors on the incident beam side and soller slits on diffracted side.

![Figure 3-10 In GIXRD, the incident beam is fixed at an angle nearly parallel to the surface of the specimen, adapted from [113].](image)

As described above, X-rays are employed as the primary beam to probe the material in XPS and XRD. The other type of source used in many materials characterisation techniques is the electron source. When an incident electron beam strikes a surface, electrons and X-rays emitted from the material surface can provide information on the surface morphology or elemental composition of the
specimen. In the next section, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) are described.

### 3.4 Scanning Electron Microscopy (SEM)

SEM is one of the main material characterisation techniques allowing high resolution (down to nm scale) images of different features on the surface to be produced and the chemical composition of such features to be determined through the collection of secondary electrons, back scattered electrons, Auger electrons or X-rays. An image of the specimen is produced by scanning a focused electron beam over the surface. Interactions of these electrons with atoms of the sample generate different signals that contain information about the structure and topography of the surface.

![Schematic diagram of a scanning electron microscope](image)

*Figure 3-11 Schematic diagram of a scanning electron microscope [114] © 2015 Arizona Board of Regents.*

A schematic diagram of an SEM is shown in Figure 3-11. An electron beam of energy between 2 keV and 40 keV is produced by an electron gun, the beam is condensed and focussed by the
condenser lens and objective lens respectively and accelerated towards the specimen. There are three types of electron sources employed in SEMs, a thermionic source, a lanthanum hexaboride emitter and a field emitter. In thermionic emission, a filament is heated such that electrons overcome the energy barrier and escape into the vacuum. In other type of source, a material with a low work function, such as LaB$_6$ is used as a much higher flux can be generated than from the thermionic emitter. In the field emission source, the width of the energy barrier (work function) of the material is narrowed by applying a strong electric field, so the electrons can quantum mechanically tunnel through the barrier and escape into the vacuum. Often SEM instruments are equipped with a thermionic source, as these are inexpensive and robust in nature and can easily be used for SE, BSE and EDX signal detection.

The primary electron beam produced at the electron source passes through lenses and then interacts with the material under investigation. The interaction volume in the material is a function of applied voltage of the electron beam and the elements present in a material. The penetration depth can be calculated by the Kanaya-Okayama principal [115] and is given in equation 3-10 below:

$$d_p = 0.0276 \frac{A E^{1.67}}{Z^{0.39} \rho} \mu m$$  \hspace{1cm} 3-10

where, $d_p$ is the penetration depth, $A$ is the atomic weight, $E$ is the applied voltage (kV), $Z$ is the atomic number and $\rho$ is the density (g/cm$^3$). This shows that the interaction volume is lower in heavy elements and for low accelerating voltages. In CdTe, the penetration depth for an incident beam of 10 keV is 1.6 µm. Figure 3-12 shows the interaction volume of a high energy electron beam as it penetrates through the specimen and types of signals that are generated during this process.

**Figure 3-12** A schematic representation of the interaction volume of a specimen that is probed by an incident electron beam and the signals generated by the electron-solid interaction.
Different emission processes are observed. Secondary electrons and X-rays were employed in this research work for characterisation purposes, so these signals are described below.

### 3.4.1 Secondary electrons

The most widely signal used in the SEM are secondary electrons. These are generated by a range of different processes, one of these is the interaction of the incident electron beam with the outer most orbital electrons of the atoms of the sample; the inelastic scattering of the primary beam dislodges valence electrons from the atoms. These excited electrons undergo additional elastic and inelastic scattering that reduce their kinetic energy. Only those electrons emerging from the sample that are close to the surface due to their low kinetic energy (< 50 eV) are considered to be secondary electrons. These electrons are then collected by a scintillator that is covered by a Faraday cage as shown in Figure 3-13. A low positive bias (~50 V) is applied to the Faraday cage to attract the secondary electrons. These electrons are then accelerated towards the scintillator by a very high voltage (+12 kV) applied at the inner surface of the Faraday cage. Photons (light) are emitted when highly accelerated electron strike the scintillator material e.g. a phosphor. The light travels through a light pipe and hits the photomultiplier tube, which absorbs photons and emits pulses of low energy photoelectrons. These are then amplified and as the spot is scanned variation in the intensity of these electrons give rise to contrast in the image which is displayed on a cathode ray tube. Most of the secondary electrons are detected, even those that are emitted from the surface in the other directions.

![Figure 3-13 A schematic diagram of a secondary electron detector. Redrawn from [116].](image)

Secondary electrons generate high resolution images of the surface topography due to firstly, the fine focussing of the beam at the surface of the specimen and secondly, their narrow depth of generation near the surface region. In addition to secondary electrons, X-rays are generated by the primary beam in the SEM and the resulting X-ray spectrum used for compositional analysis.
3.4.2 Energy dispersive X-ray Analysis (EDX)

X-rays are generated when outer shell electrons fall into the inner shell to fill the hole created by the interaction of incident electron beam with the atom of a specimen. The energy of the X-rays is unique and is characteristic of the element present in the specimen, which makes it a powerful tool for elemental identification. These X-rays can be used for both qualitative and quantitative analysis of the material under investigation. The high energy X-rays originating from the interaction volume shown in Figure 3-12 are emitted from the material and are analysed by the detector. The size of the analysis volume depends on the accelerating voltage of the incident beam, the atomic mass of the specimen and the energy of the X-ray (e.g Kα, Kβ) analysed. X-rays are uncharged radiation, so travel in a straight line. To collect a high flux of X-rays; the detector is placed near to the specimen. The most common detector shown in Figure 3-14 consists of single crystal silicon doped with a small concentration of lithium to make a p-i-n junction. Very thin gold contacts are deposited on both side of the detector to minimise the absorption of the X-rays in this layer. A thin beryllium window is placed in front of the outer gold contact to avoid contamination (gases and impurities) from the analysis chamber reaching the detector [116]. Most of the low energy x-rays are adsorbed by beryllium layer hindering the use of this detector to identify light elements.

![Figure 3-14 Schematic diagram of an EDX detector. Redrawn from [116].](image)

The X-rays interact with the Si(Li) detector exciting the valence electrons. The number of the excited electrons depends upon the X-ray energy, as the excitation of a single valence electron requires energy of 3.8 eV [117]. To reduce noise and maintain the excitation purely due to X-rays, the detector operates in reverse bias and under cryogen temperature to avoid thermal excitation. The detector not only detects elemental characteristic X-rays but also the Bremsstrahlung X-ray background. The pulse of electrons produced by an X-ray is then amplified and sent to a multichannel analyser (MCA) that assigns a channel to the pulse depending on its energy. This whole process
should be finished before the arrival of a new pulse. The X-ray count rate is dependent on this processing speed. The total time it takes to analyse the X-rays is the sum of the *live time* when the pulses were counted and the *dead time* when they were rejected. The resultant resolution of the detector is relatively poor and the peaks are broad with a width of 100-200 eV. The analysis volume is approximately 1x1x1 µm³, but is dependent on the electron beam penetration depth, as described in equation 3-10. To detect an element present in a specimen, its X-ray peak should be well above the background signal. There is a threshold level for the concentration of an element to be detected in a *bulk specimen*, which is called the *minimum detectable concentration (MDC)*. A first approximation of this is given below [116]:

\[ MDC = \frac{200\sqrt{b}}{(p-b)\sqrt{t}} \% \]  

where \( p \) is the peak counts per second of the (pure) elemental standard, \( b \) is the count rate of the background and \( t \) is the analysis time. According to this equation, as would be expected, a long analysis time will lower the MDC. Elemental quantification is not straight forward in EDX; it involves the comparison of the each element present in the specimen to the pure elemental standard. As the material being studied will be different from the individual elements in terms of atomic weight and density, ‘ZAF’ correction factors are applied, which take account of effects associated with the atomic number (Z), absorption (A) and fluorescence (F) [118].

EDX can be used for imaging and identifying the location of the different elements on the surface. The resultant EDX maps may not correspond particularly well with the SEM image as the EDX sampling volume is larger than that of the secondary electrons, and the EDX map shows the composition of the sub-surface region. The spatial resolution of EDX mapping is poorer than that of the secondary electron image as the ‘droplet’ shaped sampling volume of X-rays is broader than that of the electron spot (see Figure 3-12). This can be improved by using thin samples. It can be seen in Figure 3-15 that the interaction volume of the electron beam is reduced for a very thin sample (used in transmission electron microscopy (TEM), the beam spread would resemble a conical slice that can be calculated mathematically as follows [119]:

\[ B_s = 0.198 \left( \frac{Z}{E} \right)^{1/2} \left( \frac{p}{A} \right)^{3/2} (d_{sp})^{3/2} \]  

where \( B_s \) is the beam spread and \( d_{sp} \) is the thickness of the specimen.

For thin film analysis, most of the modern TEMs are fitted with an EDX detector. In this research work a Scanning Transmission Electron Microscope (STEM) fitted with an EDX detector was employed which is briefly described below.
3.4.3 Scanning Transmission electron microscopy

STEM is an indispensable tool for materials characterization at the nanoscale. STEM provides a range of different imaging modes that are utilized to extract information about the chemical composition and electronic structure at an atomic scale resolution. The basic principal of operation of STEM is similar to SEM, where a focussed electron beam is scanned over the specimen to collect the desired signal. However, to enable imaging and analysis in the transmission rather than secondary mode, thin samples are used. Fabrication of the thin samples required is a major task as it can require ion milling, grinding or polishing depending on the material.

Detection of transmitted electrons provides information of the bulk of the sample, but SE, BSE and EDX imaging modes are also available in the STEM. Two types of imaging modes are common with the transmitted beam, bright field (BF) and dark field (DF). In BF imaging, the directly transmitted electrons are used to form the image, while an annular DF detector collects electrons from an annulus which lies outside of the main transmitted beam [120]. These electrons have been more strongly scattered and hence this signal is sensitive to changes in atomic number.

3.5 Summary

The main materials characterisation techniques employed to study CdZnTe detectors and CdZnS/CdTe solar cells have been described in this chapter. The next chapter is related to the characterisation of MOCVD deposited ultra-thin PV solar cells and will discuss the effects of different processing parameters on the chemical composition and microstructure of the solar cell multilayer structure. This will be a standalone chapter in the thesis, but represents substantial work undertaken on a CdTe based device and hence similar in many respects to the main topic of the thesis, CdZnTe detectors.
4 Ultra-thin CdTe photovoltaic (PV) solar cells

4.1 Introduction

During the course of PhD work, it became apparent that it was important to determine the Ar⁺ ion etch rate of CdZnTe. Although a CdZnTe standard sample could not be sourced, a CdTe thin film was kindly provided by Professor Stuart Irvine’s group at the Centre for Solar Energy Research (CSER), Glyndwr University. Being a material of similar composition, this was then used to yield a relatively accurate value for the CdZnTe etch rate. In exchange for the growth of a CdTe thin film, an XPS depth profile was undertaken on a CdZnS/CdTe based thin film solar cell for CSER. The results were of particular interest to CSER and collaboration then developed between the two groups, resulting in a set of CdZnS/CdTe thin film solar cells being grown, with varying Zn contents and CdCl₂ post-growth treatments. These samples were characterised for their composition and microstructure by XPS and XRD. The results showed important changes in thin film composition as a function of CdCl₂ treatment which were further correlated with the solar cell electrical/optical performance data recorded by CSER. The work on these CdZnS/CdTe based solar cells is presented in this chapter.

The demand for renewable energy sources is increasing with the passage of time. Solar energy is a cost free gift of nature and offers an alternative source of energy. To convert this energy into electricity many different materials are used in the manufacturing of photovoltaic (PV) solar cells. A
tremendous amount of research is going on all over the world to achieve high energy conversion efficiencies with a low raw material cost. Amongst other materials, thin film CdTe based PV modules are being commercially produced on a large scale [121]. In a thin film PV solar cell, to form a p-n heterojunction: conventionally CdTe acts as the p-type (absorber) layer and CdS is usually used as the n-type (window) layer. In an ultra-thin PV solar cell, the photocurrent is reduced by the smaller absorbing volume of the ultra-thin (≤ 1 µm) CdTe absorber layer. To overcome this photocurrent loss, instead of using CdS as a window layer, a wider bandgap ternary material Cd\(_{1-x}\)Zn\(_x\)S is used to increase the photocurrent generation and to give a better response in the blue region of the solar spectrum compared to CdS [23, 24]. The appropriate amount of Zn in Cd\(_{1-x}\)Zn\(_x\)S for optimal performance of ultra-thin solar cells has been reported [122] to have a fraction (x) of 0.7 for as-grown CdTe solar cells with a thickness of 2.25 µm. For ultra-thin CdTe cells this is still under investigation.

In CdZnS/CdTe solar cells, another source of photocurrent loss is recombination at grain boundaries, as both materials have a polycrystalline structure. The grain size in both layers can be of the order of the layer thickness, as seen from Scanning Electron Microscopy (SEM) plan-view images [123]. To minimise carrier recombination, CdCl\(_2\) is deposited on the surface following deposition of the CdTe layer, which is then thermally annealed to promote Cl diffusion into the CdTe along the grain boundaries. This process acts to passivate the grain boundaries and improve the cell efficiency [25]. More work is needed to determine the optimal parameters for the CdCl\(_2\) deposition and annealing process for ultra-thin CdTe solar cells. Some of this work is published [123] (Appendix C).

4.2 Experimental procedure

4.2.1 MOCVD Thin Film Solar Cell Growth

The PV CdTe solar cells investigated in this study were grown by Metal Organic Chemical Vapour Deposition (MOCVD) at CSER. Figure 4-1 shows a schematic diagram of the ultra-thin CdTe solar cell structure. Using glass substrates coated with indium tin oxide (ITO) (supplied by Delta Technologies Ltd.), a 240 nm thick CdZnS layer was first grown as the n-type window layer. Then, a 500 nm thick CdTe layer was deposited (p-type absorber layer) and a CdCl\(_2\) treatment and annealing process was employed to improve device performance. Finally, gold was evaporated as the back contact.
Figure 4-1 Schematic diagram of the ultra-thin CdTe solar cell grown by MOCVD.

The MOCVD organometallic (OM) precursors were supplied by SAFC Hitech Ltd. These were deposited at atmospheric pressure in a horizontal chamber with a graphite susceptor using a H$_2$/(N$_2$) carrier gas. The layer thickness was monitored by an in-situ triple wavelength laser interferometer. The specific details of the CSER MOCVD solar cell fabrication process [24] are as follows:

1. **Growth of the window layer:** At 360 °C, the CdZnS layer was deposited on ITO/glass using OM precursors of dimethylcadmium (DMCd), dethyazinc (DEZn) and ditertiarybutylsulphide (DTBS).

2. **Growth of the absorber layer:** At 390 °C, the CdTe layer was deposited onto the window layer using OM precursors of dimethylcadmium (DMCd) and diisopropyltelluride (DIPTe). To make this layer p-type tris-dimethylaminoarsenic (DMAAs) was used as dopant precursor. The doping concentration was $2 \times 10^{18}$ atoms/cm$^3$.

3. **Growth of the passivating layer:** A thin layer of CdCl$_2$ was deposited using OM precursors of DMCd and tertiarybutylchloride (tBuCl).

4. The samples were then annealed and the gold contacts were deposited by thermal evaporation.

**4.2.2 Sample Details**

Six samples with varying growth parameters were prepared. The basic structure of ultra thin solar cells is glass/ITO/CdZnS (240 nm)/CdTe (500 nm) followed by CdCl$_2$ treatment and annealing. The parameters varied were the Zn content in the CdZnS layer (DEZn flow rate in the chamber was 19, 22 or 44 standard cm$^3$ min$^{-1}$ (sccm)), CdCl$_2$ treatment duration (time varied 0, 80, 120 or 179 s) and annealing period (time varied 0, 120 or 600 s).
To investigate the effect of CdCl\textsubscript{2} and annealing treatment two sets of devices of varying parameters were prepared by MOVCD. Set 1 consists of three samples numbered 201, 208 and 209 with the same amount of Zn in CdZnS layer in all three samples (DEZn flow rate 19 sccm) but with different CdCl\textsubscript{2} deposition and annealing times. Sample 209 is a reference sample and was not treated with CdCl\textsubscript{2} or annealed. Sample 208 had a CdCl\textsubscript{2} deposition time of 80 s and was annealed for 120 s. For sample 201, both the CdCl\textsubscript{2} deposition and annealing time were raised to 179 s and 600 s respectively. Set 2 had two samples, 362 and 370, prepared with a higher concentration of Zn (DEZn flow rate 22 sccm), CdCl\textsubscript{2} deposition times of 120 s and 179 s respectively and an annealing time of 600 s in both cases.

To study the effect of Zn concentration on solar cell performance, in addition to these samples, another sample 343 was prepared with a higher Zn content in the CdZnS layer (DEZn flow rate 44 sccm). For this sample, the CdCl\textsubscript{2} deposition and annealing times were 179 s and 600 s respectively. All the growth parameters are given in Table 4-1.

Table 4-1 The CdZnS/CdTe thin film solar cell growth parameters.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Growth Parameters</th>
<th>343</th>
<th>370</th>
<th>362</th>
<th>201</th>
<th>208</th>
<th>209</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEZn (sccm)</td>
<td></td>
<td>44</td>
<td>22</td>
<td>22</td>
<td>19</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>CdTe (nm)</td>
<td></td>
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<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>CdCl\textsubscript{2} (s)</td>
<td></td>
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<td>179</td>
<td>120</td>
<td>179</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>Anneal (s)</td>
<td></td>
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<td>600</td>
<td>600</td>
<td>600</td>
<td>120</td>
<td>0</td>
</tr>
</tbody>
</table>

4.3 Analytical techniques

The composition changes to the ultra-thin Cd\textsubscript{1-x}Zn\textsubscript{x}S/CdTe solar cells were determined by using a Thermo Scientific Thetaprobe XPS instrument employing a monochromatic Al K\textsubscript{α} X-ray source with a photon energy of 1486.68 eV. The diameter of the X-ray beam spot was 800 µm. Survey spectra were recorded at a pass energy of 300 eV and core-level spectra recorded at pass energy of 20 eV. Quantification of the XPS data was performed after a Shirley background subtraction using the Thermo Scientific Avantage software which employs instrument modified Wagner sensitivity factors. Spectra were charge referenced to the C1s peak at 285.0 eV. XPS depth profiling was performed to study the composition of the layers, their inter-diffusion and concentration changes of the elements. Depth profiling was undertaken using an Ar\textsuperscript{+} ion gun operating at 3 kV and current density of 11.1 µA/cm\textsuperscript{2} (1 µA induced beam current, rastered over a 3x3 mm\textsuperscript{2} area). The detailed conversion of etch
rate into depth is given in Appendix A.

The XRD patterns were acquired using a Panalytical X’Pert Pro MPD diffractometer, with Cu Ka radiation ($\lambda = 1.5406$ Å) produced with an accelerating voltage of 40 kV and a current of 30 mA. The specimen was fixed on a stainless steel holder with plasticine. The diffraction pattern was acquired in a 20 range of 15°-75°, with a step size of 0.01° and a scan step time of 6 sec.

J-V measurements of the thin film solar cells were undertaken at AM1.5 (single pass illumination) with an ABET Technologies (SUN 2000) solar simulator employing a class-A xenon lamp (450 W). The optical output power density of 100 mW/cm$^2$ was calibrated using a mono-Fraunhofer c-Si reference cell and measured with a broadband thermopile power meter. Only the front side of the cell was illuminated with no intentional back reflection.

External Quantum Efficiency (EQE) measurements were carried out using a single monochromator Bentham spectral response spectrometer (PVE300). A xenon-halogen light source with unbiased conditions over the spectral range of 0.3 – 1.0 µm was employed. J-V and EQE measurements were carried out at CSER by CSER research staff.

4.4 Results

4.4.1 XPS Depth profiles

Figure 4-2 shows the XPS depth profiles of six CdTe solar cells. CSER-209 is the untreated solar cell and hence can be taken as the control sample. The top surface is contaminated with carbon and oxygen, due to the presence of surface hydrocarbons and a surface oxide on the CdTe. After few seconds of Ar$^+$ ion sputtering, the atmospheric contamination and oxide layer are removed. In the CdTe absorber layer, the Cd:Te ratio is approximately 1.0:1.0, as expected. The Cd$_x$Zn$_{1-x}$S layer exhibits a composition of Cd$_{0.41}$Zn$_{0.59}$S and hence the Cd and Zn have near 1:1 stoichiometry. The thickness of the CdTe and CdZnS layers is in good agreement with that expected (500 nm CdTe and 240 nm CdZnS). In the CdZnS layer, the Zn and S concentrations appear to be approximately symmetric about the centre of the layer and not indicative of diffusion into the absorber CdTe or underlying ITO layer. The Cd concentration is fairly stable through the CdZnS layer.

CSER-208 is the solar cell which has undergone the mildest CdCl$_2$ treatment (80 s deposition and annealed for 120 s). The XPS depth profile shows the following differences compared to the ‘control sample’: (a) the Zn concentration has reduced to 27 at.% (compared to 32 at.% for CSER-209); (b) S has diffused from the CdZnS layer into the CdTe at a level of approximately 1 at.% in the CdTe; (c) There is a small concentration of Te diffused into the CdZnS layer; (d) Cl was observed at concentrations of 0.4 at.% at the surface and 0.5 at.% at the CdZnS/ITO interface layer. This latter observation shows that Cl has diffused from the surface right through the absorber and window layers.
even for this relatively mild CdCl$_2$ activation treatment. It should be noted that the Zn and S concentrations in the CdZnS layer are now asymmetric, indicative of S and Zn diffusion into the CdTe layer, although no Zn (up to the detection limit) was observed by XPS in the CdTe. The depth profile of CSER-201, which has been exposed to the strongest CdCl$_2$ treatment (179 s deposition and 600 s annealing time) shows a greater degree of Zn depletion (12 at.%), higher S diffusion in the CdTe layer (approximately 2 at.%) and slightly higher diffusion of Te into the CdZnS layer.

To further investigate the effect of CdCl$_2$ treatment duration, two more samples CSER-362 and CSER-370 with higher Zn (DEZn flow rate 22 sccm) content in CdZnS layer were fabricated with the same annealing time of 600 s but with different CdCl$_2$ deposition duration (120 s and 179 s respectively). All elemental concentrations of Cd$_{1-x}$Zn$_x$S are given in Table 4-2. CSER-370 with higher CdCl$_2$ deposition duration (179 s) has lower Zn ($x=0.32$) than CSER-362 ($x=0.38$) which received a reduced CdCl$_2$ deposition duration (120 s).

To investigate the effect of higher Zn proportion in the CdZnS layer on the blue region of the solar spectrum, CSER-343 was fabricated with higher Zn (DEZn flow rate 44 sccm) than the previous samples. The sample was then processed with CdCl$_2$ treatment for 179 s prior to annealing of 600 s. The depth profile shows S diffusion higher than 1.2 at.% into the CdTe layer. The profiles of S and Zn get more asymmetrical in nature. The traces of Cl found at the end of the CdZnS layer suggest that Cl diffused through the whole solar cell structure. Zn was detected in very small amount only at surface (0.25 at.%) of the CdTe layer not through it, which suggest the Zn is depleted towards the CdTe surface. Zn and S concentrations are similar in the CdZnS layer with maximum values of 44 at.% and 43 at.% respectively while Cd drops down to 12 at.% in the middle of the layer and then rise up to 16 at.% near the crossover point with O and then slowly drops down to zero. The dip in Cd profile is different from all the other solar cells depth profiles.
Figure 4-2 (Left) XPS depth profiles of differently processed glass/ITO/CdZnS (240 nm)/CdTe (500 nm) solar cells and (right) their associative growth parameters.
To understand the different level of S diffusion in different devices, S 2p spectra of CSER-201, 209 and 362 in CdTe layer are shown in Figure 4-3. The S concentration in the CdTe layer has been quantified from these core-level spectra. The neighbouring Te4s peak has been normalised. CSER-209 does not show the presence of S in CdTe, whilst CSER-201 and 362 do show S in CdTe with CSER-201 exhibiting a higher concentration (2 at.%) than CSER-362 (1.2 at.%). This correlates with CSER-201 having been treated with a thicker CdCl$_2$ layer than CSER-362, whilst CSER-209 received no CdCl$_2$ anneal treatment.

![Figure 4-3 S 2p spectra of diffused S in CdTe layer.](image)

### 4.4.2 XRD Patterns

Figure 4-4 shows the XRD patterns of all six samples in the range of 20-52° 2θ (with the different compounds being indexed in different colours). The first prominent peak is CdTe (111) at around 23.8°, which is visible for all of the six samples. Three other CdTe peaks (200), (220) and (311) are seen in most of the patterns with small variations in position, intensity and shape. The peaks which correspond to the CdZnS layer in these samples ((102), (002), (102) and (100)) exhibit variable peak positions (lattice parameter), shape and intensity. Table 4-2 compares 2θ values for the compounds present in these devices. These XRD patterns show that every solar cell has slightly different crystal structures depending on the growth parameters, as at least one of the growth parameters was varied during fabrication of the solar cells - change of Zn concentration, CdCl$_2$ deposition time or annealing time. The ITO peaks are visible in all patterns and the Au peak from the contact pads is also observed in a few patterns.
Figure 4-4 XRD patterns of six differently processed CdTe solar cells in the range of 2θ 20-52º. (The different compounds are indexed in different colours: CdTe – red, CdZnS - green, Au – orange, ITO – cyan).

To study the crystal structure in more detail, the CdTe (111) and (422) peaks of all the solar cells are plotted in Figure 4-5. All the samples show a (111) peak at 23.81º, except CSER-209 where it is slightly lower at 23.77º. There is also a difference in peak shape. CSER-209 has only one visible peak. CSER-208 has a broader shoulder to the right hand side of the main peak, whilst CSER-362 and 343 have a more distinct shoulder. Cells CSER-201 and 370 exhibit clear doublet peaks, but in both cases, the peak at higher angles is still lower in intensity compared to the main (111) peak. For reflection (422) the trends for the devices is similar but the shape and intensity are more prominent than for the (111) reflection, with clear peak doublets being observed for many of the cells.

The XPS results shown in Figure 4-2 and those reported by others [124] have shown that the S diffusion from CdZnS layer to the CdTe layer increases with annealing time. This S diffusion is the cause of the second CdTe reflection peak at higher angles. It has been proposed that the new peak represents the formation of a new CdTe$_{1-y}$S$_y$ phase [15].
Table 4-2  A Table showing the solar cell efficiency, XPS determined elemental concentrations, XRD peak positions and widths (FWHM) and associated d spacings and grain sizes.

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<th>362</th>
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<th>208</th>
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<tr>
<td>Mean eff (%)</td>
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<td>5.2</td>
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<td>~1</td>
<td>0</td>
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<tr>
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<td>33</td>
<td>37</td>
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<td>Zn at.%</td>
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<tr>
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<td>47</td>
<td>49</td>
<td>31</td>
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<tr>
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<td>2θ (°)</td>
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<td>26.99</td>
<td>26.94</td>
<td>26.78</td>
<td>26.97</td>
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<tr>
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Figure 4-5 CdTe (111) and (422) peaks for all six samples. (a) and (b) are stacked up, while (c) and (d) are overlapped plots.
Calculated d-spacing (discussed in detail in Chapter 3) is given in Table 4-2 for the peaks, which shows that lattice spacing of the processed devices is smaller than the reference device.

In the processed devices, the grain size of CdTe (111) peak is not possible to calculate directly due to the presence of the shoulder peak, which broadens the linewidth of the (111) reflection than the expected linewidth from the grain size [125]. The estimation of the grain size was done by peak fitting of the reflection (Figure 4-6) and then using FWHM of the first peak.

Figure 4-6 Peak fitting of CSER-343

It is clear from the Table 4-2 that grain size extracted from CdTe peaks increases with the level of CdCl₂ activation and annealing process.

The Zn composition of CdZnS is different in every sample due to difference in growth parameters. The CdZnS (002) reflection of every device is shown in Figure 4-7 (a). Samples CSER-201, 370 and 343 have received the same CdCl₂ deposition and annealing duration but varied Zn composition in CdZnS layer. Zn content is lowest in CSER-201, greater for CSER-370 and then highest for CSER-343. It is clear that as Zn content is increased, the CdZnS (002) reflection shifts to higher angle.

Samples CSER-209, CSER-208 and CSER-201 had the same initial amount of Zn incorporated into the CdZnS layer. CSER-209 received no CdCl₂ annealing treatment and has no CdZnS (002) peak. CSER-208 annealed for 120 s has a small and broad peak and CSER-201 annealed for the longest duration 600 s has a sharp reflection of the CdZnS (002) plane at lower angle than CSER-208. The shift of this peak could be explained by the fact that long annealing duration reduces the amount of Zn in the CdZnS layer. CSER-362 and 370 have the peak at nearly similar angle; both samples have the same Zn content and annealing duration. The only difference is in CdCl₂ deposition duration,
which slightly changes the Zn composition, so the angle variation is not noticeable. The shift of $\theta$ to higher angle with the increase in Zn content was previously reported [126].

![Figure 4-7 (a) CdZnS (002) reflection in different CdTe solar cells, (b) plot of variation of lattice spacing of CdZnS (002) with change in Zn fraction in CdZnS layer.]

Figure 4-7 (b) shows that as Zn fraction has increased in the CdZnS layer, the d-spacing decreases. The shift of the Cd$_{1-x}$Zn$_x$S reflection with the change in $x$ is due to the replacement of cadmium by zinc. The shift of the peak towards higher diffracted angle (lower d-spacing) with increasing zinc in CdZnS layer is attributed to its ionic radius, which is smaller (74 pm) than cadmium’s (97 pm) ionic radius, which in turn shortens the interatomic bond length.

The XRD study shows that for the processed devices, the CdTe reflection shift to higher angle (smaller d-spacing) and shoulder peaks appear to the right of the main peaks that vary in intensity and shape depending on the growth parameters (including CdCl$_2$ activation and annealing process and Zn content in CdZnS layer) of the device. The Grain size of the CdTe reflection increases with CdCl$_2$ activation and annealing process. Higher Zn in the CdZnS layer shifts the CdZnS peak to higher angle (reduces d-spacing). An increase in the CdCl$_2$ deposition and annealing process shifts the CdZnS to shorter diffraction angles.

The performance of the solar cells are usually characterised by open circuit voltage, short circuit current, output power, fill factor and quantum efficiency etc. of a solar cell; to measure these parameters, current density – voltage (J-V) and External Quantum Efficiency (EQE (%)) plots are analysed.
4.4.3 J-V and EQE measurements

Figure 4-8 shows the J-V curves of the solar cells. There is a large difference between the reference (CSER-209) and the other CdCl$_2$ processed samples, with the reference showing a much lower open circuit voltage ($V_{oc}$) and current density. For the CdCl$_2$ processed solar cells, there is a variation in the open circuit voltage and current density (which in turn are related to output power, fill factor (FF) and efficiency), that are attributed to different levels of CdCl$_2$ activation/annealing treatment and Zn fraction in CdZnS layer. CSER-370 shows the highest $V_{oc}$ and CSER-343 shows a slightly higher $V_{oc}$ than CSER-201. These three samples have had the same degree of CdCl$_2$ activation/annealing treatment but different Zn fraction in CdZnS layer. CSER-370 and 343 were grown with higher acceptor (As) concentrations than CSER-201 in the CdTe absorber layer, which can contribute to a rise in $V_{oc}$ [127-131] but still the $V_{oc}$ of CSER-343 is lower than that for CSER-370. This difference can be explained by the substantially higher level of Zn in the window layer of CSER-343 which would result in a low FF due to a larger series resistance [132, 133], which is also clear from the more sloping gradient of the J-V plot near $V_{oc}$. CSER-370 has a slightly higher Zn content in the window layer compared to CSER-201. This cannot explain the significant increase in $V_{oc}$ alone and suggests that other factors, such as an increase in acceptor concentration for CSER-370 compared to CSER-201 may also be contributing to the enhanced $V_{oc}$.

![Figure 4-8 J-V curves of the CdTe/CdZnS solar cells with different process parameters.](image)

One trend which is very apparent across the whole range of CdCl$_2$ processed samples is that a higher degree of CdCl$_2$ activation/annealing leads to a higher $V_{oc}$. The 3 samples with the highest $V_{oc}$ values (CSER-370, CSER-343 and CSER-201) are those which have been exposed to the same high
degree of CdCl$_2$ treatment (179 s activation, 600 s anneal). Reducing the CdCl$_2$ activation to 120 s lowers the $V_{oc}$ (CSER-362) and another decrease in the activation time (80 s) and anneal time (120 s) results in $V_{oc}$ being reduced further (CSER-208).

Figure 4-9 shows the EQE at shorter wavelengths of six differently processed samples. CSER-343 has the best spectral blue response with double absorption edge. This is representative of the window bi-layer having different levels of Zn [134]. CSER-209 has a better blue response in comparison to the other CdCl$_2$-treated devices (CSER-201, 362 & 370) but has the lowest EQE (%) overall. CSER-370 has improved blue response compared to CSER-362 and 201. An enhanced blue response (higher EQE values at lower wavelengths) is due to the wider band gap of the window layer, which can be altered by a change in the Zn fraction of the CdZnS layer. An increase in the Zn concentration in the window layer widens the bandgap resulting in blue shift of the spectral response.

Figure 4-9 EQE (%) of differently processed solar cells at shorter wavelengths.

Except CSER-343 other processed samples are red shifted at the window layer absorption edge compared to the reference sample CSER-209 (i.e. without CdCl$_2$ deposition and annealing process), this could be due to some Zn leaching out from Cd$_{1-x}$Zn$_x$S window layer after CdCl$_2$ and annealing treatment making its bandgap smaller [23].

4.5 Discussion

The composition and structural changes due to variation in growth parameters affect the solar cell performance. The device with the highest Zn concentration in the window layer gave rise to a low FF due to large series resistance [132, 133], which is also clear from the low gradient near the $V_{oc}$ of the J-V plot. The CdZnS grain size for this device is smaller than all of the other devices, which results in
a large grain boundary surface area. It has been observed that this increases the inter-grain barrier height and reduces carrier mobility [126].

It has previously been reported that high process temperatures and CdCl$_2$ activation treatment result in compositional changes such as S diffusion into the CdTe layer from Cd$_{1-x}$Zn$_x$S (or CdS) window layers [128-132]. S diffusion throughout the CdTe layer has also been observed in the XPS depth profiles in this work. The S diffusion into CdTe gives rise to changes in the XRD spectra, with a new peak emerging at higher 2-theta values. The new peak indicates a phase with a decrease in d-spacing compared to CdTe associated with the replacement of Te (large ionic radius) by S (small ionic radius). Thus, the inter-atomic bond length is reduced and as noted previously, suggests the formation of a CdTe$_{1-y}$S$_y$ phase.

Figure 4-10 (a) shows that there is a clear correlation between the S diffusion and CdCl$_2$ activation time, with a greater S diffusion into CdTe at longer annealing times. The opposite trend is found for the concentration of Zn in Cd$_{1-x}$Zn$_x$S, where the Zn concentration in the window layer decreases with longer annealing times (Figure 4-10 (b)). The presence of Cl at the CdZnS/ITO interface and small concentrations of Zn at the surface of CdTe layer, suggests that the Zn is reacting with Cl to form ZnCl$_2$ near the CdTe surface, which has a melting point below the annealing temperature, hence likely to be leading to vapourisation and desorption from the CdTe and could be why no solid product is detected by XPS.

![Graphs showing S diffusion and Zn fraction in CdTe and Cd$_{1-x}$Zn$_x$S layers](image)

*Figure 4-10 XPS results of a) S diffusion in CdTe layer and b) Zn fraction in Cd$_{1-x}$Zn$_x$S layer after different degree of CdCl$_2$ deposition and annealing duration.*
It is interesting to note that for the devices exposed to the same duration of CdCl$_2$ activation treatment but with different Zn contents during fabrication (DEZn flow rate 19, 22 or 44 sccm), the XPS compositional data show reduced S diffusion (2, 1.7 and 1.1 at.% respectively) and the XRD showed a less prominent CdTe$_{1-y}$S$_y$ peak. This suggests that higher concentrations of Zn in the CdZnS layer suppresses the degree of S diffusion, possibly due to competition between Zn and S both diffusing out from the window layer into the absorber layer.

From the XPS depth profiles and J-V curves, it is clear that the S diffusion and $V_{oc}$ both increase with stronger CdCl$_2$ activation treatments. To find the correlation between them, the $V_{oc}$ is plotted against S concentration in the CdTe absorber layer in Figure 4-11, it is clear that $V_{oc}$ increases with higher levels of S diffusion. This can be explained by intermixing of the two layers which reduces strain related defects at the p-n junction. The XPS depth profiles show that an increased S diffusion into the CdTe layer is accompanied by increased Te diffusion into the CdZnS layer. It has already been reported that interdiffusion of CdTe and CdS result in both CdTe$_{1-y}$S$_y$ and CdS$_{1-z}$Te$_z$ compounds [135]. So, it is proposed that interdiffusion of layers would result in strain relaxation between CdTe and CdZnS layer that would reduce recombination centres (strain related defects) giving improved $V_{oc}$. The XRD results have shown that compared to the reference device, the CdCl$_2$ treated devices exhibit a smaller CdTe d-spacing and this reduction in lattice parameter can be due to relaxation of the stress produced by lattice mismatch [136] between the two layers and/or due to interdiffusion of these layers [125, 136]. It can easily be seen that the $V_{oc}$ of one of the devices (circled in Figure 4-11) is higher than the others. This additional improvement can be attributed to a high concentration (~1 x 10$^{19}$ atoms/cm$^3$) of acceptor doping (As) in the CdTe absorber layer [136] in that particular device compared to the other devices which had doping levels of ~2-5 x 10$^{18}$ atoms/cm$^3$.

![Figure 4-11 Variation of $V_{oc}$ with the diffused S in CdTe$_{1-y}$S$_y$ layer.](image-url)
Hence in ultra-thin CdTe solar cells, the $V_{oc}$ can be improved by increasing the acceptor concentration in the CdTe layer and also by increasing the degree of CdCl$_2$ activation treatment. However, it has been shown previously that the CdCl$_2$ process can deteriorate the spectral response in blue region of CdZnS/CdTe cells [23]. In this work, the variation in spectral response at shorter wavelengths was found to change with Zn concentration in the CdZnS layer and the device with the highest Zn concentration exhibited a double absorption edge (Figure 4-9). It can be seen in Figure 4-10(b) that the Zn concentration in the CdZnS layer reduced with an increase in the CdCl$_2$ deposition time. It has previously been noted that a variation in the Zn concentration in CdZnS can change the bandgap of the window layer and consequently affect the blue response of the solar spectrum [23, 24]. For the devices studied here, to understand the effect of Zn composition on the blue region of the spectrum, the Zn fraction ($x$) of Cd$_{1-x}$Zn$_x$S layer was calculated from the XPS depth profile data and plotted against the wavelength at the onset of absorption in the CdTe layer (Figure 4-12).

![Figure 4-12 Wavelength at onset of absorption in CdTe layer as a function of Zn fraction $(x)$ in Cd$_{1-x}$Zn$_x$S layer.](image)

It is clear that with the increase in Zn concentration in the window layer the onset of absorption shifts towards shorter wavelength, enhancing the blue response. Usually after the CdCl$_2$ activation process, with the modest amount of Zn in the window layer, the CdS (nucleation layer) and CdZnS merge to form (via Zn diffusion) one CdZnS layer [132]. The double absorption edge at the shorter lengths could be the result of excessive amounts of Zn in the CdZnS layer and a CdS nucleation layer that remain a bi-layer after CdCl$_2$ treatment and inter-diffusion would produce two Cd$_{1-x}$Zn$_x$S layers with different Zn concentrations [134], which could be the reason of getting double edge absorption in
343. The dip of Cd 3d_{5/2} (CSER-343 in Figure 4-2) in the XPS depth profile of the Cd_{1-x}Zn_{x}S layer confirms the double layer of Cd_{1-x}Zn_{x}S layer with different Zn fraction resulting in a double absorption edge in the EQE (%) plot (Figure 4-9).

### 4.6 Conclusions

Ultra-thin Cd_{1-x}Zn_{x}S/CdTe solar cells with absorber layer thicknesses of 0.5 µm were processed under different levels of CdCl_{2} activation and annealing treatment. The composition and microstructural changes in solar cells were investigated employing XPS and XRD and correlated to optical properties. The following conclusions can be drawn from the results:

- The most prominent effect of this treatment was the interdiffusion of the window and absorber layers. S diffused throughout the CdTe absorber layer reaching the back contact, replacing Te and forming a ternary CdTe_{1-y}S_{y} phase. Te diffused through the window layer to the ITO. This interdiffusion resulted in a reduced lattice parameter. The S diffusion increases with degree of CdCl_{2} activation and annealing treatment that in turn increases V_{oc}.

- Increasing the degree of CdCl_{2} activation treatment leads to progressively more Zn being leached out of the device, which would be the result of the formation of ZnCl_{2} that has a melting point below annealing temperature.

- The Zn fraction in the Cd_{1-x}Zn_{x}S layer affects the optical properties of the solar cells. Higher Zn concentrations cause the EQE absorption edge to shift towards shorter wavelengths, enhancing the blue response. A very high Zn concentration of 44 at.% in the CdZnS layer produced a double absorption edge at shorter wavelengths. In addition, the series resistance increased due to the small grain sizes of the Cd_{1-x}Zn_{x}S layer giving rise to a poor FF. This could be due to the presence of a bilayer within the Cd_{1-x}Zn_{x}S with different Zn fractions.

- High levels of Zn within the absorber layer suppressed S diffusion in the CdTe layer due to competition between the diffusing Zn and S species.

- A significant increase in V_{oc} can be achieved with high As⁺ acceptor concentrations (~1 x 10^{19} compared to ~2.5 x 10^{18} atoms/cm³) in the absorber layer.
4.7 Summary

This chapter presented chemical and microstructural results on ultra-thin CdTe based solar cells following different degrees of CdCl₂ activation treatment. It is a stand-alone chapter in this thesis which has resulted from a collaboration between the Centre for Solar Energy Research (CSER), University of Glyndwr and the University of Surrey which took place during my PhD research. The results were found to be very useful to CSER and a clear correlation could be found between the CdCl₂ treatment process parameters, the composition/structure following the treatment and the electrical/optical properties. The work resulted in the publication of one paper (see Appendix C). The remainder chapters of this thesis will focus on developing and characterising different passivation treatments for CdZnTe single crystal detectors.
5 Bromine methanol chemical etching and H$_2$O$_2$ passivation of the CdZnTe surface

5.1 Introduction

The performance of a CZT device is dependent on charge generation, charge transport and intrinsic electric field etc. that are correlated to extended defects such as grain boundaries, cracks, pipes, tellurium inclusions [47] and surface properties of CZT [69, 137, 138]. Surface roughness induced by slicing and dicing of the crystal from its ingot, is reduced by mechanical polishing, followed by chemical polishing usually with bromine in methanol which both further improves the roughness and removes microstructural damage resulting from the mechanical polishing process. Different concentration 0.2 – 5 % of BM has been used for a duration ranging from 30 to 120 s [71, 73, 139, 140]. However, chemical polishing produces a non-stoichiometric surface (Te rich layer) and the stoichiometry can be improved by passivating the surface most commonly by H$_2$O$_2$ for a specific exposure time varying from 30 s-15 min [71, 73, 74].

In this chapter, the CZT surface is examined for the presence of growth defects and mechanically polished CZT single crystals have been chemically etched using BM concentrations. To study the effect of various concentrations and exposure durations at CZT surface, two concentrations of 0.2 and 2.0 % for varying times (5 - 120 s) were selected. For the latter, changes in surface composition have been determined by XPS depth profiling. An Ar$^+$ ion sputter rate of CZT has been evaluated by Ar$^+$ ion sputtering a CdTe thin film of known thickness. This has enabled an accurate value of the Te rich layer thickness to be determined for the different BM exposures. These BM etched surfaces were further passivated using a 30% H$_2$O$_2$ solution and the oxide thickness determined from XPS data using two different methods: (i) the standard Beer-Lambert expression employing a single photoelectron take-off angle; (ii) a Beer-Lambert based methodology using a range of photoelectron take-off angles. A comparison is made of the oxide thickness determined by the different analytical methods. Most of the work presented in this chapter is published [141] (Appendix C).
5.2 Experimental procedure

5.2.1 Sample preparation

CZT single crystal samples grown using the modified vertical Bridgman method were obtained from Yinnel Tech Inc., USA. The samples had dimensions of 8x8x5 mm$^3$. The two samples had different bulk compositions, determined by quantitative Energy Dispersive X-ray (EDX) analysis to be Cd$_{0.8}$Zn$_{0.2}$Te and Cd$_{0.9}$Zn$_{0.1}$Te. Each sample was mechanically polished, with the final polish being performed using a 0.05µm alumina suspension. The samples were then dipped in freshly prepared BM solutions with concentrations of either 0.2 or 2.0 % for different time durations (5, 15, 30, 60 or 120 s). After BM exposure, the samples were rinsed with iso-propanol and kept in methanol to avoid oxidation. The samples were removed from the methanol immediately prior to being placed in the ultra-high vacuum of the XPS instrument. After each step during the chemical treatment, the samples were blow-dried with nitrogen gas. The solution pH was determined using a pH strip indicator. For the passivation treatment, the procedure above was repeated followed by exposure in 30 wt.% of H$_2$O$_2$ for 15s. After each BM etching or passivation treatment the CZT surface was re-polished using the alumina suspension ready for the next exposure.

The surface morphology was examined by a Hitachi S3200 SEM with an additional Oxford Instruments X-ray detector for EDX and the acquired spectra were quantified using the INCA software [142]. The details of experimental parameters of XPS analysis are given in chapter 4.

5.3 Results and Discussion

5.3.1 General CZT surface

The surface of the mechanically polished CZT crystal is shown in Figure 5-1(a). Abrasive scratches, defects and some residual particles can easily be seen at the surface. Defects are produced during growth of the CZT crystal. Most of the defects (probable inclusions) found at surface were of hexagonal shape and the diameter range varied between 4 and 14 microns. Figure 5-1(b) and (c) shows such a defect and its associated EDX linescans. The defect is clearly visible at the surface of the sample and not buried in the bulk. From the linescan, in the region of the defect, the tellurium signal becomes more intense whilst the cadmium signal drops. Hence, this defect is a tellurium inclusion formed during crystal growth [66, 143]. Figure 5-1(d) and (e) shows an SEM image and EDX linescan of another hexagonal shaped defect. However, in this case the elemental signals do not change in intensity across the linescan. This suggests that a Te inclusion was present at the surface of the crystal and the process of mechanical polishing has removed it, leaving behind a crater.
Figure 5-1 SEM image of a) mechanical polished CZT surface, b) and d) are hexagonal defects found at surface, c) and e) are EDX linescans of these defects respectively.

A Zn inclusion embedded in the surface near a crack was also found at the surface which is shown in Figure 5-2. The EDX maps from this inclusion show the overall uniform distribution of Te, Cd and Zn from the general surface (coloured signal), but at the inclusion area there is an absence of Te and Cd whereas a strong Zn signal can be seen, indicating the segregation of Zn. The inclusion shape is irregular with non-uniform structure features compared to the Te inclusion. The EDX point spectra inside and outside the inclusion are shown in Figure 5-2(b). Spectrum 1 taken from the middle of the inclusion shows sharp Zn peaks and small concentrations of other elements. Spectrum 2 from the general surface shows elemental peaks of bulk CZT.

Figure 5-2 SEM image of Zn inclusion a) EDX map and, b) point spectra inside (spectrum 1) and outside(spectrum 2) of the inclusion.
It has been found that due to a higher segregation constant, Zn segregates near the heel of the ingot during the crystal growth [144]. J. Zhu et al have suggested that the growth of Zn inclusions could be due to the segregation of Zn during the crystal growth [67].

5.4 CZT surface composition after BM etching

To investigate the effect of BM etching at surface, samples were examined by XPS. Figure 5-3 compares the XPS survey spectra of 0.2% BM etched surface to a sputtered cleaned CZT surface. Both survey spectra have elemental peaks of CZT; however cadmium and zinc peaks are suppressed in 0.2% BM etched surface compared to the sputtered clean CZT surface. In addition to this, the 0.2% BM etched surface has a hydrocarbon peak of carbon and oxygen due to surface contamination.

![XPS survey spectra](image)

**Figure 5-3 XPS survey spectra of a CZT surface (black) and 0.2 % BM etched CZT surface (red) Ar+ ion sputtered for 30 s.**

Figure 5-4 shows core-level spectra of the most intense peaks of tellurium, cadmium and zinc acquired for the 0.2% BM etched and sputtered clean CZT surfaces. The binding energy of the Te 3d5/2 peak for the sputtered cleaned surface is 572.5 eV which is attributable to tellurium in CZT, whereas 0.2% BM etched surface shows a binding energy of 573 eV for this peak that corresponds to elemental tellurium. The atomic concentration of tellurium is higher, while that of cadmium and zinc are lower for the 0.2% BM etched surface compared to the CZT bulk.
The change in surface composition from exposing CZT in 0.2% BM for times of 5, 15, 30, 60 and 120 s is shown in the XPS profiles given in Figure 5-5. For all exposure times, Te is clearly enriched at the surface with a progressive decrease in the Te concentration until the bulk concentration of 50 at.% is attained. For all of the exposure times, there is little difference in surface composition and the Te rich layer has a thickness of 1.3 ± 0.2 nm. At the surface, the binding energy of the Te 3d$_{5/2}$ peak was found to be 572.9 ± 0.1 eV and this drops to a value of 572.5 eV in the bulk, consistent with Te in a CZT matrix [10]. The bulk concentrations of Cd and Zn were found on average to be 37 and 13 at.% respectively. It can be seen that Te enrichment occurs at the expense of both Cd and Zn and the XPS determined average surface concentrations for the different exposure times of Te, Cd and Zn are 66, 28 and 6 at.% respectively (except for the 5s exposure, where the Te enrichment is slightly lower and the surface concentrations of Te, Cd and Zn are 60, 30 and 10 at.% respectively).
Figure 5-5 XPS depth profiles of CZT exposed to 0.2% BM for various time periods (5s, 15s, 30s, 60s and 120s).

The XPS profiles for CZT exposed to 2.0 % BM for durations of 5, 15, 30, 60 and 120s are presented in Figure 5-6. The depth profiles again show Te to be enriched at the surface in a similar manner for all of the exposure times with a progressive decrease in the Te concentration until the bulk concentration (Te = 50 at.%) is reached. The Te enrichment for the 2.0 % BM exposure is the same as for the 0.2 % BM exposure, with the XPS results giving an average Te concentration for the different exposure times of 66 at.% at the surface. The Te enrichment layer thickness has increased slightly to 1.8 ± 0.2 nm and is again invariant with exposure time except for the 5 s exposure duration thickness.
It is clear from these results that there is no difference in outer surface composition for either the two different BM concentrations or for different exposure times. These results are consistent both with the work of Rouse et al [29] where no substantial differences in [Cd+Zn]/Te ratio were found for exposures of 1, 3 and 9 min exposures in a 5 % BM solution [71] and with Bensouici et al’s [145] plot of Te/(Cd+Zn) ratio for different BM concentrations of 1-4 % which show very similar values for all BM concentrations. However, the enriched Te layer thickness was found to increase slightly as the BM concentration was raised from 0.2 to 2.0 %, similar to the results of Özsan et al [71]. In this work, the pH of the 0.2 and 2.0 % BM solutions was found to be approximately 3 in both cases. The absence of a significant change in pH probably explains why there is very little difference in the Te enrichment region observed for the different BM concentrations, and the slight increase in the enriched Te layer thickness may be caused by the 2 % BM concentration having a slightly lower pH than the 0.2 % BM solution. The invariance of the Te enrichment with exposure time may be explained by the thickness of the Te enriched surface layer being very small (< 2 nm); thus the rate of reaction is so rapid that even very short exposure times do not influence the Cd and Zn etching process.
5.4.1 \( \text{H}_2\text{O}_2 \) Passivation treatment

The effect of the passivation treatment (15 seconds exposure in 30 wt.% \( \text{H}_2\text{O}_2 \)) on the 0.2 and 2 % BM exposed surfaces can be seen from the changes in the Te 3d\(_{5/2}\) peak presented in Figure 5-7 and Figure 5-8. In addition to the elemental Te 3d\(_{5/2}\) (Te\(_{\text{ele}}\)) component at 572.8 eV, a peak at 576.3 eV corresponding to TeO\(_2\) (Te\(_{\text{ox}}\)) is observed. For the 0.2 % BM treated surface (Figure 5-7), following passivation treatment, the Te\(_{\text{ox}}$/Te\(_{\text{ele}}\) peak intensity ratio increases with BM exposure time up to 120 s of exposure, whilst for the 2.0 % BM there is no difference in peak intensity ratio beyond an exposure time of 30s. This indicates that the oxide grown is slightly thicker for longer BM exposure times.

![Te 3d\(_{5/2}\) peaks](image)

**Figure 5-7** The Te 3d\(_{5/2}\) peak for CZT exposed in 0.2% BM for periods of 5-120 s followed by 15 s exposure in 30 wt.% \( \text{H}_2\text{O}_2 \). The CZT bulk peak occurs at a binding energy of 572.9 eV and its oxide component at 576.3 eV.
Figure 5-8 The Te 3d_{5/2} peak for CZT exposed in 2% BM for periods of 5-120 s followed by 15 s exposure in 30 wt.% H\textsubscript{2}O\textsubscript{2}. The CZT bulk peak occurs at a binding energy of 572.9 eV and its oxide component at 576.3 eV.

XPS depth profiles plotted using the Te_{ox} and Te_{ele} peaks for the 0.2 % and 2 % BM exposed samples after passivation are given in Figure 5-9 and Figure 5-10. All of the passivated surfaces show very similar behaviour, with the Te_{ox} peak intensity being stronger than the Te_{ele} at the surface (as expected from Figure 5-7 and Figure 5-8), but the Te_{ele} intensity becomes dominant within a sputter time of 5 s and beyond this the oxide intensity tails off gradually until no oxide is observed beyond a sputter time of 30 s. This somewhat diffuse oxide/bulk interface can be explained by the sample roughness. For both the 0.2 and 2.0 % BM exposures, the passivated surfaces with the shortest BM exposure time (5 s) exhibit a slightly thinner oxide layer than those exposed for longer times, indicating the kinetics of the oxide growth process is apparently slower than the BM etching process.
Figure 5-9 XPS depth profile (using Te$_{5/2}$ CZT bulk and Te$_{5/2}$ oxide peaks) of CZT surfaces exposed to 0.2 % BM for various times followed by a 15 s passivation treatment in 30 wt.% $H_2O_2$.

Figure 5-10 XPS depth profile (using Te$_{5/2}$ CZT bulk and Te$_{5/2}$ oxide peaks) of CZT surfaces exposed to 2 % BM for various times followed by a 15 s passivation treatment in 30 wt.% $H_2O_2$. 
With regard to determining the oxide thickness, metal oxides are known to generally exhibit much lower sputter rates than metals, so the TeO$_2$ thickness cannot be determined from the profile using the previously determined CZT sputter rate. Hence, oxide thicknesses have been calculated using established procedures based on the Beer-Lambert expression.

### 5.4.1.1 Oxide thickness calculation

Two methods have been used to calculate oxide thickness, a simple Beer-Lambert expression based on photoemission at a single take-off angle and a Beer-Lambert expression based methodology employing a range of take-off angles.

**(i) The Beer-Lambert Expression Employing a Single Photoelectron Take-off Angle**

The intensity of photoelectrons emitted from a depth greater than $d$ at an angle $\theta$ to the surface normal is given by the Beer-Lambert expression [103]:

$$I = I_0 \exp \left( -\frac{d}{\lambda \cos \theta} \right)  \quad 5.1$$

where $I_0$ is the intensity from an infinitely thick substrate and $\lambda$ is the photoelectron attenuation length. For calculating overlayer or oxide thicknesses, manipulation of the Beer-Lambert expression (discussed in chapter 3, section 3.2.4.1) and use of the core level elemental and oxide photoelectron peaks, $I_{el}$ and $I_{ox}$ respectively, gives rise to the following equation for the oxide thickness, $d_{ox}$:

$$d_{ox} = \lambda_{ox} \cos \theta \ln \left( \frac{I_{ox}}{I_{el}} + 1 \right)  \quad 5.2$$

The attenuation length of photoelectrons in the oxide layer, $\lambda_{ox}$, is calculated using Seah’s equation given in [146]

$$\lambda = \frac{(5.8+0.0041Z^{1.7}+0.088E^{0.93})a^{1.82}}{Z^{0.38}(1-W)}  \quad 5.3$$

where $a$ is the lattice parameter (nm), $E$ is the photoelectron kinetic energy (eV) $Z$ is the average atomic number of the oxide and $W = 0.02E_g$, which is the bandgap of the material.

**(ii) The Beer-Lambert Expression Employing Multiple Photoelectron Take-off Angles**

With the possibility of acquiring the photoelectron intensities at different take-off angles, then a more rigorous approach can be used to test for the presence of a discrete oxide overlayer and to determine the oxide thickness [103]. In this case, the Beer-Lambert expression can be manipulated to yield the following equation for the oxide thickness, $d_{ox}$:
\[ d_{ox} = \lambda \cos \theta \ln \left[ 1 + \left( \frac{I_{ox}}{I_{el}} \right) \left( \frac{I_{ox}^\infty}{I_{el}^\infty} \right) \right] \]  \hspace{1cm} 5-4

where \( I_{ox}^\infty \) and \( I_{el}^\infty \) are the intensities of bulk TeO\(_2\) and elemental Te respectively, their ratio can be represent by \( R^\infty \) that can be found by manipulating some bulk material parameters, given by [103]:

\[ R^\infty = \frac{D_{TeO_2} F_{Te} \lambda_{Te,TeO_2}}{D_{Te} F_{TeO_2} \lambda_{Te,Te}} \]  \hspace{1cm} 5-5

\( D_{Te} \) and \( D_{TeO_2} \) are the elemental Te and TeO\(_2\) bulk densities (6.24 and 5.83 g/cm\(^3\) [147] respectively), \( F_{Te} \) and \( F_{TeO_2} \) are the molar masses of elemental Te and TeO\(_2\) (127.6 and 159.6 g/mol respectively) and \( \lambda_{Te,Te} \) and \( \lambda_{Te,TeO_2} \) are the photoelectron attenuation lengths of Te 3d\(_{5/2}\) electrons in elemental Te and TeO\(_2\), calculated by the Seah’s equation [146] to be 1.7 and 1.5 nm respectively. \( I_{ox}/I_{el} \) can replace by \( R \), hence equation 5-4 can be rearranged to give:

\[ \ln \left[ 1 + \frac{R}{R^\infty} \right] = \frac{d_{ox}}{\lambda} \frac{1}{\cos \theta} \]  \hspace{1cm} 5-6

Then for a set of angle resolved XPS data recorded at different values of take-off angles, \( \theta \), on the left-hand side of the equation can be plotted against \( 1/\cos \theta \). A straight line can be drawn through the data, with the slope corresponding to \( d_{ox}/\lambda \). Knowing the attenuation length, the oxide thickness can be determined.

The XPS Thetaprobe angle resolved XPS (ARXPS) capability allows data to be recorded over 16 angles between 25 and 81° without rotation of the sample. The slope was found for the data points not exceeding an angle of 50°, to avoid interference of elastically scattered electrons (discussed in chapter 3, section 3.2.4.1). An example of the ARXPS data recorded for a 0.2 % BM exposure for 120 s seconds followed by a passivation treatment of 15 s in 30 wt.% H\(_2\)O\(_2\) when using equation 5-6 is given in Figure 5-11. The plot shows a clear linear relationship and the oxide thickness, \( d_{ox} \), calculated from the slope (0.83) of the straight line was found to be 1.25 nm.

The TeO\(_2\) thickness calculated for single angle and angle resolved data is shown in Table 5-1. The oxide thickness trends as a function of exposure time for the different calculation methods are very similar and in both cases the oxide thickness after 5 s of BM exposure is slightly smaller than for other exposure times. The oxide thicknesses calculated from the simplified Beer-Lambert expression give the same oxide thickness for 5 s of BM exposure for both concentrations (0.2 and 2%). For the 0.2% BM exposure, there is a gradual increase in oxide thickness as the exposure duration increases. While for 2% BM exposures, after 5 s there is an increase in thickness which remains the same for all
other exposure durations. In both cases (0.2 and 2% BM exposure) the highest value of oxide thickness is around 1 nm. The oxide thicknesses calculated from ARXPS data are slightly higher than the thicknesses obtained from the simplified Beer-Lambert expression except for the exposure of 0.2% BM for 5 s; otherwise the trend for both H₂O₂ concentrations is similar to that for the simplified Beer-Lambert expression. The highest value of oxide thickness in this case is around 1.25 ± 0.12 nm. Considering the methodologies employed, it is likely that the ln(1+ R/R∞) vs 1/cosθ plot will give more accurate values than the Beer-Lambert expression given in equation 5-2 as fewer assumptions are made in the former approach. The different values of D, F and λ for Te and TeO₂ are taken into account in Equation 5-5, whereas the simple Beer-Lambert expression in equation 2 assumes that λ and I∞ are the same for Te and TeO₂. Furthermore, the multiple angle approach considers photoelectron intensity data for a number of take-off angles and the linear regression fit will tend to reduce the experimental error in determination of oxide thickness compared to a single intensity measurement from one take-off angle.

![Graph](image)

**Figure 5-11 Plot to determine the oxide thickness, d_{ox}, of a CZT surface exposed in 0.2 % BM for 120 s seconds followed by passivation in 30 wt.% H₂O₂ for 15 s.**

For CZT etched in BM concentrations between 0.2 and 5 %, followed by a 30 s exposure in 30 % H₂O₂, Özsan et al reported oxide thicknesses between 1.6 and 2.8 nm [71]. Chen et al used a 5 % BM solution followed by 1 – 15 minute exposure in 15 % H₂O₂ and found oxide thicknesses between 2.1
and 4.5 nm [11]. According to Özsan et al [71], increasing the BM concentration from 2 to 5% followed by 30 s exposure in 30% H₂O₂ results in only a minimal increase in oxide thickness (from 2.7 to 2.8 nm). In this work, using the same simple Beer-Lambert expression employed by Özsan et al (equation 5-2), the oxide thickness is calculated to be 1 nm. The difference in the oxide thickness results compared to that given by the other authors [71, 73] is most probably due to the method of calculating the attenuation length, λ. Özsan et al [71] used the simpler, empirical Seah and Dench [104] approach, which yields a value of 2.63 nm, rather than the more refined Seah expression [146] employed in this work, which gives a value of 1.5 nm.

Table 5-1: Comparison of the TeO₂ thickness calculated by a simplified Beer-Lambert expression (single take-off angle) compared to ARXPS data (range of take-off angles) after exposing CZT in 0.2% and 2% BM for varying times followed by a 15 s passivation treatment in 30 wt.% H₂O₂.

<table>
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<th>BM concentration</th>
<th>5s</th>
<th>15s</th>
<th>30s</th>
<th>60s</th>
<th>120s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single angle (simplified Beer-Lambert expression)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2 %</td>
<td>0.83</td>
<td>0.93</td>
<td>0.96</td>
<td>0.97</td>
<td>1.05</td>
</tr>
<tr>
<td>2 %</td>
<td>0.84</td>
<td>0.99</td>
<td>0.98</td>
<td>0.99</td>
<td>1.00</td>
</tr>
<tr>
<td>Angle resolved data Beer-Lambert</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2 %</td>
<td>0.89</td>
<td>1.03</td>
<td>1.09</td>
<td>1.13</td>
<td>1.25</td>
</tr>
<tr>
<td>2 %</td>
<td>1.04</td>
<td>1.17</td>
<td>1.23</td>
<td>1.25</td>
<td>1.25</td>
</tr>
</tbody>
</table>
5.5 Conclusions

CZT single crystals have been exposed to etching treatments using a BM concentration of 0.2 and 2.0 % for exposure times between 5 and 120 s. XPS depth profiles have shown that both treatments resulted in the formation of a Te rich surface region. Varying the exposure time had no effect on the thickness of the Te rich region, which was found to extend to a depth of 1.3 ± 0.2 nm for the 0.2 % BM etch and 1.8 ± 0.2 nm for the 2.0 % BM etch. The invariant effect of exposure time between 5 and 120 s is considered to be due to the rapid etching process of such a thin Te enriched layer. The similarity in the surface compositions for the two different BM concentrations is ascribed to the comparable pH (pH ≈ 3) of both solutions but the increase in the Te rich layer thickness for the higher concentration of BM is probably due to this solution having a slightly lower pH.

The BM exposed surfaces were passivated using a 15 s H₂O₂ treatment. A thin TeO₂ layer was formed. XPS depth profiles showed there to be little change in the oxide thickness between the surfaces BM etched at different concentrations or etch times, but the 5s exposure in both 0.2 % and 2 % BM gave rise to a slightly thinner oxide layer than the longer BM exposure times. Determination of the oxide thickness using a Beer-Lambert expression and single photoelectron take-off angle showed a similar trend to that using Beer-Lambert expression and multiple photoelectron take-off angles. For H₂O₂ treated samples, the former method gave an oxide thickness in the range of 1.00 ± 0.07 nm whilst the latter yielded an oxide thickness of 1.25 ± 0.12 nm.

5.6 Summary

In this chapter, the effects of (i) BM chemical etching on the CZT surface and (ii) an H₂O₂ passivation treatment have been investigated. The changes in surface composition and thickness of the layers formed at the surface resulting from these treatments have been quantified and results discussed.

During this work an XPS depth profile of a commercially available Redlen’s CZT detector was acquired for an EngD student. The analysis revealed the presence of a non uniform oxide layer of average thickness of 77 nm at the electrode and the CZT interface [148] (detailed in Appendix B). The oxide thickness was thick enough compared to the oxide layer produced by H₂O₂ passivation treatment (1.25 nm). It was then decided to study the passivants that can develop thick oxide layers and later on to compare the performance of devices prepared by these passivants. In the next chapter, the effect of using different passivation agents on the surface oxide formed on CZT surface will be studied.
6 Passivation treatments

6.1 Introduction

Passivation treatments are used to reduce the surface leakage current in many technological applications. The chemical and/or physical passivation process shields the surface of a material by deactivating it electrically and/or chemically from its surrounding conditions. The passivation treatment oxidises the surface in two different ways either by producing a reaction product with the bulk elements at the surface or depositing a different material layer of appropriate properties to develop a protecting oxide layer at the surface of the semiconductor. Selection of a suitable passivation agent depends on the main characteristics required from the resultant oxide layer, but often the requirements are that it should have fewer electrically active defects and the layer should be a uniform, stoichiometric oxide, exhibiting strong adherence to the bulk material with the capability of minimising diffusion of the reactive species to the surface of the material [149].

A number of different passivating agents are used for oxidising the Te rich surface of CZT samples and a comparison of the passivation layers formed from four different treatments will be examined in this chapter. H$_2$O$_2$ is most commonly used and studied of the oxidising agents [71, 73, 74]. When using a NH$_4$F /10%H$_2$O$_2$ treatment, researchers have found that this results in a thicker, stoichiometric oxide with a lower leakage current [149, 150]. It has also been shown that instead of using just KOH as an oxidising agent, the electrical performance improves if the samples are exposed to KOH followed by a KCl or NH$_4$F/10%H$_2$O$_2$ treatment [76, 151, 152]. NaClO-DI water of varying concentration has also been employed as a passivating agent [77]. A comprehensive study is required to investigate the differences between the surfaces subjected to these passivation agents. Hence, in this chapter, the effect of the following different passivating agents: (i) 15% KOH+15% KCl; (ii) 5% NaClO-DI water; (iii) NH$_4$F/10%H$_2$O$_2$; (iv) 15% KOH + 10% NH$_4$F/10% H$_2$O$_2$ on the CZT surface will be presented. To study the difference in the thickness of the oxide layer with treatment time, two of the treatments (5% NaClO-DI water and NH$_4$F/10%H$_2$O$_2$) were exposed for different duration times (10, 20 or 40 min). These passivated samples were then characterised employing different analytical techniques.
6.2 Experimental procedure

6.2.1 Sample preparation

To study the passivation layers formed on Te rich CZT surfaces for the different treatments; the following experimental procedures were followed:

All CZT samples were mechanically polished with alumina suspensions of 3, 0.3 and 0.05µm respectively and chemically etched in 2% Bromine in Methanol for duration of 2 min followed by the different passivation treatments, given below.

1. Ammonium fluoride/ hydrogen peroxide (10%NH₄F/10% H₂O₂- DI-water)
   The sample was immersed in a solution of 10% NH₄F/10% H₂O₂ in deionised water (DI-water) for a specific duration (10, 20 or 40 min.)

2. Potassium hydroxide followed by ammonium fluoride/hydrogen peroxide (15% KOH+10% NH₄F/10% H₂O₂ in DI-water)
   The sample was immersed in a 15% KOH-DI water solution for 40 min, then rinsed with DI-water and blown dry with nitrogen, prior to exposure to 10% NH₄F/10%H₂O₂ in deionised water for 40 min.

3. Sodium hypochlorite- deionised water
   The CZT crystal was exposed to 5% NaClO-DI water for a specific duration (10, 20 or 40 min.)

4. Potassium hydroxide-deionised water followed by potassium chloride- deionised water solution (15% KOH+15% KCl)
   The sample was immersed in solution of 15% KOH- DI water for 40 min then rinsed with DI-water and blown dry with nitrogen, prior to exposure to 15% KCl in DI-water for 40 min. duration.

6.3 Analytical techniques

The surfaces of the passivated samples were mostly examined by XPS, but to provide information on the structure of the surface, a few passivated surfaces were also analysed employing SEM, XRD and atomic force microscopy (AFM). The SEM micrographs were acquired with a Quanta FEG 200 microscope by FEI, operating in high vacuum with a beam voltage of 20 to 30 kV. The GIXRD patterns were acquired using a Panlytical X’Pert Pro MPD diffractometer, with Cu Kα radiation (λ = 1.5406 Å) generated using an accelerating voltage of 40 kV and a current of 30 mA. The specimen was fixed on a stainless steel holder with plasticine. The diffraction pattern was acquired in a 2θ range of 15°- 65°, with a step size of 0.1° and a scan step time of 6 sec.

The AFM images were recorded using an NT-MDT Solver Magnetic Force Microscope in tapping, 'topology' mode. Standard silicon carbide tips were employed with a resonant frequency around 270 kHz.
6.4 Results

6.4.1 SEM, AFM and XRD

An SEM micrograph, AFM 3D image and GIXRD pattern of a 15% KOH + 10%NH₄F/10%H₂O₂ passivated surface are shown in Figure 6-1. The SEM image in Figure 6-1(a) shows an irregular morphology with a large density of island features. Figure 6-1(b) is the AFM 3D image. The average surface roughness is 12.9 nm. GIXRD has been employed to observe any structural changes occurring to the CZT passivated surfaces. Figure 6-1(c) shows a typical XRD pattern of an oxidised surface. The XRD results show a main CZT (111) peak with another small CZT (220) peak. In addition to these peaks, the 15% KOH (40 min) + 10%NH₄F/H₂O₂ (40 min) treatment has a broad hump between 24°-35° 2θ, which is above the usual background. X-rays generated from an amorphous phase scatter in many directions leading to a broad hump, instead of intense narrow peaks as in a crystalline structure. The references for TeO₂ (01-074-1131), TeO₃, CdTeO₅ (00-049-1757) and CdO all have peaks between 24°-35°, which suggest that the passivated surface contains oxide of either tellurium oxide and CdO or CdTeO₅ or could be a combination of both type of oxides. The roughness of the surface is probably a result of the growth of a thicker oxide layer and hence greater chemical etching of the CZT, leading to an increased roughness.

Figure 6-1 Analytical results for the 15% KOH + 10%NH₄F/10%H₂O₂ passivated surface: a) SEM image b) AFM 3D image, and c) GIXRD pattern.

6.4.2 XPS analysis and depth profiling

XPS has been employed as the main tool to examine the different passivated CZT samples. The core-level photoelectron peaks, photoelectron-induced Auger peaks (of Te and Cd) and valence band spectra were all recorded. To investigate the composition and thickness of the oxide film formed, depth profiles were also acquired.
6.4.2.1 **Shallow core levels and valence band**

Shallow core-level spectra (Te 4d and Cd 4d) of the 5% NaClO-DI water (10, 20 and 40 min) and 15% KOH + 15% KCl treated samples are plotted in Figure 6-2(a). The Cd and Te 4d peak binding energies and their FWHM, together with the binding energy of the valence band maximum are given in Table 6-1. The spin-orbit splitting of the Cd 4d peak could not be resolved by the XPS spectrometer, whereas the Te 4d \( \frac{5}{2} \) and Te 4d \( \frac{3}{2} \) are clearly resolvable and binding energy values are given for both peaks. For the spectra shown in Figure 6-2 (a), there are two components present for the Te 4d \( \frac{5}{2} \) and Te 4d \( \frac{3}{2} \) peaks. The lower and higher binding energy peak pairs represent the Te elemental (Te-element) and Te oxide (Te-ox - TeO\(_2\)/CdTeO\(_3\)) peaks respectively [76]. The binding energies of the Cd 4d and Te 4d\( \frac{5}{2} \) peaks between the 5% NaClO (10, 20 and 40 min) and KOH + KCl are similar but the relative intensity ratio of the Te 4d\( \frac{5}{2} \) elemental and oxide peak pairs is different in each case. Following the KOH + KCl treatment, the oxide/metal peak ratio is higher than for the 5% NaClO treatment peak, indicating that a thicker oxide layer has formed on the KOH + KCl surface compared to the NaClO treated surfaces.

![Figure 6-2 Shallow core level spectra (a) NaClO-DI (10, 20 and 40 min) and KOH+ KCl, (b) NH\(_4\)F passivated surfaces](image)

The Te 4d and Cd 4d peaks for the NH\(_4\)F/10%H\(_2\)O\(_2\) (10, 20, 40 min) and KOH+ NH\(_4\)F/10%H\(_2\)O\(_2\)
treated samples are shown in Figure 6-2(b) and their binding energies are compared in Table 6-1. The Te 4d$\frac{3}{2}$, 4d$\frac{5}{2}$-element peak pairs can be easily seen at the lower edge of Te 4d$\frac{3}{2}$, 4d$\frac{5}{2}$-ox peaks for NH$_4$F/10%H$_2$O$_2$ -10 min treatment and are just visible for NH$_4$F/10%H$_2$O$_2$- 20 min and KOH- NH$_4$F/10%H$_2$O$_2$ treated samples, while for NH$_4$F/10%H$_2$O$_2$- 40 min treatment there is no evidence of the Te 4d$\frac{3}{2}$, 4d$\frac{5}{2}$-element peaks. The reduction in the intensity of the Te 4d- element peak at longer exposure times and for the KOH+NH$_4$F/10%H$_2$O$_2$ treated samples suggests that the oxide is much thicker for these samples compared to the NH$_4$F/10%H$_2$O$_2$ -10 min, 5% NaClO and 15% KOH+ 15% KCl treated samples.

The Te 4d$\frac{3}{2}$, 4d$\frac{5}{2}$-ox spin-orbit pair are distinguishable for the NH$_4$F/10%H$_2$O$_2$ -10 min treatment sample, but the peaks broaden, such that the 4d$\frac{3}{2}$ becomes a shoulder on the 4d$\frac{5}{2}$ peak with an increase in the exposure time and there is just a single broad peak for the KOH+NH$_4$F/10%H$_2$O$_2$ treatment.

**Table 6-1 Binding energy (BE), FWHM of the Te 4d and Cd 4d peaks and measured valence band maximum (VBM) values for the different passivated CZT surfaces and a standard CdO thin film grown by MOCVD in CSER.**

<table>
<thead>
<tr>
<th>Elements</th>
<th>KOH- KCl</th>
<th>NaClO-10</th>
<th>NaClO-20</th>
<th>NaClO-40</th>
<th>NH$_4$F-10</th>
<th>NH$_4$F-20</th>
<th>KOH-NH$_4$F-40</th>
<th>CdO</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE 4d$\frac{3}{2}$</td>
<td>40.0</td>
<td>39.8</td>
<td>40.1</td>
<td>40.0</td>
<td>40.1</td>
<td>42.0</td>
<td>40.8</td>
<td>----</td>
</tr>
<tr>
<td>TE 4d$\frac{5}{2}$</td>
<td>41.3</td>
<td>41.0</td>
<td>41.6</td>
<td>41.9</td>
<td>41.5</td>
<td>44.0</td>
<td>43.9</td>
<td>----</td>
</tr>
<tr>
<td>TE 4d$\frac{3}{2}$-oxide</td>
<td>43.4</td>
<td>43.1</td>
<td>43.6</td>
<td>43.7</td>
<td>43.5</td>
<td>44.3</td>
<td>45.7</td>
<td>45.3</td>
</tr>
<tr>
<td>TE 4d$\frac{5}{2}$-oxide</td>
<td>44.7</td>
<td>44.6</td>
<td>45.0</td>
<td>44.9</td>
<td>45.0</td>
<td>45.7</td>
<td>45.5</td>
<td>45.3</td>
</tr>
<tr>
<td>Cd 4d</td>
<td>10.6</td>
<td>10.7</td>
<td>11.1</td>
<td>11.1</td>
<td>11.0</td>
<td>11.7</td>
<td>11.3</td>
<td>10.7</td>
</tr>
<tr>
<td>VBM</td>
<td>0.43</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
<td>1.3</td>
<td>2.5</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Cd 4d-VBM</td>
<td>10.2</td>
<td>10.3</td>
<td>10.6</td>
<td>10.6</td>
<td>9.7</td>
<td>9.2</td>
<td>9.0</td>
<td>9.10</td>
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<tr>
<td>FWHM (eV)</td>
<td>Te 4d</td>
<td>1.6</td>
<td>1.4</td>
<td>1.3</td>
<td>1.6</td>
<td>1.5</td>
<td>2.7</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>Cd 4d</td>
<td>1.5</td>
<td>1.6</td>
<td>1.5</td>
<td>1.5</td>
<td>1.6</td>
<td>1.6</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The Te 4d$\frac{3}{2}$ - 4d$\frac{5}{2}$ peaks broaden and overlap for the NH$_4$F/10%H$_2$O$_2$ surface treatments and particularly for long exposure times compared to the KOH + KCl and NaClO-DI water treated surfaces. There could be several factors that may enhance the peak width, i) variation in oxide composition, i.e. there may be different Te oxides present in NH$_4$F/10%H$_2$O$_2$ samples, ii) surface roughness can result in differential charging i.e. variation in localised charge state of the surface, iii)
spin-orbit splitting in outer $d$ levels would be more prominent than the closely bond core level $d$ shells due to the variation in crystal environment known as crystal field effect [153]. There is an observable spin-orbit splitting in KOH + KCl and NaClO-DI water treated surfaces which could be due to a crystal field effect suggesting that the thin oxide layer could have defined (crystalline) structure. For long exposure of NH$_4$F/10%H$_2$O$_2$ treated surfaces the Te 4d$_{3/2}$ and Te 4d$_{5/2}$ merge into one broad peak which could be the result of a weak crystal field effect, giving an indication of an amorphous oxide at the surface which is in agreement with the XRD results.

The region at the start of an XPS spectrum (i.e. 0-15 eV) is known as the valence band (VB) region. In the valence band, many closely spaced energy levels are occupied by electrons of low binding energy, which can be de-localized and participate in chemical bonding. In insulators and conductors, the density of electron states differ in such a way that occupied valence band and empty conduction band are separated by the band gap, while for the conductors, the overlap of these bands occur with the higher occupied state being the Fermi level ($E_f$). This makes the valence band useful in the study of chemical bonding and electronic structure of materials related to device applications, and to compare with band structure calculations [153-155]. The valence band region of differently passivated CZT surfaces was examined.

For the passivated CZT crystals, this region includes O 2p peak and 5s, 5p peaks of Cd and Te as well as the Cd 4d peaks (at a binding energy of ~11 eV). The VB region between 0 - 6 eV for all of the passivated samples together with that of Ar$^+$ ion sputtered clean CdZnTe (as reference) is given in Figure 6-3.

For the CZT crystal native surface, the 5s and 5p valence orbitals exhibit two main peaks. The valence band maximum (VBM) is determined by linearly extrapolating the sharp drop of the VB edge to the baseline. Values of the VBM and the difference between the Cd 4d peak binding energy and the VBM of all treated surfaces are given in Table 6-1. Considering first the general VB spectral shape, the two main peaks observed for the CZT sample, are no longer present for the passivated surfaces (Figure 6-3(b) and (c)) and have been replaced by a broad peak with the VBM shifted away from the Fermi level. The shape of the VB region for the KOH + KCl, NaClO - DI water and NH$_4$F/10%H$_2$O$_2$-10 minute treated surfaces is similar, most probably due to the oxide thickness being thinner for these samples compared to the 20/40 minute NH$_4$F/10%H$_2$O$_2$ and KOH+ NH$_4$F/H$_2$O$_2$ treated surfaces. The latter samples also have the VB further away from Fermi level, as would be expected for a thicker oxide.

The reduction of peak P1 and shifting of the VBM away from the Fermi energy in passivated surfaces suggest that some valence electrons are consumed in bonding to develop an insulating layer. The consumption of more electrons moves the VB edge further away from Fermi level, which suggests that 15%KOH + 15%KCl and 5%NaClO-DI water treated surfaces have thinner insulating layers compared to 10%NH$_4$F/10%H$_2$O$_2$ and 15%KOH + 10%NH$_4$F/10%H$_2$O$_2$ treated surfaces. This insulating nature of the surface is more prominent in long exposed NH$_4$F/10%H$_2$O$_2$ treated surfaces.
Figure 6-3 Valence band spectra (a) CZT crystal, (b) 5%NaClO-DI (10, 20 and 40 min) and 15%KOH+ 15%KCl, c) NH₄F/10%H₂O₂ passivated surfaces.

6.4.2.2 Auger parameter analysis

As the chemical state of an element changes, this generally leads to a shift in core-level binding energies, but there is also a change in the X-ray generated Auger peak binding energy. For some elements, the shift in the core levels BEs are notable (e.g. Te) but this is not the case for some other elements (e.g. Cd). However, Auger peak shifts can be considerable due to the involvement of three electrons in the Auger electron emission process. The addition of the binding energy of core-level photoelectron and the kinetic energy of the X-ray excited Auger electron is known as the Auger parameter (AP), given the symbol $\alpha$, which is a useful additional tool in identifying chemical states at surfaces/interfaces using XPS. The shift in the AP, $\Delta \alpha$, for different chemical states is related to the
final state effect given by:

$$\Delta \alpha = 2\Delta R$$

where $\Delta R$ represents shift in extra atomic relaxation energy (related to the polarization energy) of the neighbouring environment affecting the core-ionized atom [156-158]. For non-conductive surfaces, charging effects under the X-ray beam, make it difficult to see the real change in core level binding energy. But, charging shifts the core level and the Auger peak by an equal amount, so use of the AP to identify chemical states make it very useful in the study of insulators even without the use of valid charge referencing [157]. Hence, in principle, the AP will only change if there is a change of chemical state.

The AP alone is a powerful tool; however it is a ‘one dimensional’ value. To make it more useful, the kinetic energy of the Auger transition is plotted against the binding energy of the core level electron and the Auger parameter (AP) is plotted diagonally on the 2nd vertical axis. This is called the Wagner plot [157]. Figure 6-4 (a) and (b) show Auger (KE) and core (BE) peaks of Te and Cd. As an increase in charging due to the presence of a non-conducting material shifts the binding energy to a higher value and the kinetic energy to a lower value, the distribution of the data points in a Wagner
plot can be analysed as follow

a) If a set of data points, lying along one of the diagonal (AP) lines in the diagram is selected, then moving up the line towards the top right of the diagram, the points higher up the line will have a higher conductivity than those lower on the line.

b) Moving perpendicular to these diagonal lines gives an indication of chemical shift.

The Wagner plot has been used to study the different chemical states of Cd and Te for various Cd and Te compounds and surface treatments associated with this work. The different treated surfaces plotted were: CdZnTe–mechanical polished, BM etched, subjected to the different passivation treatments, CdTe and standards of Cd, Te and CdO. For the elemental Cd and Te standards, the surface was first analysed to give values for its native oxide, CdO and TeO$_2$ respectively, and then the surface was Ar$^+$ ion sputtered to analyse the elemental bulk. In the Wagner diagram, for Cd and Te; the kinetic energy of the Cd M$_{4,5}$N$_{4,5}$ and Te M$_{4,5}$N$_{4,5}$ peaks are plotted against the binding energy of Cd 3d$_{5/2}$ and Te 3d$_{5/2}$ (without charge correction). The Wagner plots for the different compounds and treated surfaces of Cd and Te are given in Figure 6-5 and Figure 6-6 respectively. For comparison AP data from the NIST XPS database is also plotted [159].

Figure 6-5 shows that pure Cd has the highest AP at around 789 eV, CZT and CdTe are dispersed along the 788 eV line, BM etched surfaces have a slightly lower value at 787.6 eV. The oxidised surfaces have lower AP values. CdO has an AP of 786.9 eV and the passivated CZT surfaces are dispersed around an average AP of 786.5 eV.

The AP of CZT and CdTe are 1 eV lower than Cd due to the low polarization energy of Te, dragging down the relaxation energy of CdTe (CZT). BM etched surfaces are Te enriched, dropping the AP value further. The AP of the oxidised CdZnTe surfaces is significantly lower; this is attributed to lower polarizability of the oxygen atom, which has high electronegativity ($X_O = 3.5, X_{Te} = 2.1$ [160]) ; this results in a low relaxation energy due to the small contribution of electron density available to screen the Cd 3d$_{5/2}$ core-hole. The passivated surface points lie around the AP line of CdO in a range of ± 0.2 eV, suggesting the same chemical state. The distribution of points for the passivated surfaces along the AP line is most probably due to the thickness of the oxide layer formed which varies for the different treatments, as it is known that a very thin insulating layer on conductive materials may shift to higher kinetic energy (lower binding energy) due to an increase in the polarization energy or extra atomic relaxation energy [161] compared to the thick insulating layer. The thicker oxide layer for the 10%NH$_4$F/10%H$_2$O$_2$-water (20 and 40 min) and KOH + 10%NH$_4$F/10%H$_2$O$_2$-water (40 min) treated surfaces located on the lower left of the AP line compared to the thinner oxide layers grown on the 10%NH$_4$F/10%H$_2$O$_2$-water (10 min) and 5% NaClO/DI water (10, 20 and 40 min) treated surfaces, which lie along the top right of the AP line.
Figure 6-5 Wagner plot of different Cd compounds

Figure 6-6 shows the Te 3d$_{5/2}$ Wagner plot. Standard Te has an AP greater than 1065 eV, BM etched surfaces have an average AP value of 1064.5 eV and CZT/CdTe exhibit an average AP of 1063.7 eV. Again, the oxidised surfaces lie to the bottom left of the Wagner plot. The native oxide of standard Te has an AP value of 1063.5 eV. The NH$_4$F/H$_2$O$_2$ (10, 20 and 40 min) and KOH+ NH$_4$F/H$_2$O$_2$ treated surfaces lie lower on the AP line, again due to the presence of a thicker oxide layer. The NH$_4$F/H$_2$O$_2$ (10 min) treatment lies higher up on the line than the NH$_4$F/H$_2$O$_2$ (20 and 40 min) and the KOH+ NH$_4$F/H$_2$O$_2$ (40 min) treated surfaces representing a thin TeO$_2$ layer for the shorter treatment time. The AP value for CdTeO$_3$ at 1061.4 eV is similar, but slightly lower in energy compared to TeO$_2$ and TeO$_3$. The consistency of the AP for different oxidation states and neighbouring environment of Te could be due to localized shielding [162].
The Cd Wagner plot suggests that for all passivated surfaces, Cd most probably exists in the form of CdO, as these points within a small range (± 0.2 eV) around the AP line of CdO. Te is probably found in two different chemical states, TeO$_2$ and TeO$_3$, depending on the passivation treatment and its duration. The similarity in the AP for TeO$_2$ and TeO$_3$, combined with the movement along the AP line caused by different oxide thicknesses makes any assignment tentative. But, for KOH+KCl, NaClO/DI-water (10, 20 and 40 min) and NH$_4$F/H$_2$O$_2$ (10 min) treated surfaces, Te is possibly found more in the TeO$_3$ state whereas for the KOH + NH$_4$F/H$_2$O$_2$ (40 min) and NH$_4$F/H$_2$O$_2$ (10, 20 and 40 min) processed surfaces, it could be mostly TeO$_2$. 

Figure 6-6 Wagner plot of different Te compounds
The valence band and Auger parameter study have shown there to be different chemical states and varied insulator layer thicknesses at the surface depending on the passivation treatment and its exposure duration. To investigate the composition with depth and thickness of these layers, all the passivated surfaces were depth profiled.

6.4.2.3 XPS depth profiles of passivated surfaces

XPS depth profiling was performed for passivated surfaces under the same sputtering conditions as previously described. After charge correction and peak fitting, the elemental atomic concentrations were plotted against sputtered time which was then converted into depth using a defined sputter rate. To find the thickness of the profiled depth, the sputtering rate must be known. In XPS, usually the sputter rate of a standard sample of known thickness is used to calibrate the depth. In this study, the passivated surfaces were metal oxides, to examine the oxide thickness in cross-section; TEM, SEM and EDX were employed on a FIB sectioned passivated CZT surface. The analytical results and calculations used to determine the oxide thickness are described in detail in Appendix A. It was decided that it was best to employ the sputter rate based on the oxide thickness determined by the SEM cross-section. This method is based on a direct measurement of the oxide thickness, is not composition dependent and appeared to give sputter rate values for the profiles which agreed best with the acquired XPS depth profile data.

6.4.2.3.1 15% KOH (40min) + KCl (40 min) passivation treatment

The elemental core-level spectra of carbon, oxygen, tellurium, cadmium, and zinc for the 15% KOH+15% KCl treated CZT surface at different sputter levels are shown in Figure 6-7. At the surface; adventitious carbon was found. The O 1s peak was resolved into three components, the main peak at 530.3 eV (29 at.%), is attributed to metal oxide, the second peak observed at 531.5 eV (5 at.%) is associated with the presence of hydroxide (OH\(^{-}\)) and third peak observed at 532.9 eV (3 at.%) is due to adsorbed water [163]. For the Te 3d\(_{5/2}\) peak, at higher binding energy, the 576 eV peak represents tellurium oxide (8 at.%), while the lower binding energy peak at 573 eV corresponds to metallic tellurium (4 at.%). For the Cd 3d\(_{5/2}\) peak, there was just a single component at a binding energy of 405 eV (8 at.%) and zinc was found at 1021.6 eV (2 at.%). The hydroxide peak of O 1s indicates the formation of metal hydroxide that could be either Cd(OH)\(_{2}\) or Te(OH)\(_{6}\) or combination of both. To get the right stoichiometry, the molar ratio of metal to oxygen concentration should be 1:2 and 1:6 for cadmium and tellurium, respectively. As the available oxygen for hydroxide is 5 at.%, the amount of oxygen associated with hydroxide is either 2.5 at.% of Cd or 0.83 at.% of Te or less than these values in case the formation of combination of both metal hydroxides. The remaining Cd(Te) would be 5.5 at% (~7 at.%). For the Te, Cd, and Zn based oxide compounds at the surface, there are different possibilities based on the XPS results obtained and these will be examined in terms of a stoichiometric evaluation. Firstly; considering the formation of CdTeO\(_{3}\); as 7 at.% of Te oxide was
present, then for CdTeO$_3$, this requires a further 7 at.% of Cd and 24 at.% of O. This analysis suggests that the presence of single oxide CdTeO$_3$ is not favourable as 5 at.% of O remains unaccounted for. Furthermore, as elemental Te can be observed then some fraction of the Cd signal corresponds to the bulk CZT (as cadmium cannot be resolved in its oxide and elemental components due to the small difference in binding energy between Cd and CdO), hence there is a further excess of oxygen. A second possibility is a combination of metal oxides, TeO$_2$ (Te-ox: 7 at.% and O: 14 at.%), CdO (Cd: 8 at.% and O: 8 at.%), and ZnO (Zn: 2 at.%, O: 2 at.%). This stoichiometric analysis leaves a smaller excess of oxygen (3 at.%) and is possible. Another group of metal oxides could be TeO$_3$ (Te-ox: 7 at.% and O: 21 at.%), leaving an excess of 8 at.% of oxygen, which could combine with Cd and Zn to form CdO and ZnO. This stoichiometric analysis results in some cadmium and zinc remaining which could represent bulk CZT, so this combination may be more appropriate. At a depth of 1 nm; carbon and oxygen due to adsorbed water are removed. This pure oxide surface exhibits an O concentration of 46 at.%, Cd 21 at.%, Te (metal) 13.5 at.%, Te (oxide) 9.5 at.% and Zn 7 at.%. The Te 3d$_{5/2}$ peak shows a new peak at 573.7 eV, which is usually attributed as mixed tellurium oxide. The high concentration of oxygen and lower intensity of tellurium oxide would suggest the presence of metal oxides TeO$_3$, CdO and ZnO. At 2.5 nm of depth there is still a high concentration of oxygen (40 at.%), again suggesting a high proportion of oxygen in the metal oxide. Further sputtering leads to the bulk CZT being reached. The compositional changes in surface layer up to a few nm in the depth profile could be due to preferential sputtering, as it is reported that during sputtering process of an oxide layer; preferential sputtering is an issue that can reduce oxidation states [164, 165]. During the sputtering, the elemental Te peak exhibited a binding energy corresponding to CZT not to metallic Te and the O/OH peak was found with oxide peak that could vary the oxide concentration at surface. Surface roughness due to the passivation treatment can also contribute to the variation in oxide composition.
Figure 6-7 Elemental core-level spectra of carbon, oxygen, tellurium, cadmium and zinc for the 15% KOH (40 min) + KCl (40 min) passivated surface at different depths.

Figure 6-8 (a) shows the depth profile of the 15% KOH +15% KCl. The adventitious carbon at the surface has a thickness of 1 nm. As the carbon signal decreases, the oxygen (oxide) and Te (oxide) signals increase. There is a small amount of oxygen related to hydroxide which disappears at a depth of 3 nm. Tellurium oxide is removed at nearly 4.5 nm. However, elemental tellurium is seen at the surface, which is an indication of the variation in oxide thickness across the surface. As the sputtering proceeds, the Te elemental peak increases in intensity until in the bulk CZT, where tellurium, cadmium and zinc attain their bulk stoichiometry. The depth profile is replotted in Figure 6-8 (b), now considering the total tellurium (oxide + elemental) concentration. Te concentration profile is higher than that of Cd in the oxide layer. However, Te/(Cd+Zn) ratio is less than 1 due to the presence of a high Zn concentration. In XPS, the average oxide thickness is generally taken where the oxygen and metal peaks cross-over in the profile. It is interesting to note that the tellurium and cadmium intensities are very similar throughout the profile, but for all of the profiles given in this thesis for surfaces which have been passivated, the oxide thickness is taken at the point where the O signal first crosses over with one of the metal signals. Hence, in Figure 6-8 (b), this is O 1s and Te 3d_{5/2} signals. This gives an average oxide thickness of 3.0 nm.
6.4.2.3.2 5% NaClO/DI water (10, 20 or 40 min) passivation treatment

Figure 6-9 (a), shows XPS depth profiles of CZT samples treated with 5% NaClO for durations of 10, 20 or 40 min. For the O signal, the atomic concentration of peaks related to OH/H$_2$O is not included in the oxygen profile. After a 10 min exposure, at the surface, the concentrations of the different elements are O (oxide) is 20 at.%, Cd 9 at.%, Te-oxide 4 at.% Te-elemental 2 at.% and Zn 1 at.%, with the remainder due to surface C contamination. After few seconds of Ar$^+$ ion sputtering, the C contamination is removed and the atomic concentration for the cleaned surface has changed to O 46 at.%, Cd 28 at.%, Te-elemental 14 at.%, Te-oxide 8 at.% and Zn 4 at.%. Subsequently, profiling deeper into the surface, the O decreases slowly and after 8 nm it completely disappears, to give the expected bulk Te, Cd and Zn stoichiometry. The depth profiles for all three exposure times are very similar. To examine if there is any noticeable change in the oxide layer composition or thickness, the profiles have been redrawn using the total tellurium (oxide + elemental) concentration in Figure 6-9 (b). For the 10 min exposure, the Te/(Cd+Zn) ratio at the surface is 0.6, which slightly increases to 0.7 around the interface and then to approximately 1.0 in the CZT bulk. For the 20 min exposure time, the Te/(Cd+Zn) ratio at the surface is 0.87, dropping down to 0.75 at interface and attains a value of approximately 1.0 in the CZT bulk. Increasing the treatment time to 40 min gives a Te/(Cd+Zn) ratio of 0.99 at the surface which reduces to 0.8 at interface and yields a value of approximately 1.0 in the CZT bulk. The average oxide thickness is similar for all exposure durations, but appears to decrease slightly with exposure time. The values determined from the profiles in Figure 6-9 (b) are 2.7, 2.4 and 1.7 nm for 10, 20 and 40 min durations respectively.
Figure 6-9 XPS depth profile of 5% NaClO-DI water (10, 20 or 40 min): a) all elements and, b) with total Te (Te 3d$_{5/2}$-el + Te 3d$_{5/2}$-oxide).

The large O concentration observed in the oxide layer would be consistent with the presence of the oxides TeO$_3$/TeO$_2$, CdO and ZnO to form the oxide layer. Again, the substrate CZT signal is observed in the XPS spectra from the surface and the long O tail up to 8 nm is indicative of an oxide which has substantial variation in thickness across the surface.

6.4.2.3.3 10% NH$_4$F/10% H$_2$O$_2$ (10, 20 or 40 min) passivation treatment

Detailed elemental analysis is presented for the 40 min 10% NH$_4$F/10% H$_2$O$_2$ passivation treatment, as the 10, 20 and 40 min processed samples showed very similar results. The elemental core-level (charge corrected and peak fitted) spectra of carbon, oxygen, tellurium, cadmium and zinc of 10%NH$_4$F/10%H$_2$O$_2$ (40 min) treated CZT surface at different sputter levels are shown in Figure 6-10 and corresponding binding energies and atomic concentrations are given in Table 6-2.
Figure 6-10 Elemental core-level spectra of carbon, oxygen, tellurium, cadmium and zinc for the NH$_4$F/H$_2$O$_2$ (40 min) passivated surface  a) at surface, b) after 20 s of sputtering and c) in the middle of the oxide layer.

Adventitious carbon found at the surface is removed after few seconds of Ar$^+$ ion sputtering. Oxygen was resolved into three peaks. The main peak is attributed to oxide, the binding energy of which varied in the range of 530.5 – 530.1 eV, the second peak was observed up to few nanometers in depth associated with hydroxide (OH$^-$) and the third peak observed only at surface is due adsorbed water. At the surface, the Te 3d$^{5/2}$ peak at higher binding energy (576.3 eV) represents tellurium oxide, while the elemental tellurium peak at lower binding energy (573.5 eV) corresponds to metallic tellurium. As sputtering proceeds (in to the middle of the oxide layer), the tellurium oxide peak shifts...
to 576 eV, whereas the elemental tellurium peak is shifted to a binding energy of 572.6 eV with an increase in intensity representing bulk CZT. For cadmium, a broader Cd 3d$_{5/2}$ peak (FWHM 1.15 eV) was observed at the surface with a binding energy of 405.1 eV. In the bulk, the peak became sharper (FWHM 0.92 eV) and was observed at 405 eV, representing bulk CZT. The Zn 2p$_{3/2}$ peak was observed at 1021.8 eV at the surface and shifts to a lower value of 1021.5 eV in the oxide layer, but back to 1021.8 eV in bulk CZT.

Table 6-2 XPS carbon, oxygen, tellurium, cadmium and zinc peak binding energies and concentrations for CZT following 40 mins passivation in 10%NH$_4$F/10%H$_2$O$_2$. Values are given at different points in the depth profile.

<table>
<thead>
<tr>
<th></th>
<th>Peak binding energy (FWHM)</th>
<th>Atomic percent (%) ± 2%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At the surface After 20 s of sputtering In the middle of the oxide layer Bulk CZT</td>
<td>At the surface After 20 s of sputtering In the middle of the oxide layer Bulk CZT</td>
</tr>
<tr>
<td>C 1s (total)</td>
<td>285 (-) - - -</td>
<td>29 (-) - - -</td>
</tr>
<tr>
<td>O 1s</td>
<td>530.5 (1.31) 530.1 (1.26) 530.2 (1.34) -</td>
<td>42 (-) 60 (-) 60 (-) -</td>
</tr>
<tr>
<td>O (OH)</td>
<td>531.6 (1.19) 531.2 (0.7) - -</td>
<td>4 (-) 1 (-) - -</td>
</tr>
<tr>
<td>O-H$_2$O</td>
<td>532.8 (1.50) - - - -</td>
<td>2 (-) - - - -</td>
</tr>
<tr>
<td>Te 3d$_{5/2}$-el</td>
<td>573.5 (2.19) 572.8 (1.95) 572.6 (1.71) 572.5 (1.0)</td>
<td>0.4 (-) 4 (-) 3 (-) 51 (-)</td>
</tr>
<tr>
<td>Te 3d$_{5/2}$- oxide</td>
<td>576.3 (1.38) 576 (1.28) 576 (1.31) -</td>
<td>13 (-) 17 (-) 13 (-) -</td>
</tr>
<tr>
<td>Cd 3d$_{5/2}$</td>
<td>405.1 (1.15) 405 (1.16) 405 (1.18) 405 (0.78)</td>
<td>7 (-) 16 (-) 20 (-) 44 (-)</td>
</tr>
<tr>
<td>Zn 2p$_{3/2}$</td>
<td>1021.8 (1.92) 1021.6 (1.7) 1021.5 (1.41) 1021.8 (1.2)</td>
<td>1.6 (-) 3 (-) 4 (-) 6 (-)</td>
</tr>
</tbody>
</table>

Figure 6-11 shows the XPS depth profile for the CZT passivated with 10%NH$_4$F/10%H$_2$O$_2$ for durations of 10, 20 and 40 minutes. The inset shows the profile in the surface region. The oxygen profile represents the concentration of the O 1s main peak, associated with oxide only. The oxide layer clearly increases in thickness with passivation treatment time. The differences in oxide layer for the
different treatment times are the following: i) in the surface region (~10 nm), there is a small sharp peak in the O profile for the 10 min treated sample, but this is either not so noticeable or not present for the 20 and 40 min treatments respectively; ii) the intensity of the O 1s signal decreases almost linearly towards the interface for the 10 min treated sample, there is a slower decrease for the 20 min treatment, whereas for 40 min treated sample the O signal is stable for up to ~70 nm. The oxygen concentration in oxide layer is 48 at.% in the 10 min treated sample, which increases to 55 at.% and 60 at.% for the longer durations of 20 and 40 min respectively; iii) the oxide layer becomes progressively thicker as the treatment time increases; The depth profiles are replotted in Figure 6-11 (b) with the total tellurium (oxide + elemental) signal for more rigorous analysis. It can be seen that at the surface, the total Te concentration is greater than the (Cd + Zn) concentration, but throughout the rest of the oxide, the total Te is lower than the (Cd + Zn) concentration. For both the 10 and 20 min exposure times, the ratio of Te to (Cd + Zn) concentration is 1.2 at the surface and dropping down to 0.7 in the oxide layer, whereas for the 40 min treated sample; the ratio is higher (1.4) at the surface and drops to 0.65 in the oxide layer. From the profiles in Figure 6-11 (b), the average oxide thickness is found to be 43, 108 and 135 nm for 10, 20 and 40 min treated samples respectively.

Apart from the 40 minute passivation treatment, which forms the thickest oxide layer, for the shorter treatments, a small amount of elemental tellurium is observed at the surface, with its binding energy corresponding to metallic tellurium. For a stoichiometric analysis, from the elemental concentrations available at surface (Table 6-2) to form the oxide at the surface for the 10%NH₄F/10%H₂O₂ (40 min) treatment; the most appropriate oxides are metal oxides would be CdO (Cd: 7 at.% and O: 7 at.%) and ZnO (Zn: 1.6 at.%, O: 1.6 at.%), the remaining available oxygen is 33.4 at.%. The two possibilities for tellurium oxide are TeO₂ (Te: 13 at.% and O: 26 at.%) or TeO₃ (Te: 13 at.% and O: 39 at.%); if only TeO₂ was formed there would still oxygen available(7.4 at.%) but not any other element to form the oxide and there is not enough oxygen to form only TeO₃ (Te: 13 at.% and O: 39 at.%). This suggests that both types of tellurium oxide (TeO₂ and TeO₃) would form along with cadmium oxide and zinc oxide at the surface of the passivated sample. There would also be very small amount of Cd(OH)₂ and Te(OH)₆ formation due to the 4 at.% of OH available In the middle of the oxide layer, the binding energy of elemental tellurium is very similar to that of bulk CZT (Table 6-2) and is caused by the varying oxide thickness due to chemical passivation treatment. As the elemental Te concentration is 3 at.%, then 2.7 at.%, Cd and 0.3 at.% Zn should correspond to the molar ratio of bulk C₀.₉Z₀.₁T and the remainder to the oxides. Hence, the metal oxides which fit this stoichiometry are CdO (Cd: 17.3 at.% and O: 17.3 at.%), ZnO (Zn: 3.7 at.%, O: 3.7 at.%) and TeO₃ (Te: 13 at.% and O: 39 at.%). Similar composition of oxides was found for the 10 and 20 min exposure times.
Figure 6-11 XPS depth profile of 10%NH₄F/10%H₂O₂ (10, 20 and 40 min): (a) all elements, (b) with total Te (elemental + oxide).
6.4.2.3.4 15% KOH (40 min) + 10% NH₄F/10% H₂O₂ (40 min) passivation treatment

The elemental core-level (charge corrected and peak fitted) spectra for carbon, oxygen, tellurium, cadmium and zinc of the CZT sample treated with 15% KOH followed by dipping in 10% NH₄F/10% H₂O₂-water is shown in Figure 6-12. The depth profiles constructed from these spectra at each depth are plotted in Figure 6-13.

![Elemental core-level spectra](image.png)

**Figure 6-12** Elemental core-level spectra of oxygen, tellurium, cadmium and zinc of 15%KOH+ 10%NH₄F/10%H₂O₂ processed CZT surface at different depths. The binding energy of the peaks varies by ±0.1 eV.
From Figure 6-12, at the surface the most favourable oxide composition calculated from the stoichiometric analysis is TeO$_2$, CdO and ZnO in addition to Te(OH)$_6$ and Cd(OH)$_2$. After removal of the surface contamination layer, the concentration of cadmium, zinc and tellurium has increased. The concentration of oxygen as oxide has also increased to 55 at.% while OH decreased to 4 at.%, suggesting the formation of TeO$_3$ (Te: ∼14 at.% and O: 42 at.%), with the remaining 13 at.% O associated with the formation of CdO and ZnO. This condition remains stable to a depth of 50 nm, beyond which the oxygen concentration gradually drops off. The Te/(Cd + Zn) ratio is 1.3 at the surface and drops to 0.77 in the oxide layer, where Cd is slightly more enriched than Te. From Figure 6-13, the average oxide thickness is determined to be 142 nm.

6.5 Discussion

The effects of oxidising the CZT surface with different chemicals have been investigated. Some treatments have produced thin oxide layers (even for longer exposure durations); however others clearly lead to the formation of thicker oxide layers as the exposure time is increased. Furthermore, it is clear from the XPS spectra and profiles that this chemical treatment leads to an oxide layer which is variable in thickness over the surface. The oxide thickness obtained from various passivation treatments are given in Table 6-3.
Table 6-3 Oxide layer thickness calculated from XPS depth profiling.

<table>
<thead>
<tr>
<th>Passivating agents</th>
<th>Average oxide layer thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% NaClO\ DI water</td>
<td>2.2</td>
</tr>
<tr>
<td>15% KOH + 15% KCl (40 min)</td>
<td>3.0</td>
</tr>
<tr>
<td>10% NH₄F/10% H₂O₂-water (10, 20 min)</td>
<td>43, 108</td>
</tr>
<tr>
<td>10% NH₄F/10% H₂O₂-water (40 min)</td>
<td>135</td>
</tr>
<tr>
<td>15% KOH+10% NH₄F/10% H₂O₂-water (40 min)</td>
<td>142</td>
</tr>
</tbody>
</table>

A 5% NaClO\ DI water treatment develops a very thin oxide layer (average thickness of 2.2 ± 0.5 nm), which shows a small dependence on the treatment time (10, 20 or 40 min), and is similar to the average oxide thickness (3.0 nm) produced by 15% KOH + 15% KCl (40 min) treatment. This is in good agreement with valence band results and Wagner plots. It is clear that the NH₄F/H₂O₂ based treatments lead to thicker oxides compared to the previous NaClO and KOH + KCl treatments and the oxide thickness was increased by increasing the treatment time (10, 20 or 40 min). The KOH+ NH₄F/H₂O₂ passivated surface exhibited an average oxide thickness of 142 nm, thicker than any of 10% NH₄F/10% H₂O₂-water (10, 20 or 40 min) passivated oxide thicknesses (43, 108 and 135 nm respectively). The formation of this thick oxide layer is in agreement with the shifting of the valence band maximum to higher binding energies and the data points to the lower left of the AP line of Wagner plots of Cd and Te. The diffuse interface in the XPS depth profile could be due to rough and inhomogeneous surface produced by oxidation process as shown in SEM and AFM studies. The Te/(Cd+Zn) ratio at the surface and in the middle of the oxide layer of these passivated samples is compared in Table 6-4 to observe the effect on the stoichiometry of CZT in oxide layer.

Table 6-4  Te/(Cd+Zn) ratio of CZT processed by various chemical agents.

<table>
<thead>
<tr>
<th>Chemical agents</th>
<th>Te/(Cd+Zn)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At the surface</td>
</tr>
<tr>
<td>2%BM (2 min)</td>
<td>~2</td>
</tr>
<tr>
<td>5% NaClO\ DI water (40 min)</td>
<td>~1.0</td>
</tr>
<tr>
<td>15% KOH + 15% KCl (40 min)</td>
<td>1.4</td>
</tr>
<tr>
<td>10% NH₄F/10% H₂O₂-water (10, 20 min)</td>
<td>1.2</td>
</tr>
<tr>
<td>10% NH₄F/10% H₂O₂-water (40 min)</td>
<td>1.4</td>
</tr>
<tr>
<td>15% KOH+10% NH₄F/10% H₂O₂-water (40 min)</td>
<td>1.3</td>
</tr>
</tbody>
</table>
The surface layer of the CZT (~2 nm) was tellurium enriched due to a 2% BM exposure for 2 min prior to passivation treatment and the Te/(Cd+Zn) ratio was 1.6. All the passivating agents improved the Te/(Cd+Zn) stiochiometry at the surface, particularly the long exposure (40 min) 5% NaClO\ DI water treatment, bringing the Te/(Cd+Zn) ratio to a value of ~ 1.0. However the composition of the oxide layer is different in each case. Although these passivating agents have somewhat consumed the Te enrichment at surface, these have also consumed Te and the Te/(Cd+Zn) ratio has dropped to a non-stoichiometric value in the oxide layer. This is most probably due to the O/Te ratio in its oxides being 2:1 (TeO$_2$) or 3:1 (TeO$_3$) compared to 1:1 for CdO and ZnO. The effect of the more aggressive NH$_4$F/ H$_2$O$_2$ treatment on the CZT surface could be explained as follows. It is known that NH$_4$F and H$_2$O$_2$ dissociate to ammonia and hydrogen fluoride ions in addition to reaction products, one of which is hyponitrous acid (H$_2$N$_2$O$_2$) that acts as more efficient oxidising agent than H$_2$O$_2$. Fluoride compounds formed at the surface, oxidise more quickly than the bare CZT surface and TeF$_6$ (which exists as a gas at room temperature) reduces the Te in the oxide layer [149]. [166]. A 20 nm thick Cd enriched region at the surface of the oxide layer has been reported for NH$_4$F/H$_2$O$_2$ treatment compared to the KOH + NH$_4$F/H$_2$O$_2$ treated sample that slightly improved the stoichiometry of oxide layer [152]. It is also reported that soluble H$_2$TeO$_3$ and K$_2$TeO$_3$ products formed during passivation reduce Te enrichment at surface [150]. As every oxide layer developed is thicker (smallest is 3 nm) than Te enrich surface layer (~2 nm), these soluble products would also be formed beyond the 2 nm layer (in stoichiometric CZT) resulting in Cd enrichment in the non-stoichiometric oxide layer.

The highly oxidising nature of the passivating solutions, favours the formation of the primary metal oxides (TeO$_2$/TeO$_3$, CdO and ZnO (with higher overall O/Me ratios)) compared to CdTeO$_3$ which has a lower overall O/Me ratio. This is supported by the high O concentration observed in the oxides during depth profiling. The possible oxides formed at the surface and in the middle of the oxide layer calculated from the available atomic concentration of the elements of passivated layers are presented in Table 6-5.

Table 6-5 Possible oxides formed after the various passivation treatments.

<table>
<thead>
<tr>
<th>Passivating agents</th>
<th>Possible oxides formation</th>
<th>At surface</th>
<th>In the middle of oxide layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% NaClO/ DI water (40 min)</td>
<td>5% NaClO/ DI water (40 min)</td>
<td>TeO$_2$, CdO and ZnO</td>
<td>TeO$_2$/TeO$_3$, CdO and ZnO</td>
</tr>
<tr>
<td>15% KOH + 15% KCl (40 min)</td>
<td>15% KOH + 15% KCl (40 min)</td>
<td>TeO$_2$ or TeO$_3$, CdO and ZnO</td>
<td>TeO$_3$, CdO and ZnO</td>
</tr>
<tr>
<td>10% NH$_4$F/10% H$_2$O$_2$-water (40 min)</td>
<td>10% NH$_4$F/10% H$_2$O$_2$-water (40 min)</td>
<td>TeO$_2$ and TeO$_3$, CdO and ZnO</td>
<td>TeO$_3$, CdO and ZnO</td>
</tr>
<tr>
<td>15% KOH+10% NH$_4$F/10% H$_2$O$_2$-water (40 min)</td>
<td>15% KOH+10% NH$_4$F/10% H$_2$O$_2$-water (40 min)</td>
<td>TeO$_2$ or TeO$_3$, CdO and ZnO</td>
<td>TeO$_3$, CdO and ZnO</td>
</tr>
</tbody>
</table>
According to the stoichiometric analysis and Wagner plots, at the top surface, the composition is probably a combination of the TeO$_3$/TeO$_2$, CdO and ZnO oxides at the surface depending on the available Te and Cd after the formation of Cd(OH)$_2$ and/or Te(OH)$_6$. It has been reported by Wang et al that an 10%NH$_4$F/10%H$_2$O$_2$ treatment (15 min) on a 2% BM etched CZT surface leads to the formation of a thick oxide layer of TeO$_2$ [150] and Wright et al have reported a 30 - 45 nm of oxide layer composed of CdO with a top layer of TeO$_2$ and a small amount of ZnO [149]. Other authors have reported that oxidisation of CdTe/CdZnTe surfaces by different chemical methods leads to the formation of a mixed oxide with a composition of TeO$_2$, TeO$_3$ and CdO [167, 168], similar to that proposed here. Shen et al [169] have reported that in strong alkaline solutions, TeO$_2$ dissolves and forms TeO$_3$ ions and this could then be the mechanism through which TeO$_3$ is formed following this KOH + KCl and 5% NaClO/DI water treatment. Chattopadhyay et al have seen an improvement in the surface stoichiometry for the 15% KOH + 15% KCl (40 min) passivation treatment when using this treatment on the Te enriched CZT layer following BM etching [151]. The binding energy of the tellurium oxide for passivated samples varied from 576 to 575.7 eV, which according to Mekki et al corresponds to TeO$_3$ [170].

6.6 Conclusions

- The oxide layer produced by the passivating treatments does not produce a layer of uniform oxide thickness, rather one that has a substantial thickness variation across the surface and the interface may also be diffuse going into the CZT bulk.
- The composition of the layer and stoichiometry of the metal oxides formed is similar for the different passivating agents. An XPS stoichiometric analysis combined with the Wagner plots indicate that the oxides formed for all treatments are generally a mix of TeO$_3$/TeO$_2$, CdO and ZnO.
- The 5%NaClO-DI water treatment produces a thin oxide layer (2.2 ± 0.5 nm). The thickness does not show a strong dependence on the treatment duration time. The KOH + KCl treatment produces an oxide layer of similar thickness (3.0 nm) to that for the 5%NaClO-DI water treatment. The 5%NaClO-DI water and KOH + KCl passivated surfaces have a surface composition of TeO$_3$, CdO and ZnO.
- The NH$_4$F/H$_2$O$_2$ passivation treatment gives an oxide thickness which shows a clear dependence on the exposure time. Treatment times of 10, 20 and 40 minutes lead to oxide thicknesses of 43, 108 and 135 nm respectively. The increase in thickness with exposure time is attributed to the particularly aggressive oxidation processes associated with this treatment. The KOH+NH$_4$F/H$_2$O$_2$ (40 mins) passivation treatment results in an oxide thickness of 142 nm. The stoichiometric analysis and Wagner plots indicate that the
NH₄F/H₂O₂ and KOH+NH₄F/H₂O₂ passivated surfaces are comprised of TeO₃, TeO₂, CdO and ZnO at the surface and TeO₃, CdO and ZnO in the oxide layer bulk.

- 5%NaClO-DI water treatment among other passivating agents fully recover the stoichiometry at the surface. For KOH-KCl, Te concentration is higher than Cd. However, all of passivating agents produced non-stoichiometric Cd enriched oxide layer.

6.7 Summary

In this chapter, different oxidising agents have been investigated in an attempt to grow a thick surface oxide layer. Some passivating agents have been shown to develop a thin oxide layer independent of exposure time, whilst others show a marked oxide thickness dependence on exposure time and thick oxides up to 140 nm can be grown. The oxide composition as a function of depth has been examined through XPS depth profiling. The results of the profiles have been used to perform a stoichiometric evaluation of the total oxide composition. These results have been considered together with those from Wagner plots for Cd and Te oxides to provide an assessment of the different oxides present in the layers grown by the passivating treatments.

In next chapter characterisation of the devices fabricated prior to (or followed by) these passivating agents will be presented.
7 Fabrication and characterisation of CZT detectors

7.1 Introduction

The performance of the CZT room temperature detectors is often restrained by two main factors i) partial charge collection of the mobile carrier, causing spectral broadening and ii) electronic noise, related to dark current. An increase in bias voltage can improve charge collection (decrease in spectral broadening), but at the cost of a higher leakage current [6]. The major reason for the leakage current is a layer of partially conducting material present at the surface of the CZT material after chemical polishing of the surface. Mobility lifetime (µτ) product (a charge transport property of the material) is one of the primary indicators for the quality of the material. The reported values vary between $6 \times 10^{-3}$ and $8 \times 10^{-4}$ cm$^2$/V for electrons and $3-9 \times 10^{-5}$ cm$^2$/V for holes [63, 64]. In this chapter, two different CZT contact configurations have been prepared to identify the optimum process for improving the performance of such CZT detectors. The two configurations are: i) metal-semiconductor (MS) (used commonly to fabricate CZT detectors); ii) metal-insulator-semiconductor (MIS). These CZT surfaces were prepared using different passivating agents and the contacts then fabricated. The structure and interfaces of the different contacts were examined using XPS and TEM/EDX. The electrical and spectroscopic properties were recorded and the performance considered based on the different structures fabricated.

7.2 Experimental detail

7.2.1 Device Preparation

A Redlen CZT detector of size 10 x 10 x 5 mm$^3$ was used. The electrodes were ground down using a standard polishing process (described in Chapter 5). The CZT crystal was sectioned into eight pieces of $\sim 5 \times 5 \times 2.5$ mm$^3$. Every CZT crystal was chemically etched in 2% of bromine methanol (BM) solution for 2 minutes and then two different fabrication processes were used to form the CZT contacts. The first method involves the Au electrodes being deposited prior to passivation treatment (directly on BM etched surfaces) to avoid any oxidation at the metal-semiconductor (MS) interface shown in Figure 7-1 (a). This is the most common way to form the CZT contact. The second method is to passivate the chemically etched CZT crystal prior to electrode deposition to develop a metal-
insulator-semiconductor (MIS) interface as shown in Figure 7-1(b). This method is not widely used; but this process is being investigated here based upon the results found from the Redlen’s detector study (Appendix B), where a thick oxide layer was observed at the contact/bulk interface. The bulk characteristics of these detectors are identical as they are from same source.

![Figure 7-1 Schematic of a) MS and, b) MIS configuration of CZT devices.](image)

Au electrodes of 70 nm were deposited onto both upper and lower surfaces of the CZT crystals through RF sputter deposition for a planar electrode configuration. The lateral sides were covered with photoresist, as any Au deposited on top of the photoresist can easily be removed by an acetone dip. CZT devices fabricated employing different processes are as follows.

### 7.2.2 MS configuration

The different passivation treatments after deposition of the Au electrodes are given below.

1. 10% NH$_4$F/H$_2$O$_2$ (40 min) (oxide layer thickness 135 nm)
2. 15% KOH (40 min) + KCl (40 min) (3 nm)
3. 5% NaClO+ DI water (2.2 nm)
4. 30% H$_2$O$_2$ (15 s) (1.2 nm)

### 7.2.3 MIS configuration

The passivation treatments prior to Au deposition are

1. 10% NH$_4$F/H$_2$O$_2$ (40 min)
2. 15% KOH (40 min) + KCl (40 min)
3. 30% H$_2$O$_2$ (15 s)

Details of the reaction of these passivating agents at CZT surface are given in Chapter 5 and 6. Once the device was ready, it was mounted onto a ceramic substrate with silver dag paint. A metal wire was connected to the top contact (anode) with the same paint and the other end was soldered to the separate conducting part of the substrate shown in Figure 7-2.

The device was then characterised by:

1. XPS (depth profiling)
2. TEM/EDX
3. I-V measurements
4. Alpha particle spectroscopy

**Figure 7-2 CZT detector mounted onto ceramic substrate.**

### 7.2.4 Materials Characterisation

The Focussed Ion Beam (FIB) milling experiments were undertaken in an FEI Nova 600 NanoLab DualBeam FIB system, which is comprised of a high-resolution field emission scanning electron microscope (FESEM) and a scanning gallium ion beam column. This machine used a focused Ga\(^+\) ion beam with a probe current of 3 nA to cut the sections and polish them in two stages at 1 nA and then 300 pA. The high-resolution field emission SEM column was able to use acceleration voltages between 0.2 and 30 kV and beam currents up to 20 nA. A ‘protective strap’ (a thin layer with a thickness of approximately 100 nm of Pt) was first deposited on the Au contact to prevent the sample surface from damage and then a thicker layer (> 1 µm) of Pt was ion beam deposited.

A Hitachi HD2300A STEM employing a high performance Schottky field emission gun (FEG) source and a Gatan Enfina electron spectrometer, operated at 200 kV, also equipped with energy dispersive X-ray (EDX) analysis was used to study the detector-contact interface region in more detail.

### 7.2.5 Device Characterisation and Performance

A set of I-V measurements was performed to investigate the operating properties of the CZT detector and to observe which of the passivating treatments minimise the leakage current. To reduce the electronic noise, the device was placed inside a metal box and then covered by a piece of black cloth to block out any interference from light. A Keithley DC power unit was used as an electrometer to bias the detector and the resultant dark current was recorded by a PC computer using Labview software. Two ranges of bias voltage were selected i) -1 V to 1 (to find the resistivity); ii) -200 V to 200 V, to see the effect of different passivation treatments on the detector leakage current (surface + bulk).
7.3 Results and discussion

7.3.1 XPS analysis

To determine the effect of the passivation treatment on the surface composition, XPS analysis was undertaken on CZT detectors passivated prior to/after Au deposition.

7.3.1.1 CZT detector of metal-semiconductor (MS) configuration

In this sample set, only one detector was depth profiled to investigate the metal-semiconductor interface as in this group of samples, the passivation treatments were performed only on the lateral sides of the device, not at the interface between the Au and CZT, so the interface configuration is the same for all of the passivated detectors. The device subjected to the 10% NH$_4$F/10% H$_2$O$_2$ (40 min) passivation treatment was selected. Figure 7-3 shows the XPS depth profile (DP) of the metal-semiconductor interface. In the figure, the profile has been divided into four sections $S1$, $S2$, $S3$ and $S4$ to better understand the interface regions.

![Figure 7-3 XPS depth profile of a CZT device passivated with 10% NH$_4$F/10% H$_2$O$_2$ for 40 minutes after Au contact deposition.](image)

Region $S1$ corresponds to the Au electrode. The surface of this layer shows the presence of hydrocarbon contamination, which is removed after a few seconds of sputtering. $S2$ is the interface region. The Au signal drops rapidly between 250 and 500 nm, with the Te, and Cd emerging at the same time, Te signal being slightly higher than Cd. However, as the Zn signal appears and rise up there is a drop of Te/(Cd+Zn) ratio to below 1, i.e. non-stoichiometric proportion. Beyond 500 nm, in $S3$ region, the Au signal exhibits a long tail to 1000 nm. As the gold layer is RF sputtered deposited, the chance of diffusion of Au into the CZT is negligible due to the low energy of Au atoms that are deposited on the material. The most probable reason of this tailing is either the roughness of the CZT
surface or induced roughness produced during the Ar\(^+\) ion sputtering process at a greater depth. The \(S4\) region represents the bulk CZT.

### 7.3.1.2 CZT detectors with a metal-insulator-semiconductor configuration

The XPS depth profiling was performed on two of the MIS detectors with, i) a very thin oxide layer developed by 30% \(\text{H}_2\text{O}_2\) treatment and, ii) thick oxide developed by 10% \(\text{NH}_4\text{F}\)/10% \(\text{H}_2\text{O}_2\) at Au/CZT interface. No XPS DP data was recorded for other passivation treatments because this was the end of PhD and there was no time left to record further data.

#### 7.3.1.2.1 30% \(\text{H}_2\text{O}_2\) passivation treatment

This sample was etched in 2% BM and passivated in 30% \(\text{H}_2\text{O}_2\) for 15 s followed by Au electrode deposition on the top and bottom surfaces. The XPS DP is plotted in Figure 7-4. The profile is again divided into three sections with \(S1\), \(S2\) and \(S3\) representing the Au layer, interface and CZT bulk respectively. In the interface region, Au begins to decay, with Te, Cd and Zn emerging at the same time with Te slightly higher that Cd, but then near the middle of the interface, the \((\text{Cd}+\text{Zn})\) concentration is higher than Te concentration. The Au signal disappears at 700-800 nm. Despite the presence of an oxide layer at the Au and CZT interface; there is no oxygen seen in the profile throughout the interface region. The 30% \(\text{H}_2\text{O}_2\) treatment only develops a very thin oxide layer of 1.25 nm on the CZT surface (see chapter 5) and the sputter interval during Ar\(^+\) etching is approximately 15 nm, which is larger than the oxide layer thickness at the Au/CZT interface. To detect the O signal at the interface; at the time, when the Te and Cd signals appeared in the presence of the Au signal, the sputter rate was reduced to 0.3 nm. The profile was acquired with this sputter rate for the next 12 nm. However, during this period no O signal was detected. Although, the intensity of the Te and the Cd signals were increased. Despite the presence of the oxide layer, the absence of the O signal at the interface suggest that the oxide layer (1.25 nm) has been removed within a single sputter interval (15 nm) before the sputtering rate was reduced. Hence, resulting in there being no evidence of O found in the DP.
Figure 7-4 XPS depth profile of CZT device passivated with 30% H\textsubscript{2}O\textsubscript{2} prior to Au contact deposition. No O signal is detected at interface due to a very thin oxide layer of 1.25 nm compared to the sputtering interval of 12 nm.

7.3.1.2.2 10% NH\textsubscript{4}F-10% H\textsubscript{2}O\textsubscript{2} passivation treatment

The depth profile is shown in of the device which is etched in 2 % BM and passivated with 10% NH\textsubscript{4}F/10% H\textsubscript{2}O\textsubscript{2} (40 min) prior to electrode deposition is shown in Figure 7-5a). Sections S\textsubscript{1} and S\textsubscript{3} again represent the Au electrode and bulk CZT. In section S\textsubscript{2}, the interface region, the total Te signal has been broken down into the Te elemental peak (Te-\textsubscript{ele}) and the Te oxide peak (Te-\textsubscript{ox}). Where the Au starts to decay, in addition to Cd, Zn and Te-\textsubscript{ele}, Te-\textsubscript{ox} and O can be seen. The behaviour of the oxide layer is discussed in chapter 6. To investigate the Au–oxide interface in detail, the region where the oxide first appears, is magnified and shown in Figure 7-5b). The Te-\textsubscript{ele} and Cd peaks appear first and then the O and Te-\textsubscript{ox} peaks become visible at a slightly lower depth. Once the oxide layer is established, the Cd+Zn concentration is higher than the Te-\textsubscript{ele} concentration. At the end of S\textsubscript{2} interface region, the Au and O signals disappear at 500 nm and 700 nm respectively and Te, Cd and Zn concentrations attain their correct proportion in S\textsubscript{3}. 
Figure 7-5 XPS DP of a CZT device, a) in MS configuration passivated with NH₄F/H₂O₂ (40 mins), and b) is magnified interface section.

7.3.2 FIB and TEM/EDX analysis

FIB sectioning was carried out on both sets of CZT detector configurations. Figure 7-6 shows an SEM image of the FIB milling process of the NH₄F/H₂O₂ treated device in the MIS configuration. Even though this passivation treatment leads to a thicker oxide layer (~135 nm) at Au/CZT interface compared to the other treatments, it is not possible to observe this oxide in the interface region in Figure 7-6. So a thin strip was sectioned to undertake STEM analysis.
Figure 7-6 SEM image of the FIB section preparation for a CZT device of MIS configuration, where oxide layer is developed by 10% NH$_4$F/10% H$_2$O$_2$.

The FIB prepared MIS CZT device treated with 10% NH$_4$F/10% H$_2$O$_2$ was examined using STEM. Figure 7-7 shows secondary electron (SE) and transmission emission (TE) images of two different regions of the Au/CZT interface. The images show the different layers; the top layer is platinum, second layer is the sputtered Au layer, with a thickness of 140 ± 3 nm. The oxide layer is clearly seen at the Au-CZT interface. The thickness of the oxide layer is quite variable, varying between 50 and 130 nm and the interface between the oxide and Au layer is also slightly rough. The SE images show the morphology and topography of the sample and are less dependent on Z contrast as these are low energy electrons. The presence of voids in the oxide layer is clear in the SE image shown in Figure 7-7 (d). In the TE images, the Au layer appears dark as this dense layer attenuates the beam and the brighter regions in oxide layer could be due to the generally less dense oxide and/or the presence of voids. The lower region of the oxide, between the oxide and bulk CZT and some regions of the oxide layer are darker than the CZT bulk. From the results given in Table 7-1(below), this is most probably due to these regions having a higher Te/(Cd+Zn) ratio compared to the CZT bulk.
Figure 7-7 (a) and (c) secondary electron, (b) and (d) transmitted electron images of the Au-oxide-CZT interface for a CZT device treated with 10% NH₄F/10% H₂O₂ followed by the sputtered deposition of a Au layer.

EDX point analysis was performed at different points of the FIB prepared section of the CZT detector. The points analysed are shown in Figure 7-8 and the quantified EDX results given Table 7-1.

Figure 7-8  TE image of Au-CZT interface of FIB sectioned sample
Table 7-1 EDX determined atomic concentrations (%) of the elements present at different points

<table>
<thead>
<tr>
<th>Point #</th>
<th>CdL</th>
<th>TeL</th>
<th>ZnK</th>
<th>PtL</th>
<th>AuL</th>
<th>Te/(Cd+Zn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>1.3</td>
<td>1.5</td>
<td>94.0</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>0.6</td>
<td>1.6</td>
<td>2.4</td>
<td>94.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>31.4</td>
<td>58.2</td>
<td>5.3</td>
<td>2.6</td>
<td>2.5</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>40.1</td>
<td>47.7</td>
<td>5.9</td>
<td>3.2</td>
<td>3.1</td>
<td>1.02</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>1.9</td>
<td>0.4</td>
<td>94.6</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.2</td>
<td>1.5</td>
<td>2.3</td>
<td>3.3</td>
<td>91.6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>37.8</td>
<td>55.1</td>
<td>5</td>
<td>1.49</td>
<td>1.22</td>
<td>1.3</td>
</tr>
<tr>
<td>8</td>
<td>43.1</td>
<td>52.0</td>
<td>3.82</td>
<td>0.35</td>
<td>0.64</td>
<td>1.1</td>
</tr>
<tr>
<td>9</td>
<td>1.71</td>
<td>2.19</td>
<td>0</td>
<td>95.16</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.9</td>
<td>1.7</td>
<td>2.2</td>
<td>2.6</td>
<td>92.5</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>33.4</td>
<td>56.4</td>
<td>6.4</td>
<td>1.9</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>12</td>
<td>40.5</td>
<td>47.4</td>
<td>6.0</td>
<td>3.1</td>
<td>3.1</td>
<td>1.02</td>
</tr>
</tbody>
</table>

The EDX point analyses show that points 1, 5 and 9 correspond to the Pt layer; points 2, 6 and 10 represent the Au layer; points 3, 7 and 11 are from the Te rich oxide and points 4, 8 and 12 correspond to bulk CZT. Figure 7-9 is EDX elemental map of the Au-CZT interface. The ‘protective strap’ of Pt is evident at the top and Au electrode layer is homogenous and has not diffused into the oxide layer. The elemental map of O clearly confirms the non-homogenous thickness of the passivated layer. The O signal also seems to weaken in some areas near the Au interface. These regions of lower O intensity could be due to the increased occurrence of voids as the oxide increases in thickness, as seen from the TE images of Figure 7-7. The voids also affect the Te and Cd signals, but are both clearly weaker in the oxide compared to the bulk CZT. The Cd intensity is slightly weaker than the Te at the interface between the bulk CZT and oxide. This is in agreement with the EDX point analyses showing the higher Te/(Cd + Zn) ratio in the oxide region.
Two EDX linescans are shown in Figure 7-10 where normalised elemental intensities are plotted against depth. In Figure 7-10 (a) and (b), linescans were performed at two different places across Au-CZT interface where in TE image bright and dark spots appear respectively.

In Figure 7-10 (a), below the Pt there is a 140 nm thick layer of Au. Below the Au layer, signals from O, Cd, Te and Zn appear. There is a dip in these elemental intensities at the point where there is bright spot in TE image, probably indicative of a void at this point. The oxide region shows a variation in O intensity, similar to the XPS depth profile (Figure 7-5). The oxide layer extends about 125 nm in depth until the CZT bulk is observed. There is no Au diffusion into the oxide layer. The linescan shown in Figure 7-10 (b) is very similar to the linescan given in Figure 7-10 (a) except that a Au signal can be seen at the dark spot in oxide layer. This is most probably due to the presence of a void at this point on the oxide surface, which has been filled by Au during the deposition of the Au layer.

*Figure 7-9  EDX elemental mapping of the Au-CZT interface of FIB sectioned sample.*
7.3.3 Electrical Characterisation and Spectroscopic Properties

Although XPS depth profiling and STEM analysis were performed on specific detectors, the electrical and spectroscopic performance was examined for every detector fabricated with a different configuration, either MS or MIS, and passivated with one of the passivating agents described in the device preparation section.

7.3.3.1 Resistivity

The resistivity can be measured at a low voltage range (-1 to 1 V) [171]. The I-V characteristics at room temperature (290 K) for the MS configuration is plotted in Figure 7-11. The leakage current of the KOH-KCl treated device is about five times higher than any other device. The NH₄F/ H₂O₂ treated sample has a slightly higher leakage current than NaClO and H₂O₂ treated device.
Figure 7-11 I-V curves of CZT devices: MS configuration.

Figure 7-12 shows the I-V relation of MIS configuration devices. At lower voltages, NH$_4$F/H$_2$O$_2$ and H$_2$O$_2$ have identical I-V relationships and the leakage current is a factor of two lower than that of the KOH-KCl treated device.

Figure 7-12 I-V curves of CZT devices: MIS configuration.

It can easily be seen that the leakage current for every device is reduced for the MIS configuration compared to the MS devices. Particularly, for KOH-KCl treatment, the drop in leakage current is observed by factor of four.
These plots are used to calculate the resistivity of a device by employing equation 7-1,

$$\rho = R \frac{A}{d}$$  \hspace{1cm} 7-1

where $A$ is the area ($\text{cm}^2$) of the metal contact and $d$ (cm) is the thickness of the detector. $R$ is the resistance ($\Omega$), which is calculated from the inverse of the slope of the fitted I-V curve in between the voltage range of -1 to 1 V.

The calculated resistivities of the processed detectors are given in Table 7-2. For the MS configuration, the resistivity of the KOH+KCl is lowest, being $3 \times 10^9 \Omega \cdot \text{cm}$. This increases to $1 \times 10^{10} \Omega \cdot \text{cm}$ in MIS configuration. Other passivation treatments have resistivity values in range of 1.0-2.5x$10^{10} \Omega \cdot \text{cm}$ for both configurations. It should be noted that all the samples were from the same source, so the intrinsic material properties should be similar including bulk resistivity. The difference in leakage current and apparent resistivity could be attributed to the series resistance associated with different device configurations and for a specific type of a configuration; it is related to the variation in the passivation treatment.

7.3.3.2 J-V relationship

To study the effect at higher voltages, the dependence of the current density on the voltage for the MS configuration is plotted in Figure 7-13(a). The NaClO and $\text{H}_2\text{O}_2$ passivation treatments show a somewhat similar rectifying behaviour; the KOH+KCl treatment exhibits an ohmic behaviour, whilst the $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treatment shows a reverse rectifying behaviour. In the MIS configuration, the $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treatment shows the lowest leakage current.

The reverse leakage current densities at an electric field of -500 V/cm$^2$ for different devices are given in Table 7-2, which shows that the KOH-KCl treated devices in both configurations have similar and higher current densities than the other devices. The $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treated device in the MIS configuration show a substantial decrease in leakage current. While, the $\text{H}_2\text{O}_2$ treated device in the MS configuration has the lowest leakage current density $\sim 4 \text{nA/cm}^2$ compared to all the other devices irrespective of device configuration. However, there is a significant decrease in the overall leakage current for the MIS relative to the MS configuration.
Figure 7-13  J-V curves of CZT devices, a) MS configuration. b) MIS configuration
Table 7-2 Resistivity, current density, Au/CZT barrier height and mobility-lifetime product for the CZT detectors.

<table>
<thead>
<tr>
<th>Passivating agent</th>
<th>Resistivity (Ω·cm) (extracted from I-V data)</th>
<th>Reverse leakage current density (J) (nA/cm²) At -500 V/cm</th>
<th>Au/CZT barrier height ( \phi_{Au/CZT} ) ±0.02 (eV)</th>
<th>( \mu \tau_e ) (cm²/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MS configuration</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KOH+KCl</td>
<td>3x10⁹</td>
<td>168</td>
<td>0.81</td>
<td>9.1x10⁻⁵</td>
</tr>
<tr>
<td>NH₄F/H₂O₂</td>
<td>1x10¹⁰</td>
<td>145</td>
<td>0.83</td>
<td>3.2x10⁴</td>
</tr>
<tr>
<td>NaClO</td>
<td>2.5x10¹⁰</td>
<td>97.2</td>
<td>0.84</td>
<td>1.2x10⁴</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>2.3x10¹⁰</td>
<td>3.79</td>
<td>0.84</td>
<td>1.6x10⁴</td>
</tr>
<tr>
<td><strong>MIS configuration</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KOH+KCl</td>
<td>1.0x10¹⁰</td>
<td>169</td>
<td>0.83</td>
<td>4x10⁴</td>
</tr>
<tr>
<td>NH₄F/H₂O₂</td>
<td>2.6x10¹⁰</td>
<td>13.6</td>
<td>0.86</td>
<td>4.9x10⁴</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>2.6x10¹⁰</td>
<td>131</td>
<td>0.84</td>
<td>4.8x10⁴</td>
</tr>
</tbody>
</table>

7.3.3.2.1 Au/CZT barrier height calculation

One of the parameters that control the charge transport through the interface between the contact and the semiconductor is the magnitude of the barrier height. The Schottky barrier height (SBH) calculated using equation 2-6 (given in chapter 2). The saturation current density was obtained by the straight line intercept of ln \( J \) at V=0 for the forward bias of a ln \( J-V \) plot as shown in Figure 7-14.

The calculated values of SBH are given in Table 7-2. For the **MS configuration**, the SBH values of all treatments are similar around ~ 0.84 ± 0.02 eV except for the KOH-KCl treatment, where it is slightly lower i.e. 0.81 ± 0.02 eV. In these devices, gold has a planer configuration and has been deposited directly on top of CZT surface that would result in an identical Au/CZT interface excluding the edges due to the passivation of lateral sides, which may cause the difference in SBH seen in KOH-KCl. For the **MIS configuration**, the thick interfacial oxide layer (~135 nm) developed by NH₄F/H₂O₂ has a higher SBH of 0.86 ± 0.02 eV than the value of 0.84 ± 0.02 eV for a very thin oxide layer (~3 nm) present at interface developed by the other passivation treatments. Other researchers have also reported an increased barrier height due to an interfacial oxide layer [82, 172] The similarity of SBH for a very thin oxide layer and **MS configuration** devices could be attributed to the surface roughness produced during passivation treatment that could be in the order of these very thin oxide thickness and/or for the MS configuration, there will still be a thin layer of native oxide formed on the surface of the CZT, which would then give a similar response to the passivated surfaces where the oxide formed is also very thin.
7.3.4 Charge transport and radiation spectroscopy

The mobility-lifetime ($\mu \tau_e$) product and charge collection efficiency (CCE) of the differently treated Au/CZT/Au devices were investigated employing alpha particle spectroscopy. When the detector is irradiated by alpha particles from $^{241}$Am radioisotope source with average emission energy of 4.95 MeV (reduced due to self attenuation in the source) and 180 kBq activity [173]. The alpha particles have shallow penetration depth (~20 µm) [171] compared to the thickness of the CZT devices, the signal generated is due to the drift of one type of charge carrier (either electrons or holes) that moves to the electrode under the influence of an applied potential difference. For negative bias, the induced signal is dominated by electron drift with the drift length of $\lambda_e$ given by

$$\lambda_e = \mu_e \tau_e E$$  \hspace{1cm} (7.2)

where E is the electric field.

The resultant signal is passed through pre-amplifier followed by a shaping amplifier (gain 20 and shaping time 1 µs), and then recorded on a multi-channel analyser (MCA). The multi-channel analyser (MCA) spectrum was energy calibrated prior to the spectroscopic measurements. Figure 7-15 (a) and (b) show the pulse height spectra (PHS) of CZT devices at a fixed acquisition time of 500 s, at indicated voltages, where x and y-axes show channel number and count rate respectively. Figure 7-15 (a) shows the PHS of the CZT devices of MS configuration, in which the passivation treatments NaClO, KOH+KCl and H$_2$O$_2$ show a strong shift of the spectra to lower channel numbers broader and attenuated peaks at lower biases, all of these treatments produce thin oxide layer (2-5 nm). For the NaClO treatment, broadening of the peaks can be seen at higher voltages as well. The NH$_4$F/ H$_2$O$_2$ treated device exhibits a lower shift and broadening of the peaks (produce thick oxide layer of 130
nm) compared to the other treatments. The MIS configuration devices show an improved performance and reduced broadening of the peaks compared to MS configuration (Figure 7-15 (b)). For the H₂O₂ treated device, both the peak shift is reduced and the intensity is improved up to 75 V; for the KOH+KCl treatment, only the peak shift is improved (for all voltages) and for the device exposed to the NH₄F/H₂O₂ treatment, a high intensity is attained for every voltage with no tailing off of the peaks towards the lower channels. The PHS of the NH₄F/H₂O₂ treatment is better than the PHS of other treatments in both the MS and MIS configuration.

The leakage current was also measured during the acquisition of PHS at every bias voltage. In the MS configuration, the leakage current rose with increasing bias voltage for the H₂O₂, KOH+KCl and NaClO treatments and leakage current values of 0.24, 0.27 and 0.68 µA were respectively obtained at a bias voltage of 400 V, whilst the NH₄F/ H₂O₂ treatment gave a substantially lower value of 0.02 µA at 400 V. For the MIS configuration the leakage current reduced to 0.01, 0.02 0.01 µA at 400 V for the H₂O₂, KOH+KCl and NH₄F/H₂O₂ treated surfaces respectively.

Another parameter which can be extracted from the PHS to assess the performance of the device is the charge collection efficiency (CCE), which is related to mobility-lifetime product. The following procedure was adopted for various bias voltages from 50-400 V at an interval of 25 V; the energy peaks of the PHS were peak fitted using a Gaussian function and the centroid was calculated for every peak. The centroids were determined initially as channel numbers; then to find the CCE, the channel numbers were converted to an energy scale. The relationship between the bias voltage and the peak centroid (in terms of the CCE) is plotted in Figure 7-15 (c) and (d). The experimental data was then fitted using the Hecht equation [174] given below to yield the electron mobility-lifetime product, \( \mu_e \tau_e \).

\[
CCE = \left( \frac{\mu_e \tau_e V}{d^2} \right) \left[ 1 - \exp \left( -\frac{d^2}{\mu_e \tau_e V} \right) \right]
\]

where \( V \) is applied bias voltage and \( d \) is the device thickness.

In Figure 7-15 (c), the Hecht plot gives an excellent fit to the CCE data points for NH₄F/H₂O₂ and NaClO treatments in the MS configuration. The passivating agents that develop a thin oxide layer along their lateral sides (2-5 nm) i.e. NaClO, KOH+KCl and H₂O₂ treated devices, exhibit poor CCE at lower bias voltages relative to the device with a 150 nm thick oxide layer for the NH₄F/ H₂O₂ treatment. In the MIS configuration (Figure 7-15 (d)), all of the three passivation treatments fit the Hecht model exactly and also at higher voltages (> 200 V) demonstrate similar high CCE (~ 95%). However at lower voltages, NH₄F/H₂O₂ and KOH+KCl treated devices show better CCE than the H₂O₂ passivation treatment. The overall CCE of every device is much enhanced for the MIS configuration.

The measured mobility-lifetime product of every device is given in Table 7-2. For the MS configuration, the KOH+KCl treated device has the lowest \( \mu_e \tau_e \) value, whereas the NH₄F/H₂O₂ exposed device has a better \( \mu_e \tau_e \) than the others. For the MIS configuration, all the devices have
similar $\mu_e \tau_e$, but higher than the devices of MS configuration.

Figure 7-15 (a) and (b) show the spectroscopic response of CZT devices of MS (passivated after Au deposition) and MIS configuration (passivated prior to Au contact deposition) respectively. (c) and (d) show the charge collection efficiency (CCE) of MS and MIS configurations respectively.

7.4 Discussion

The MS configuration results in the deposition of gold on BM etched CZT surfaces. No interfacial layer has been observed at the Au/CZT interface in the XPS depth profile and FIB sections analysis show that there is no Au diffusion into CZT. In the MS configuration, the lateral sides of every device were passivated with a different passivant to reduce the shunt current produced by Te enriched
surfaces. All the samples were from the same source and were prepared by the same method suggesting that the variation in device performance could be the result of different passivation treatments. The KOH-KCl treated device showed the highest reverse leakage current, poor charge collection efficiency, lowest resistivity and barrier height. For this treatment, a slightly higher Te concentration relative to other treatments was observed in the 3 nm oxide layer as well as higher electron density was observed at valence band (Chapter 6). Dharmadasa et al [175] have reported a lower barrier height of the surface with Cd vacancies (Te excess). NaClO, H$_2$O$_2$ and NH$_4$F/H$_2$O$_2$ treated devices show similar resistivity, $\mu_e\tau_e$, and barrier heights. However, the NaClO and H$_2$O$_2$ treatments produce a very thin oxide layer of ~2 nm whereas NH$_4$F/H$_2$O$_2$ treated device developed a thick oxide layer up to 180 nm. This has resulted in the leakage current density being the lowest (i.e. 3.8 nA/cm$^2$) at -500 V/cm for the H$_2$O$_2$ treatment, whilst charge collection is improved for the NH$_4$F/H$_2$O$_2$ treated device.

In the MIS configuration, along with the lateral sides of the device, the interface of the Au/CZT is also oxidised and this interfacial oxide layer thickness depends on the passivant used in the surface treatment. The KOH-KCl treated device has a slightly lower resistivity and $\mu_e\tau_e$ and higher leakage current than the H$_2$O$_2$ and NH$_4$F/H$_2$O$_2$ treated devices which have high resistivity (2.6 x 10$^{10}$ Ω.cm) and $\mu_e\tau_e$ (~4.9 x 10$^{-4}$ cm$^2$/V). The NH$_4$F/H$_2$O$_2$ treated device has a reduced leakage current density of 13 nA/cm$^2$ at -500 V/cm, increased barrier height of 0.86 ± 0.02 eV and enhanced charge collection efficiency relative to the KOH-KCl and H$_2$O$_2$ devices. XPS and STEM analysis have revealed that the oxide layer is inhomogeneous and of varying thickness in the range of 30 – 180 nm and the interface region contain voids. It is known that the overall resistivity of a detector increases and the leakage current decreases after a passivation treatment [75, 150] due to an increase in the surface barrier height, which fixes the surface potential with immobile interface charges, minimizing the escape of electrons through oxide layer. Consequently, the amount of leakage current depends on the quality of passivated layer [82, 152]. It has been reported that a stable phase of TeO$_2$ is formed during oxidation of a Te rich CZT surface and this results in a low leakage current [176]. Low leakage currents reduce the detector noise and enhance the performance of the detector [151, 177] and this is the probable explanation for the enhanced performance of the (NH$_4$F/H$_2$O$_2$ treated) device with a thick oxide layer on the lateral side of the device in MIS configuration. The overall improved performance of MIS configuration devices with both the lateral sides and interface oxidised) compare to MS devices could be due to blocking of electrons passing through the Au/CZT barrier, as it has been reported previously that improved blocking at the Au/CZT interface results in less peak tailing and enhances the signal-to-noise ratio, energy resolution and better performance of radiation detector [178]. This is in agreement with the results recorded for the MIS devices, where the Au/CZT blocking increases as the oxide layer becomes thicker i.e. 135 nm of NH$_4$F/H$_2$O$_2$ relative to ~3 nm of KOH+KCl and 30% H$_2$O$_2$ treated devices). This suggests that the passivation treatment altered the composition and structure of the
surface layer of the CZT and nature of these variations depend on passivant and/or its exposure
duration that could result in the difference in apparent resistivities and leakage currents of the
processed detectors.

The spectral response depends on the bias voltage. An increasing bias voltage shifts the peaks to
higher energies. The amount of shift is different in all the spectra. The broadening of the spectra at
low bias voltage is due to partial charge collection [179], as the possibility of the electrons becoming
trapped or recombined at the traps is greater due to a longer drift-time [180].

The charge transport in the bulk of the devices which gives rise to the PHS is due to electron
transport. The PHS of the MS CZT devices show larger differences in the peak shifts with an
increasing bias voltage and a greater broadening of the peaks at low bias voltages compared to the
MIS devices. The broadening and the asymmetrical shape of the peak is due to charge trapping or
recombination [6]. The overall CCE and leakage current are improved for MIS configuration and for
the NH₄F/H₂O₂ treatment in the MS configuration. Consequently, the two limiting factors of CZT
device performance i.e. incomplete charge collection of mobile carriers and leakage current can be
improved by passivating the sample prior to contact deposition. Amongst the passivating agents
employed in this work, NH₄F/H₂O₂ gives the best result in both the MS and MIS configurations due to
the thicker oxide layer developed with this treatment.

7.5 Summary

CZT detectors were fabricated in two different configurations i) metal-semiconductor (MS) (used
commonly to fabricate CZT detectors) ii) metal-insulator-semiconductor (MIS), processed with
different passivating agents. The passivating layer has a diffuse and non-homogenous nature, which is
confirmed by the XPS DPs, SE/TE imaging and EDX compositional mapping of this interface region.
The SE/TE images show that thickness of the layer formed by the NH₄F/H₂O₂ treatment varies (30-
130 nm) across the surface of the bulk CZT. There are voids present in the oxide layer, which are
more prevalent at the oxide/Au interface.

The resistivity of a detector was improved and leakage current reduced for the MIS configuration.
Amongst the passivating agents, the NH₄F/H₂O₂ (40 min) treated device shows the minimum leakage
current in the MIS configuration. The MIS configuration also improves the mobility-lifetime product
and the two limiting factors: i) partial charge collection and ii) electronic noise related to leakage
current of a CZT device. Thus, the NH₄F/H₂O₂ treated detectors in both the MS and MIS
configurations gives increased charge collection and exhibits reduced electronic noise and a higher
mobility-life time product.
8 Conclusions and future work

The main aim of this thesis was to study the effect of different surface treatments on CdZnTe radiation detector materials; to characterise the composition and thickness of surface layers formed and determine their effect on device performance. In Chapter 5, a very common surface preparation technique of Br in methanol chemical polishing followed by H$_2$O$_2$ passivation was investigated. The passivation work was then extended to consider the different passivants in Chapter 6. Then, in Chapter 7, the performance of the devices fabricated using these passivants in two different configurations, MS and MIS have been compared. During the PhD work, some time was also spent on the characterisation of ultra-thin CdTe/CdZnS solar cells and the effect of different CdCl$_2$ activation parameters on the photovoltaic device composition, microstructure and performance is presented in Chapter 4.

8.1 Conclusions

1. Surface modification of CZT through BM etching gives rise to a Te enriched surface, due to selective dissolution of Cd by the BM solution. XPS analysis has shown that the enriched Te layer thickness was similar irrespective of exposure time (between 5 and 120 s). However, the BM concentration did affect the Te enriched layer thickness, with a 2.0 % BM etch giving a
thickness of 1.8 ± 0.2 nm, slightly higher than the 1.3 ± 0.2 nm layer thickness for the 0.2 % BM etch. This chemical etching results in a non-stoichiometric conducting surface with the Te/(Cd+Zn) ratio rising to ~2. XPS results show that subsequent exposure in 30 % H$_2$O$_2$ results in an oxide thickness of 1.0 ± 0.07 nm calculated using the Beer-Lambert expression with a single photoelectron take-off angle and 1.25 ± 0.12 nm employing the Beer-Lambert expression and multiple photoelectron take-off angles.

2. CZT surfaces prepared using different passivants with various exposure durations were compared. From analysis of the XPS DPs and SEM/STEM cross-section results, it was observed that all the passivants develop non-uniform, rough oxide layers with a substantial thickness variation across the surface and exhibit a diffuse interface with the underlying bulk CZT. The metal oxides formed for all treatments are generally a mix of TeO$_3$/TeO$_2$, CdO and ZnO. The 5%NaClO-DI water treatment produces a thin oxide layer (2.2 ± 0.5 nm) that does not show any change by varying the treatment duration time. However, long exposure times improve the surface stoichiometry. The thickness was also similar to that for the KOH + KCl treatment. The NH$_4$F/H$_2$O$_2$ passivation treatment gives an oxide thickness which shows a strong dependence on the exposure duration. Treatment times of 10, 20 and 40 minutes lead to oxide thicknesses of 43, 108 and 135 nm respectively. The KOH+NH$_4$F/H$_2$O$_2$ (40 mins) passivation treatment results in an oxide thickness of 142 nm. The NH$_4$F/H$_2$O$_2$ related passivated surfaces are comprised of TeO$_3$, TeO$_2$, CdO and ZnO at the surface and TeO$_3$, CdO and ZnO in the oxide layer bulk.

3. Using different passivants, CZT detectors were fabricated by depositing a planar gold contact in two configurations: i) metal-semiconductor (MS) (used commonly to fabricate CZT detectors); ii) metal-insulator-semiconductor (MIS). The diffuse and non-homogenous nature of the passivating layer was confirmed by the XPS DPs and SEM/STEM/EDX compositional mapping of this interface region. The SE/TE images show that thickness of the layer formed by the NH$_4$F/ H$_2$O$_2$ treatment varies (50 - 130 nm) across the surface of the bulk CZT. There are voids present in the oxide layer, which are more prominent at the oxide/Au interface and there was no Au diffusion in oxide layer. The resistivity was improved and leakage current (surface + bulk) reduced in the MIS configuration. Amongst the passivating agents, the NH$_4$F/ H$_2$O$_2$ (40 min) treated device shows the minimum leakage current in the MIS configuration. The MIS configuration also improves the mobility-lifetime product and the two limiting factors: i) partial charge collection and ii) electronic noise related to leakage current of a CZT device. The NH$_4$F/H$_2$O$_2$ treated detectors gives increased charge collection and exhibits reduced electronic noise and a higher mobility-life time product. The barrier heights of MIS devices were determined to be 0.83 ± 0.02 eV and 0.86 ± 0.02 eV for very thin and thick oxide layers respectively.

4. The effect of CdCl$_2$ activation parameters on the composition, microstructure and performance
of MOCVD grown ultra-thin CdTe/CdZnS solar cells were investigated. XPS DP and XRD data showed that the increase in degree of CdCl$_2$ activation and annealing treatment results in increased S diffusion into the absorber layer (CdTe) from the window layer (CdZnS) that in turn enhanced $V_{oc}$. A ternary CdTe$_{1-y}$S$_y$ phase was formed with the CdTe and the maximum S concentration observed in the CdTe layer was approximately 2.0 at.%. The diffused S species reached the back contact whilst Te diffused to the ITO layer. The CdCl$_2$ treatments also allow Zn to leach out the device. Using modified MOCVD deposition parameters to give a slightly higher initial Zn concentration in the CdZnS layer improves the blue spectral response. However, higher Zn concentrations in the CdZnS layer deteriorates the performance and results in a poor FF. Increasing the As$^+$ acceptor concentration in the absorber layer leads to a better $V_{oc}$.

8.2 Future work

Research work related to different passivation treatments and device configurations have been presented in this thesis. Although, a number of passivated CZT surfaces were generated, only some were used for device fabrication and XPS DPs and STEM studies were also performed only on selected devices. Characterisation of the other devices should be carried out. Alpha spectroscopy was performed to measure CCE and leakage current for the fabricated devices; the performance of the devices should also be extended to determine the X/gamma ray response. The electrode configuration employed for the devices was planar; however, for different application purposes, other configurations such as pixellated and co-planer grid are also used in practice. This work should be taken further to consider these configurations. This study employed sputter deposited gold. Other deposition methods such as evaporation and electroless deposition of gold could be investigated to compare with the results for the passivated surfaces with sputtered gold.

This investigation was performed on small size crystals. Large crystals should also be analysed to ensure that the results are potentially transferable for industrial application. Furthermore, the durability of the passivated surfaces should also be determined. In this work, the time between surface preparation, device fabrication and characterisation were short. For commercial exploitation, the electrical and spectroscopic response of the devices should be characterised over a much longer time period. Finally, The IV characteristics of the detectors should be obtained at high voltages to observe the stability in the presence of strong electric fields.
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Appendix A

Sputter rate conversion

A.1 CdTe sputter rate

To determine the Ar$^+$ sputter rate of CZT; a CdTe layer was deposited by metal organic chemical vapour deposition (MOCVD) onto a Si (100) wafer at the Centre for Solar Energy Research, Glyndŵr University, UK. Details of the process can be found in [181]. The nominal CdTe layer thickness, measured by *in-situ* laser interference reflectometry was 120 nm. Using *ex-situ* mechanical profilometry, the thickness of the area to be Ar$^+$ sputtered was determined to be 135 nm. An XPS depth profile of the MOCVD CdTe thin film is shown in Figure A.1. The Cd:Te ratio exhibits a stoichiometry of 1.0:1.0 and the sputter rate for CdTe for a 3 kV Ar$^+$ ion bombardment energy and beam current density of 11.1 µA/cm$^2$ was determined to be 0.15 nm/s. This etch rate was then used to calibrate the depth scale for all the XPS depth profiles of BM etched CZT surfaces.

Figure A.1. XPS depth profile of an MOCVD deposited CdTe layer of 135 nm thickness. The CdTe etch rate of 3 kV Ar$^+$ ions at a beam current density of 11.1 µA/cm$^2$ was determined to be 0.15 nm/s.
A.2 Oxide layer sputter rate

A thick oxide layer was developed at the surface for some of the passivating agents. Usually, in XPS the sputter rate of a standard metal oxide sample of known thickness and composition is used to calibrate the depth for oxide layers.

The average etch time between 84% and 16% of concentration A depth profile of the CZT device fabricated after the NH\textsubscript{4}F/H\textsubscript{2}O\textsubscript{2} (40 min) passivation treatment is shown in Figure A.2. The oxide layer spans around 1200 s of sputtering time.

![XPS depth profile of CZT device passivated with 10% NH\textsubscript{4}F/10% H\textsubscript{2}O\textsubscript{2} prior to Au contact deposition, b) magnified plot of (a) after 4000 s of sputter time.](image1.png)

A.2. XPS depth profile of CZT device passivated with 10% NH\textsubscript{4}F/10% H\textsubscript{2}O\textsubscript{2} prior to Au contact deposition, b) magnified plot of (a) after 4000 s of sputter time.

This device was also FIB sectioned and characterised by STEM. The SE image shows the oxide layer to have a large thickness variation, being between 50 and 130 nm as shown in Figure A.3. The analysis volume of the XPS is larger than that of the SE. The sputter rate calculated for the largest oxide thickness is 0.11 nm/s.

![SE image of a FIB sectioned Au and passivated CZT interface.](image2.png)

Figure A.3. SE image of a FIB sectioned Au and passivated CZT interface.
A.3 Au layer thickness calculation

Gold contact of 70 nm thickness was deposited on CZT surfaces employing RF sputtering method. However, the SE image in Figure A.3 indicates the presence of an Au layer of thickness~140 ±3 nm. The Au signal in the XPS depth profile of Figure A.2 decays after 4200 s of etch time. Hence, the sputter rate is 140 nm/4200 s=0.033 nm/s. The sputter rate was also calculated from sputter rate equation given below [154]

\[
\frac{d}{t} (\text{m/s}) = \frac{M}{\rho N_A e} S j_p
\]

where

\[ M = \text{atomic mass number} = 196.97 \]
\[ \rho (\text{kg/m}^3) = 19.3 \times 10^3 \]
\[ N_A = 6.022 \times 10^{26} \]
\[ e = 1.6 \times 10^{-19} \]
\[ S \text{ sputter yield} = 7 \text{ [182]} \]
\[ j_p (\text{A/m}^2) = 111.1 \times 10^{-3} \text{ (1 \mu A induced beam current, rastered over a 3x3 mm}^2 \text{ area)} \]
\[ \text{Ar}^+ \text{ ion energy = 3 keV} \]

\[
\frac{d}{t} (\text{m/s}) = \frac{196.97}{19.3 \times 10^3 \times 6.022 \times 10^{26} \times 1.6 \times 10^{-19}} \times 7 \times 111.1 \times 10^{-3}
\]

\[
\frac{d}{t} = 0.082 \text{ nm/s}
\]

The Au signal in the XPS depth profile of Figure A.2 decays after 4200 s of etch time. Hence, the Au layer thickness = 0.082 x 4200= 344.4 nm.

The gold layer thickness obtained from this sputter rate is much higher than the found from SE image. It was suggested to calibrate the XPS depth profiles with the sputter rate determined from SE image.

The conversion of the sputter time to depth of the XPS DP was done in the following manner. The depth resolution was used 84 – 16% of the element profile. The sputter rate of Au was applied to the Au profile till the 84% of the atomic concentration. For the oxide layer the sputter rate of oxide was applied between the 84 – 16% of the O profile. For the interface of Au/oxide-CZT (between the 84% of Au and 84% of O) the average of sputter rates of Au and oxide layer was used and for the interface of oxide (16% of O) and CZT bulk, it was the average of oxide and CdTe.
Appendix B

Characterisation of Redlen detectors

B.1 Introduction

For a University of Surrey EngD project, commercially available efficient and high performance CZT detectors grown and fabricated by Redlen technologies were provided to the EngD sponsor (Rutherford Appleton Laboratory (RAL)). The detectors showed very high resistivity in the order of $10^{11} \, \Omega \cdot \text{cm}$ and very low leakage current $2.36 \text{–} 3.95 \, \text{nA/cm}^2$ [183]. All of the detectors were of the same dimensions - $1.95 \times 1.95 \times 0.5 \, \text{cm}$. Configuration of the anode electrode was pixellated, while the cathode was planar. The I-V performance was asymmetric which affects the spectroscopic response of the detectors. To understand the behavior of the interface between the contact and bulk of the material different characterisation techniques were employed.

Initial XPS depth profiling of a Redlen detector was performed for the EngD project, this work being further carried out by the EngD student, Steven Bell. Other characterisation techniques such as STEM and EDX were utilised to examine a FIB sectioned thin section of the detector.

The detailed work is published by S. Bell [172, 183]. A brief overview is presented here as this work became the basis of further development in passivation treatment of CZT surfaces during my PhD.

B.2 XPS depth profiling

XPS depth profiling was undertaken on both sides of the contact i.e. anode and cathode. The parameters of the sputtering process are given in detail in chapter 5. An XPS depth profile of an anode of one of the detectors is shown in Figure B.1. The thicknesses of the layers are not defined, as the depth profile is in sputter time not in depth.

Three different layers can easily be seen in the profile. The top layer is gold corresponding to the electrode. In the next layer high intensity oxygen signal can be seen in addition of the non-stoichiometric proportions of tellurium, cadmium and zinc and in the third layer, Cd, Te and Zn are attaining their stoichiometric concentration while oxygen is reducing in intensity. At the Au/CZT interface, the tellurium concentration is also high. The oxide formed would be metal oxide. This
The oxide layer is thick compared to the oxide layer developed by the passivation treatment of 30% H$_2$O$_2$. Similar results were found for other Redlen’s detectors.

![Graph showing XPS depth profile](image)

*Figure B.1 XPS depth profile of the pixellated anode of a Redlen CZT detector*

### B.3 STEM analysis

A thin section of the CZT detector was prepared by FIB and analysed by STEM. A secondary electron image of this strip is shown in Figure B.2. EDX was used for elemental quantification, whereas TEM was used to obtain the diffraction pattern from the oxide layer.

The variation in the gold layer thickness was between 30 and 50 nm with a mean value of 35 nm, while the oxide layer thickness varied from 30 to 120 nm with a mean value of 77 nm. It was found that oxide layer was not uniform. The diffraction patterns revealed that the oxides present in the oxide layer were a combination of CdTeO$_3$ and/or Te$_2$, TeO$_3$ [183].
Figure B.2 Secondary electron image of FIB section taken from a Redlen CZT detector. Image reproduced from the work of S. Bell [148].

B.4 Summary

High performance Redlen CZT detectors were analysed due to their asymmetric I-V behaviour. The Au/CZT interface of the detectors was examined by XPS depth profiling and STEM. It was revealed that a non-uniform thick oxide layer was present the gold contact. It was earlier found that the 30 % H$_2$O$_2$ passivation treatment develops only a very thin layer of oxide 1.25 nm [141]. Hence, the focus of this PhD work was then turned to find the passivation agents that can develop thick oxide layers (similar to the good performing Redlen detectors) and to find the effect of this oxide thickness on the performance of the CZT detector.
Appendix C

Published work
An XPS study of bromine in methanol etching and hydrogen peroxide passivation treatments for cadmium zinc telluride radiation detectors

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ABSTRACT
The performance of single crystal CdZnTe radiation detectors is dependent on both the bulk and the surface properties of the material. After single crystal fabrication and mechanical polishing, modification of the surface to remove damage and reduce the surface leakage current is generally achieved through chemical etching followed by a passivation treatment. In this work, CdZnTe single crystals have been chemically etched using a bromine in methanol (BM) treatment. The BM concentrations employed were 0.2 and 2.0 (v/v) % and exposure times varied between 5 and 120 s. Angle resolved XPS and sputter depth profiling has been employed to characterize the surfaces for the different exposure conditions. A Te rich surface layer was formed for all exposures and the layer thickness was found to be independent of exposure time. The enriched Te layer thickness was accurately determined by calibrating the sputter rate against a CdTe layer of known thickness. For BM concentrations of 0.2 (v/v) % and 2 (v/v) %, the Te layer thickness was determined to be 1.3 ± 0.2 and 1.8 ± 0.2 nm, respectively. The BM etched surfaces have subsequently been passivated in a 30 wt.% H2O2 solution employing exposure time of 15 s. The oxide layer thickness has been calculated using two standard XPS methodologies, based on the Beer–Lambert expression. The TeO2 thickness calculated from ARXPS data are slightly higher than the thickness obtained by the simplified Beer–Lambert expression. For BM exposures of 30–120 s followed by a passivation treatment of 30 wt. % H2O2 solution employing an exposure time 15 s, the ARXPS method gave an average TeO2 thickness value of 1.20 nm and the simplified Beer–Lambert expression gave an average thickness value of 0.99 nm.

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1. Introduction
X-ray and gamma rays detectors fabricated from single crystal cadmium zinc telluride (CZT) are able to operate at room temperature with low leakage currents [1]. The energy resolution of such detectors is enhanced by the wide band gap (1.5–2.2 eV) and the higher atomic number (Z) density of CZT [2,3]. There is a correlation between the performance (charge generation, charge transport and intrinsic electric field) and the surface properties of CZT, hence optimizing the specific surface properties are important to the detector performance [4–6]. After slicing and dicing of the crystal from its ingot, it is mechanically polished to reduce surface roughness. This is followed by chemical polishing which both further improves the roughness and removes microstructural damage resulting from the mechanical polishing process. The surface composition after chemical treatment depends on the chemical solution employed. A chemical treatment using an acidic solution produces a Te-rich surface, whilst an alkaline solution etch gives a Cd-rich surface [7]. Most commonly, bromine in methanol (BM) of varying

concentrations is used. Özsan et al. found that the Cd/Te ratio at the surface was invariant after a 2 min exposure in 0.2 and 1.0% BM solution, but the graded Te layer increased in thickness as the BM concentration was increased [8]. However, the enriched Te layer thickness was not quantified. Ageing of the BM solution increases its acidity, resulting in an enrichment of elemental Te at the surface. Rouse et al. found that once the Te layer reaches a thickness of approximately 2 nm, it is independent of chemical etching duration and the acidity of BM solution [9]. The authors used XPS depth profiling to determine the thickness, but do not describe how the Ar+ ion sputter rate employed was determined. Accurate quantification of the Te layer thickness is one of the primary aims of the work undertaken in this study.

Bensalah et al. have shown that variation in BM exposure affects the surface roughness and leakage current [10]. The Te enrichment changes the stoichiometry of the surface and due to a smaller band gap (~0.3 eV), increases the leakage current, deteriorating the radiation detector performance. To minimize the leakage current, the Te-rich surface is passivated to develop a thin insulating oxide layer. Özsan et al. showed that passivation of BM etched surfaces with 30 wt.% H2O2 produces an oxide thickness which is dependent on BM concentration up to a BM concentration of 2% [8]. The oxide thickness dependence on exposure time of the passivating agent

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was only measured for a 0.2\% BM concentration, but was found to be similar, for all exposure times [8]. Considering a number of authors' work, the thickness of the H2O2 generated oxide is in the range of 1.6–4.5 nm, depending on the BM concentration and oxide thickness calculation method employed [8,11,12].

In this paper, CZT single crystals have been chemically etched using BM concentrations of 0.2 and 2.0 (v/v) % for varying times (5–120 s) and changes in surface composition determined by XPS depth profiling. An Ar+ ion sputter rate of CZT has been evaluated by Ar+ ion sputtering a CdTe thin film of known thickness. This has enabled an accurate value of the Te layer thickness to be determined for the different BM exposures. These BM etched surfaces were further passivated using a 30 wt.% H2O2 solution and the oxide thickness determined from XPS data using two different methods: (i) the standard Beer–Lambert expression employing a single photoelectron take-off angle; (ii) a Beer–Lambert based methodology using a range of photoelectron take-off angles. A comparison is made of the oxide thickness determined by these different analytical methods.

2. Experimental procedure

2.1. Sample preparation

Cadmium zinc telluride (CZT) single crystal samples grown using the modified vertical Bridgman method were obtained from Yinnel Tech Inc., USA. The samples had dimensions of 8 mm × 8 mm × 5 mm. The two samples had different bulk compositions, determined by quantitative energy dispersive X-ray (EDX) analysis to be Cd0.9Zn0.1Te and Cd0.9Zn0.1Te. (The quantified EDX data was recorded using a Hitachi S3200 SEM employing an Oxford Instruments X-ray detector and the spectra quantified using the INCA software.) Each sample was mechanically polished, with the final polish being performed using a 0.05 μm alumina suspension in ethanediol. The samples were then dipped in freshly prepared BM solutions with concentrations of either 0.2 or 2.0 (v/v) % for different time durations (5, 15, 30, 60 or 120 s). After BM exposure, the samples were rinsed with iso-propanol and kept in methanol to avoid oxidation. The samples were removed from the methanol immediately prior to being placed in the ultra-high vacuum of the XPS instrument. After each step during the chemical treatment, the samples were blow-dried with nitrogen gas. The solution pH was determined using universal pH indicator paper. The accuracy of the pH indicator was estimated to be the measured pH ± 1. For the passivation treatment the procedure above was repeated followed by exposure in 30 wt.% of H2O2 for 15 s. After each BM or passivation treatment the CZT surface was re-polished using the alumina suspension ready for the next exposure.

To determine the Ar+ sputter rate of CZT; a CdTe layer was deposited by metal organic chemical vapour deposition (MOCVD) onto a Si (1 0 0) wafer at the Centre for Solar Energy Research, Glyndwr University, UK. Details of the process can be found in [13]. The nominal CdTe layer thickness, measured by in situ laser interference reflectometry was 120 nm. Using ex situ mechanical profilometry, the thickness of the area to be Ar+ sputtered was determined to be 135 nm.

2.2. XPS analysis

A Thermo Scientific Thetaprobe XPS instrument employing a monochromatic Al Kα X-ray source with a photon energy of 1486.68 eV was used in this work. The diameter of the X-ray beam spot was 800 μm. Survey spectra were recorded at a pass energy of 300 eV and high resolution core level spectra recorded at pass energy of 20 eV. Quantification of the XPS data was performed after a Shirley background subtraction using the Thermo Scientific Avantage software which employs instrument modified Wagner sensitivity factors. Depth profiling was undertaken using an EX05 Ar+ ion gun operating at 3 kV and current density of 11.1 μA/cm² (1 μA induced beam current, rastered over a 3 mm × 3 mm area). Spectra were charge referenced to the C 1s peak at 285.0 eV.

3. Results and discussion

3.1. CdTe sputter rate

A depth profile of the MOCVD CdTe thin film is shown in Fig. 1. The Cd:Te ratio exhibits a stoichiometry of 1.0:1.0 and the sputter rate for CdTe at Ar+ ion bombardment at an energy of 3 kV and beam current density of 11.1 μA/cm² was determined to be 0.15 nm/s. This etch rate was then used to calibrate the depth scale for all the XPS depth profiles of BM etched CZT surfaces.

3.2. CZT surface composition after BM etching

The changes in surface composition from exposing CZT in 0.2 (v/v) % BM for times of 5, 15, 30, 60 and 120 s is shown by the XPS profiles given in Fig. 2. For all exposure times, Te is clearly enriched at the surface with a progressive decrease in the Te concentration until the bulk concentration of 50 at.\% is attained. For all of the exposure times, there is little difference in surface composition and the Te rich layer has a thickness of 1.3 ± 0.2 nm. At the surface, the binding energy of the Te 3d5/2 peak was found to be 572.9 ± 0.1 eV and this drops to a value of 572.5 eV in the bulk, consistent with Te in a CZT matrix [10]. The bulk concentrations of Cd and Zn were found on average to be 37 and 13 at.\% respectively. It can be seen that Te enrichment occurs at the expense of both Cd and Zn and the XPS determined average surface concentrations for the different exposure times of Te, Cd and Zn are 66, 28 and 6 at.\% respectively (except for the 5 s exposure, where the Te enrichment is slightly lower and the surface concentrations of Te, Cd and Zn are 60, 30 and 10 at.\% respectively).

The XPS profiles for CZT exposed to 2.0 (v/v) % BM for times of 5, 15, 30, 60 and 120 s are presented in Fig. 3. The profiles again show Te to be enriched at the surface in a similar manner for all of the exposure times with a progressive decrease in the Te concentration until the bulk concentration (Te = 50 at.\%) is reached. The Te enrichment for the 2.0 (v/v) % BM exposure is the same as for the 0.2 (v/v) % BM exposure, with the XPS results giving an average Te concentration for the different exposure times of 66 at.\% at the surface.

![Fig. 1. XPS depth profile of an MOCVD deposited CdTe layer of 135 nm thickness. The CdTe etch rate of 3 kV Ar+ ions at a beam current density of 11.1 μA/cm² was determined to be 0.15 nm/s.](image-url)
The Te enrichment layer thickness has increased to 1.8 ± 0.2 nm and is again invariant with exposure time except for the 5 s exposure duration.

It is clear from these results that there is no difference in the outer surface composition for either the two different BM concentrations or for different exposure times. These results are consistent both with the work of Rouse et al. where no substantial differences in [Cd + Zn]/Te ratio were found for exposures of 1, 3 and 9 min exposures in a 5% BM solution [8] and with Bensouici et al.’s [14] plot of Te/[Cd + Zn]) ratio for different BM concentrations of 1–4% which show very similar values for all BM concentrations [13,14]. However, the enriched Te layer thickness was found to increase slightly as the BM concentration was raised from 0.2 to 2.0%, similar to the results of Özsan et al. [8]. In our study, the pH of the 0.2 and 2.0% BM solutions is approximately 3 in both cases. The absence of a significant change in pH probably explains why there is not a large difference in the Te enrichment region observed for the different BM concentrations, and the relatively small increase in the enriched Te layer thickness may be caused by the 2 (v/v) % BM concentration having a slightly lower pH than the 0.2 (v/v) % BM solution. The invariance of the Te enrichment with exposure time may be explained by the thickness of the Te enriched surface layer being very small (<2 nm): thus the rate of reaction is so rapid that even very short exposure times do not influence the Cd and Zn etching process.

3.3. Passivation treatment

The effect of the passivation treatment (15 s exposure in 30 wt.% H₂O₂) on the 0.2 and 2 (v/v) % BM exposed surfaces can be seen from the changes in the Te 3d⁵/₂ peak presented in Figs. 4 and 5. In addition to the elemental Te 3d⁵/₂ component at 572.8 eV, a peak at 576.3 eV corresponding to TeO₂ is observed. For the 0.2 (v/v) % BM treated surface (Fig. 4), following passivation, the ratio of Te oxide peak to Te elemental peak (TeO₂/Teₚ) increases with BM exposure time up to 120 s of exposure, whilst for the 2.0 (v/v) % BM there is no difference in peak intensity ratio beyond an exposure time of 30 s. This indicates that the oxide grown is slightly thicker for longer BM exposure times. XPS depth profiles plotted using the TeO₂ and Teₚ peaks for the 0.2 (v/v) % and 2 (v/v) % BM exposed samples after passivation are given in Figs. 6 and 7. All of the passivated surfaces show
very similar behaviour, with the Te$_{\text{ox}}$ peak intensity being stronger than the Te$_r$ at the surface (as expected from Figs. 4 and 5), but the Te$_r$ intensity becomes dominant within a sputter time of 5 s and beyond this the oxide intensity tails off exponentially until no oxide is observed beyond a sputter time of 30 s. This somewhat diffuse oxide/bulk interface can be explained by the sample roughness. For both the 0.2 and 2.0 (v/v) % BM exposures, the passivated surfaces with the shortest BM exposure time (5 s) exhibit a slightly thinner oxide layer than those exposed for longer times, probably due to there being a slightly thinner Te enriched layer for these surfaces. With regard to determining the oxide thickness, metal oxides are known to generally exhibit much lower sputter rates than metals, so the TeO$_2$ thickness cannot be determined from the profile using the previously determined CZT sputter rate. Hence, oxide thicknesses have been calculated using established procedures based on the Beer–Lambert expression.

### 3.4. Oxide thickness calculation

Two methods have been used to calculate oxide thickness, a simple Beer–Lambert expression based on photoemission at a single take-off angle and a Beer–Lambert expression based methodology employing a range of take-off angles.

#### 3.4.1. The Beer–Lambert expression employing a single photoelectron take-off angle

The intensity of photoelectrons emitted from a depth greater than d at an angle $\theta$ to the surface normal is given by the Beer–Lambert expression [15]:

$$ l = l_0 \exp \left( \frac{-d}{\lambda \cos \theta} \right) $$

(1)

where $l_0$ is the intensity from an infinitely thick substrate and $\lambda$ is the photoelectron attenuation length. Manipulation of the Beer–Lambert expression and use of the core level elemental and oxide photoelectron peaks, $I_{\text{el}}$ and $I_{\text{ox}}$ respectively, gives rise to the following equation for the oxide thickness, $d_{\text{ox}}$:

$$ d_{\text{ox}} = \lambda \cos \theta \ln \left[ 1 + \frac{(I_{\text{el}}/I_{\text{ox}})}{(I_{\text{el}}/I_{\text{el}})} \right] $$

(2)

where $I_{\text{el}}$ and $I_{\text{ox}}$ are the intensities of the bulk TeO$_2$ and elemental Te peaks respectively. For calculating overlayer or oxide thicknesses, assuming that $\lambda$ and $\lambda_{\text{ox}}$ are the same for Te and TeO$_2$ gives rise to the following simplified expression:

$$ d_{\text{ox}} = \lambda_{\text{ox}} \cos \theta \ln \left( \frac{I_{\text{ox}}}{I_{\text{el}}} + 1 \right) $$

(3)

The attenuation length of photoelectrons in the oxide layer, $\lambda_{\text{ox}}$, is calculated using Cumpson and Seah’s equation given in [16]

$$ \lambda = 0.316a^{3/2}\left[ \frac{E}{20.45\sin(E/27) + 4} \right] $$

(4)

where $a$ is the lattice parameter (nm), $E$ is the photoelectron kinetic energy (eV) and $Z$ is the average atomic number of the oxide.

#### 3.4.2. The Beer–Lambert expression employing multiple photoelectron take-off angles

With the possibility of acquiring the photoelectron intensities at different take-off angles, then a more rigorous approach can be used to test for the presence of a discrete oxide overlayer and to determine the oxide thickness [15]. The ratio of $I_{\text{el}}$ and $I_{\text{ox}}$ can be represented by $R_{\text{ox}}$ which can be found by manipulating some bulk material parameters, given by:

$$ R_{\text{ox}} = \frac{D_{\text{Te}}F_{\text{Te}}\lambda_{\text{Te},\text{TeO}_2}}{D_{\text{TeO}_2}F_{\text{TeO}_2}\lambda_{\text{Te},\text{Te}}} $$

(5)

where $D_{\text{Te}}$ and $D_{\text{TeO}_2}$ are the elemental Te and TeO$_2$ bulk densities (6.24 and 5.90 g/cm$^3$, respectively), $F_{\text{Te}}$ and $F_{\text{TeO}_2}$ are the molar masses of elemental Te and TeO$_2$ (127.6 and 159.6, respectively) and $\lambda_{\text{Te},\text{Te}}$ and $\lambda_{\text{Te},\text{TeO}_2}$ are the photoelectron attenuation lengths of Te $3d_{5/2}$ electrons in elemental Te and TeO$_2$, calculated by the Cumpson and Seah equation [16] to be 1.6 and 1.5 nm respectively. $I_{\text{ox}}/I_{\text{el}}$ can be replaced by $R$ and Eq. (2) rearranged to give:

$$ \ln \left[ 1 + \frac{R}{R_{\text{ox}}} \right] = \frac{d_{\text{ox}}}{\lambda} \frac{1}{\cos \theta} $$

(6)

Then for a set of angle resolved XPS data recorded at different values of take-off angles, $\theta$, the left-hand side of the equation can be plotted against $1/\cos \theta$. A straight line can be drawn through the data, with the slope corresponding to $d_{\text{ox}}/\lambda$. Knowing the attenuation length, the oxide thickness can be determined.

The XPS Thetaprobe angle resolved XPS (ARXPS) capability allows data to be recorded over 16 angles between 25$^\circ$ and 81$^\circ$ relative to the sample surface normal without rotation of the sample. The slope was determined for take-off angles not exceeding the 50$^\circ$, to avoid elastic scattering effects. An example of the ARXPS data.

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**Fig. 6.** XPS depth profile (using CZT Te$_{3d_{5/2}}$ bulk and oxide peaks) of CZT surfaces exposed to 0.2 (v/v) % BM for various times followed by a 15 s passivation treatment in 30 wt.% H$_2$O$_2$.

**Fig. 7.** XPS depth profile (using CZT Te$_{3d_{5/2}}$ bulk and oxide peaks) of CZT surfaces exposed to 2.0 (v/v) % BM for various times followed by a 15 s passivation treatment in 30 wt.% H$_2$O$_2$. 

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recorded for a 0.2 (v/v) % BM exposure for 120 s followed by a passivation treatment of 15 s in 30 wt.% H₂O₂ when using equation 6 is given in Fig. 8. The plot shows a clear linear relationship and the oxide thickness, \( d_{\text{ox}} \), calculated from the slope of the straight line was found to be 1.25 nm.

The TeO₂ thickness calculated for the single angle and angle resolved data is shown in Table 1. The oxide thickness trends as a function of exposure time for the different calculation methods are very similar and in both cases the oxide thickness after 5 s of BM exposure is slightly smaller than other exposure times. The oxide thicknesses calculated from simplified Beer–Lambert expression gives the same oxide thickness for 5 s of BM exposure for both concentration (0.2 and 2.0, v/v %). For longer exposure times, the 0.2 (v/v) % BM exposure exhibits a gradual increase in oxide thickness as the duration time increases. While for 2.0 (v/v) % BM exposures, beyond 5 s there is an increase in thickness which remains essentially unchanged for all other exposure times. In both cases (0.2 and 2.0, v/v % BM exposure) the highest value of oxide thickness is around 1 nm.

The oxide thicknesses calculated from ARXPS data are slightly higher than the thickness obtained by simplified Beer–Lambert expression and the trend of increasing oxide thickness for longer BM exposure times is similar to that found for the simplified Beer–Lambert expression. The highest value of oxide thickness for the ARXPS data is 1.25 nm. Considering the methodologies employed, it is likely that the ln[(1 + R/R∞) vs. 1/\( \cos \theta \)] plot will give more accurate values than the Beer–Lambert expression given in equation 3 as fewer assumptions are made in the former approach. The different values of \( D, F \) and \( \lambda \) for Te and TeO₂ are taken into account in Eq. (5), whereas the simplified Beer–Lambert expression in Eq. (3) assumes that \( \lambda \) and R∞ are the same for Te and TeO₂. Furthermore, the multiple angle approach considers the photoelectron intensity data for a number of take-off angles and the linear regression fit will tend to reduce the experimental error in determination of oxide thickness compared to a single intensity measurement from one take-off angle.

For CZT etched in BM concentrations between 0.2 and 5%, followed by a 30 s exposure in 30 wt.% H₂O₂, Özsan et al. reported oxide thicknesses between 1.6 and 2.8 nm [8]. Chen et al. used a 5% BM solution followed by 1–15 min exposure in 15% H₂O₂ and found oxide thicknesses of between 2.1 and 4.5 nm [11]. According to Özsan et al, increasing the BM concentration from 2 to 5% followed by 30 s exposure in 30 wt.% H₂O₂ results in only a minimal increase in oxide thickness (from 2.7 to 2.8 nm). In this work, using the same simple Beer–Lambert expression employed by the other authors (Eq. (2)), a thickness of 1.0 nm is reported for exposure in BM concentrations of 0.2 and 2.0 (v/v) % followed by exposure in 30 wt.% H₂O₂ for 15 s. The lower oxide thicknesses reported here compared to those given by the other authors [8,11] could result from the shorter H₂O₂ exposure time, but the different attenuation lengths, \( \lambda \), are probably the major cause of discrepancy. Özsan et al. [8] used the simpler, empirical Seah and Dench [17] approach, which yields a value of 2.6 nm for \( \lambda \), rather than the more refined Cumpson and Seah expression [16] employed in this work, which gives a value of 1.5 nm.

### 4. Conclusions

CZT single crystals have been exposed to etching treatments using a BM concentration of 0.2 and 2.0 (v/v) % for exposure times between 5 and 120 s. XPS depth profiles have shown that both treatments resulted in the formation of a Te rich surface region. The enriched Te layer thickness was accurately determined by calibrating the CZT sputter rate against a CdTe layer of known thickness. Varying the exposure time had no effect on the thickness of the Te rich region, which was found to extend to a depth of 1.3 ± 0.2 nm for the 0.2 (v/v) % BM etch and 1.8 ± 0.2 nm for the 2.0 (v/v) % BM etch. The invariant effect of exposure time between 5 and 120 s is considered to be due to the rapid etching process of such a thin Te enriched layer. The similarity in the surface compositions for the two different BM concentrations is ascribed to the comparable pH (pH ≈ 3) of both solutions but the increase in the Te rich layer thickness for the higher concentration of BM is probably due to this solution having a slightly lower pH.

The BM exposed surfaces were passivated using a 15 s H₂O₂ treatment. A thin TeO₂ layer was formed. XPS depth profiles showed there to be little change in the oxide thickness between the surfaces BM etched at different concentrations or etch times, but the 5 s exposure in both 0.2% and 2 (v/v) % BM gave rise to a slightly thinner oxide layer than the longer BM exposure times. Determination of the oxide thickness using a Beer–Lambert expression and single photoelectron take-off angle showed a similar trend to that using Beer–Lambert expression and multiple photoelectron take-off angles. For BM exposures of 30–120 s followed by a passivation treatment of 30 wt. % H₂O₂ solution employing an exposure time 15 s, the former method gave an average TeO₂ thickness value of

### Table 1
Comparison of the TeO₂ thickness calculated by a simplified Beer–Lambert expression (single take-off angle) compared to ARXPS data (range of take-off angles) after exposing CZT in 0.2 (v/v) % and 2 (v/v) % BM for varying times followed by a 15 s passivation treatment in 30 wt.% H₂O₂.

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Average oxide thickness (nm) for BM exposure durations of 5, 15, 30, 60 and 120 s (±0.07 nm for single angle and ±0.12 nm for ARXPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 s</td>
</tr>
<tr>
<td>Single angle (simplified Beer–Lambert expression)</td>
<td>(0.2)</td>
</tr>
<tr>
<td>Angle resolved XPS</td>
<td>(0.2)</td>
</tr>
<tr>
<td></td>
<td>(2)</td>
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<td></td>
<td>(2)</td>
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</tbody>
</table>

![Fig. 8. ARXPS plot to determine the oxide thickness, \( d_{\text{ox}} \), of a CZT surface exposed in 0.2 (v/v) % BM for 120 s followed by passivation in 30 wt.% H₂O₂ for 15 s.](image-url)
0.99 nm and the latter method yielded an average thickness value of 1.20 nm. For H$_2$O$_2$ treated samples, the former method gave an oxide thickness in the range of 1.0 ± 0.07 nm whilst the latter yielded an oxide thickness of 1.25 ± 0.12 nm.

The results presented in this paper give accurate values for the thickness of both the enriched Te layer (following BM exposure at different concentrations) and the H$_2$O$_2$ generated oxide layer. Such data is important to workers in the field of device fabrication where a balance between low leakage current and good charge collection is required from this surface region. Hence, this study is of importance for further research work on the determination of optimum oxide thickness and composition for improved device performance.

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References

Influence of CdCl₂ activation treatment on ultra-thin Cd₁₋ₓZnₓS/CdTe solar cells

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Abstract

Ultra-thin CdTe photovoltaic solar cells with an absorber thickness of 0.5 μm were produced by metal organic chemical vapour deposition onto indium tin oxide coated boroaluminosilicate glass. A wide band gap Cd₁₋ₓZnₓS alloy window layer was employed to improve spectral response in the blue region of the solar spectrum. X-ray photoelectron spectroscopy, X-ray diffraction and scanning electron microscopy were used to monitor changes in the chemical composition and microstructure of the Cd₁₋ₓZnₓS/CdTe solar cell after varying the post-deposition CdCl₂ activation treatment time and annealing temperature. The CdCl₂ treatment leached Zn from the Cd₁₋ₓZnₓS layer causing a redshift in the spectral response onset of window absorption. S diffusion occurred across the Cd₁₋ₓZnₓS/CdTe interface, which was more pronounced as the CdCl₂ treatment was increased. A CdTe₁₋ₓSₓ alloy was formed at the interface, which thickened with CdCl₂ treatment time. Small concentrations of S (up to 2 at.%) were observed throughout the CdTe layer as the degree of CdCl₂ treatment was increased. Greater S diffusion across the Cd₁₋ₓZnₓS/CdTe interface caused the device open-circuit voltage (V_oc) to increase. The higher V_oc is attributed to enhanced strain relaxation and associated reduction of defects in the interface region as well as the increase in CdTe grain size.

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1. Introduction

CdTe solar module production is the most successful thin film technology for commercial photovoltaics (PV) [1]. This has much to do with the relative ease of industrial scale-up [2] as well as its near optimum band gap for solar absorption [3]. Recent developments led by industry have resulted in improvements to world records for both cell (21.0%) and module (17.5%) conversion efficiencies [4]. In order to produce CdTe solar cells without the effects of pinholes, the absorber thickness is typically 2–7 μm [5,6], but the majority of photons are absorbed in the first 1 μm [7,8]. However, the performance of ultra-thin CdTe solar cells (absorber thickness ≤1 μm) can be optically limited with loss of longer wavelength photons towards the CdTe band gap [8–10]. For future large scale production of CdTe solar modules to remain sustainable, consideration has to be given to the global availability of tellurium [1,8,11]. Hence, there is currently great interest in improving the performance of ultra-thin CdTe solar cells.

Ultra-thin CdTe solar cells can be susceptible to a drop in open circuit voltage (V_oc) and fill factor (FF) [12,13]. For the latter, this is typically associated with an increased number of micro-shunts [9,13] due to the ultra-thin CdTe absorber layer having a large density of pinholes. It has also been suggested [14] that recombination at the back contact becomes more prominent when reducing the CdTe absorber thickness for ultra-thin solar cells, which has an adverse effect on V_oc. In addition, reports have shown [13,15] that ultra-thin CdTe solar cells are more sensitive to the effects of CdCl₂ activation treatment, which can significantly affect the wide band gap Cd₁₋ₓZnₓS alloy window layer composition.

It has been demonstrated [15] that the CdCl₂ layer deposited prior to the annealing treatment needs to be sufficiently thick to induce an appropriate level of intermixing across the Cd₁₋ₓZnₓS/CdTe interface in order to reduce strain related defects for enhancement of the V_oc. This study uses X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM) to examine in detail the compositional and structural changes to ultra-thin Cd₁₋ₓZnₓS/CdTe solar cells after different levels of CdCl₂ activation treatment. The changes in individual layer and interface compositions following the different CdCl₂ activation treatments have been correlated with device PV properties.

2. Experimental

Ultra-thin Cd₁₋ₓZnₓS/CdTe solar cells were produced using metal organic chemical vapour deposition (MOCVD) in a single growth chamber.

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Boroaluminosilicate glass coated with indium tin oxide (ITO) was used as the substrate, with glass thickness of 1.1 mm and an ITO sheet resistance of 4–8 Ω/sq. The ultra-thin CdTe solar cell spectral response in the blue region of the solar spectrum was enhanced by using a wide band gap Cd1−xZn1−xS window layer, 0.24 μm in thickness [5,13,16]. As was used as the CdTe acceptor dopant with concentration [As] in the range of ~10¹⁸–10¹⁹ atoms/cm³. An in situ CdCl₂ treatment process [17] was used with variable deposition time for control of the relative CdCl₂ layer thickness and hence level of CI diffusion into the CdTe layer during anneal at 420 °C for activation of the solar cell. A CdTe absorber thickness of 0.5 μm was employed for all ultra-thin solar cells due to high sensitivity of the spectral response to the CdCl₂ activation treatments. Each ultra-thin CdTe solar cell device consisted of 8 × 0.25 cm² cells defined by evaporating Au through a shadow mask.

Compositional changes to the ultra-thin Cd₁₋ₓZnₓS/CdTe solar cells were determined by using a Thermo Scientific Thetaprobe XPS instrument employing a monochromatic Al Kα X-ray source with a photon energy of 1486.7 eV. The diameter of the X-ray beam spot was 800 μm. Wide scan spectra were recorded at a pass energy of 300 eV and narrow scan spectra recorded at pass energy of 20 eV. Quantification of the XPS data was performed after a Shirley background subtraction using the Thermo Scientific Avantage software which employs instrument modified Wagner sensitivity factors. Depth profiling was undertaken using an Ar⁺ ion gun operating at 3 keV and current density of 11.1 μA/cm² (1 μA induced beam current, rastered over a 3 × 3 mm² area). Spectra were charge referenced to the C 1 s peak at 285.0 eV.

XRD analysis was carried out with a Bruker D8 Discover instrument, equipped with twin primary and secondary optics. Copper Kα radiation was used, together with a Lynx-eye position sensitive detector. All scans reported here were made in the parafocussing mode due to instrumental resolution being much higher than in the parallel beam mode. Following data collection, the instrumental software was used to strip the Kα₂ component from the diffraction patterns. XRD peak fitting was based on the least-squares fitting of broadened peaks to a pseudo-Voigt function enabling the grain size to be estimated from the Lorentzian component based on the Scherrer equation [18,19]. SEM was performed using a Jeol JSM-7100 F instrument, employing a Schottky field emission gun, operated at 10 keV.

Current density–voltage (J–V) measurements were carried out at AM1.5 using an Abet Technologies Ltd. solar simulator with light power density output equal to 100 mW/cm² calibrated using a Fraunhofer c-Si reference cell. Only single pass illumination from the front side of the cell was carried out with no intentional back reflection, but with possibility of this occurring from the Au back contacts. External quantum efficiency (EQE) measurements were carried out using a Bentham spectral response spectrometer under unbiased conditions over the spectral range of 0.3–1.0 μm.

3. Results and discussion

The different times (s) for the CdCl₂ layer deposition and 420 °C anneal used for the activation treatment of the ultra-thin CdTe solar cell devices are outlined in Table 1. Pre-anneal CdCl₂ layer thickness ranged from 0.9–2.0 μm between 80 and 179 s deposition time, respectively, based on a growth rate of 11 nm/s at 420 °C [17]. The treatment parameters typical for a solar cell device with baseline-MOCVD CdTe thickness of 2.25 μm are also shown. No ultra-thin device which has only received the high temperature anneal has been included in this study. A previous study [20] showed that annealing induces interdiffusion, but that without the presence of CdCl₂, the effects were not as prominent. The study reported here focuses on the effects of the CdCl₂ activation treatment only.

3.1. J–V and EQE curves

J–V curves for best cells from two ultra-thin CdTe PV devices having received the largest variation in CdCl₂ treatment are given in Fig. 1. The results show an improvement in V_oc as the CdCl₂ deposition time was increased, whereas little change in J_sc was observed to occur. Comparison to the reference ultra-thin device and a baseline device (CdTe = 2.25 μm) has also been made. It is clear that the V_oc drops significantly as the absorber thickness is reduced from the baseline to the ultra-thin CdTe. The large degree to which V_oc falls may suggest additional mechanisms to the effects of CdCl₂ treatment, such as back surface recombination [14], which is not addressed in this paper. Table 2 shows mean J–V parameters for the devices with best cells represented in Fig. 1.

Ultra-thin solar cells can suffer from a large variation in shunt resistance (R_sh) due to the presence of pin-holes from incomplete CdTe coverage. However, Table 2 shows similar FF values between the CdCl₂ treated ultra-thin cells suggesting little variation in R_sh between the ultra-thin PV cells. The reference ultra-thin cell has a more significant reduction in FF, which is attributed to the absence of CdCl₂ activation treatment. This showed some effect on series resistance (R_s), which increased, but may also be due to an increase in reverse saturation current density.

EQE of a cell from each sample is shown below in Fig. 2. In general, as previously reported [15], the window layer absorption edge shifts further into the blue region of the solar spectrum as the CdCl₂ deposition was reduced. This has a direct correlation to the level of Zn in the Cd₁₋ₓZnₓS alloy detected by XPS. There is a discrepancy between samples T080A10 and T080A02, which had the same levels of CdCl₂, but different anneal times. Sample T080A10, which was annealed for

![Fig. 1. J-V curves for cells from ultra-thin CdTe PV devices after CdCl₂ activation treatment; comparison to a baseline CdTe PV cell and reference ultra-thin PV cell.](image)
10 min, has better blue response than sample T080A02. One would expect the shorter anneal time to yield better blue response due to a lesser influence of the Zn leaching effect by the Cl during diffusion. Greater Cl diffusion may be assumed after a longer annealing time. Another observation is the different EQE levels over the red region of the solar spectrum relating to the collection of generated photocurrent in the CdTe absorber layer. For the most part, samples with a red-shifted window layer absorption edge have higher EQE over the red region. This is not the case for sample T120A10 which shows loss of photocurrent generation towards longer photon wavelengths, similar to what has been reported previously [8,10].

The $J_{sc}$ has been calculated for each solar cell by integrating the area under the EQE curves shown in Fig. 2. When comparing to Table 1 from $J$–$V$ measurements, the calculated $J_{sc}$ reveals an over-estimation for the baseline solar cell, but under-estimation for the ultra-thin solar cells, with the exception of the T120A10 cell where loss of photocurrent generation towards the longer wavelengths was evident in the EQE curve. The $J_{sc}$ from the EQE curve calculation for samples T179A10, T080A10 and T080A02 differ slightly, compared to the same values obtained from the $J$–$V$ curves. Interestingly, sample T179A10 has red-shifted at the CdTe band edge relative to all other samples. This may have something to do with the increased level of S diffusion towards the back contact, as determined by the XPS analysis, due to the thin CdTe thickness and treatment with thicker CdCl$_2$ layer.

Fig. 3 shows a simplified energy band diagram produced by Solar Cell Capacitance Software (SCAPS) [21] for a CdTe/Cd$_{1-x}$Zn$_x$S junction for solar cells with different Zn levels in the Cd$_{1-x}$Zn$_x$S window layer. The band gaps for the different Zn levels in Cd$_{1-x}$Zn$_x$S have been taken from Ref. [16]. It illustrates a drop in Cd$_{1-x}$Zn$_x$S valence band energy with Zn incorporation into the window layer. More significantly, the conduction band offset is reduced when comparing the CdS/CdTe junction with Cd$_{1-x}$Zn$_x$S/CdTe. This results from a reduced electron affinity in the window layer with the addition of Zn. Previous reports [12,13] have shown that $V_{oc}$ increases for Cd$_{1-x}$Zn$_x$S/CdTe solar cells in comparison to equivalent CdS/CdTe devices. The difference in $V_{oc}$ between the ultra-thin devices reported here are small, with values being low in general compared to the baseline CdTe device (Table 2). This shows recombination in the ultra-thin cells is high and the small improvement in $V_{oc}$ with greater CdCl$_2$ treatment is likely to be due to a reduction in defect density coupled with strain relaxation.

### 3.2. XPS depth profiles

XPS depth profiling was performed to understand the effect of the various CdCl$_2$ activation treatments on the ultra-thin CdTe solar cell multilayer composition. The depth profiles for the reference device (no CdCl$_2$ activation treatment), device T080A02 (CdCl$_2$ deposited for 80 s and annealed for 120 s) and device T179A10 (CdCl$_2$ deposited for 179 s and annealed for 600 s) are shown in Fig. 4. It has been assumed that the ion etching rate for all samples is the same, although differences may occur due to variation in sample surface roughness. The results for the reference device show that the Cd$_{1-x}$Zn$_x$S alloy contained a notable amount of Zn (Cd$_{0.41}$Zn$_{0.59}$S). This composition was chosen to achieve a wide band gap of ~2.7–2.9 eV for the window layer [16]. Cl was omitted from these profiles as it was not detected for all of the samples. In the cases where it was detected the signal dropped in and out and the level was generally very low.
A number of changes in the CdTe and Cd$_{1-x}$Zn$_x$S layer compositions can be observed from the XPS profiles as a result of the CdCl$_2$ activation treatment. As the thickness and anneal time of the CdCl$_2$ activation treatment is increased three effects are observed: (i) a reduction in the Zn concentration in the Cd$_{1-x}$Zn$_x$S layer; (ii) increased diffusion of S into the CdTe layer (with S diffusing through the CdTe layer to back contact region); (iii) Cd and Te diffusion into the Cd$_{1-x}$Zn$_x$S layer.

The Cd concentration in the Cd$_{1-x}$Zn$_x$S can be seen to drop from Cd$_{0.41}$Zn$_{0.59}$S for the reference sample with no CdCl$_2$ treatment to Cd$_{0.50}$Zn$_{0.50}$S after 80 s of CdCl$_2$ deposition and a 120 s anneal and Cd$_{0.76}$Zn$_{0.24}$S after 179 s deposition and a 600 s anneal. Fig. 5 shows the spectral response absorption edge as a function of the Zn content in the Cd$_{1-x}$Zn$_x$S window layer. The onset of absorption for the Cd$_{1-x}$Zn$_x$S window layer edge shifts to longer wavelengths with a drop in Zn content, indicative of a reduced band gap. This is consistent with the lower concentrations of Zn remaining in the Cd$_{1-x}$Zn$_x$S layer following the CdCl$_2$ treatment.

Interestingly, from the XPS profiles, there is no clear indication of where the Zn has migrated to from the Cd$_{1-x}$Zn$_x$S layer. The loss of Zn correlates with a proportional gain in Cd content in the Cd$_{1-x}$Zn$_x$S layer (Fig. 5), which must also be due to the CdCl$_2$ deposition and anneal treatment. It is known that metal chlorides are used to leach Zn from ZnS [22] and the progressive decrease in Zn concentration with increasing CdCl$_2$ treatment would also suggest that the reaction of Cl$^-$ species with the Cd$_{1-x}$Zn$_x$S layer is the probable cause of this Zn depletion. It is well-known that Cl$^-$ diffuses along grain boundaries within the CdTe layer during the CdCl$_2$ treatment. The particularly thin layer of CdTe in these devices is allowing Cl$^-$ species to easily diffuse to the underlying Cd$_{1-x}$Zn$_x$S layer. Hence, Cl$^-$ attack is resulting in Zn$^{2+}$ species being released from Cd$_{1-x}$Zn$_x$S [20]. The low melting point of ZnCl$_2$ (293 °C) may prevent the deposition of a solid reaction product and the Zn$^{2+}$ species diffuse outwards along the CdTe grain boundaries to the surface. At the high temperature (420 °C) during the anneal treatment the Cd$_{1-x}$Zn$_x$S formed at the back surface most likely desorbs into the gas phase, removing it from the growth chamber. The Zn$^{2+}$ diffusion process is probably being enhanced by the Cl$^-$ concentration gradient.

The diffusion of S from the Cd$_{1-x}$Zn$_x$S (or CdS) layer into the CdTe layer has been reported previously by a number of authors [e.g., 23–28] and can occur as a result of high process temperatures [23] as well as a post-deposition CdCl$_2$ treatment. Fig. 6 shows the close correlation between CdCl$_2$ layer deposition time and S content in the CdTe absorber layer. A constant S content of approximately 2 at.% within the CdTe layer is observed when CdCl$_2$ is deposited for 179 s and annealed for 600 s. $V_{oc}$ clearly increases with greater S diffusion across the Cd$_{1-x}$Zn$_x$S/CdTe interface.

With regard to the influence of anneal time on S diffusion and $V_{oc}$, devices T080A02 and T080A10 were activated using the same CdCl$_2$ layer thickness but were annealed at 420 °C for different times (2 and 10 min, respectively). The longer anneal (device T080A10), gave rise to a small increase in $V_{oc}$ and slightly higher S concentration in CdTe compared to the shorter anneal (device T080A02). The annealing times used in this study were relatively short and more significant changes in the degree of S diffusion have been observed after employing longer annealing times [23].

From the profiles shown in Fig. 4, it can be seen that there is a small but detectable Te concentration in the window layer as the deposition/anneal time for the CdCl$_2$ activation treatment is increased for the ultra-thin solar cells. For device T179A10, a Te concentration of 1–2 at.% is present in the Cd$_{1-x}$Zn$_x$S layer. It has previously been reported that the intermixing of CdTe and CdS leads to formation of both Cd$_{1-x}$Zn$_x$S and Cd$_{1-x}$Te$_x$S$_{1-y}$ layers [22]. Hence, Te diffusion into the Cd$_{1-x}$Zn$_x$S layer is expected with concomitant diffusion of S into CdTe. Similar to the formation of Cd$_{1-x}$Zn$_x$S, the diffusion of Te into Cd$_{1-x}$Zn$_x$S may promote strain relaxation between the Cd$_{1-x}$Zn$_x$S and CdTe layers and contribute to the higher $V_{oc}$ after greater CdCl$_2$ activation treatment [15].

### 3.3 XRD

For CdS/CdTe solar cells, it has previously been demonstrated [22] using grazing incidence XRD that the diffraction peaks associated with
CdTe split after annealing due to interdiffusion across the CdS/CdTe interface. A shoulder on the CdTe peak became more prominent with increasing annealing time, with the new peak resulting from the formation of a CdTe$_{1-x}$S$_x$ alloy in the solar cell junction region. An increase in the CdTe$_{1-x}$S$_x$ layer thickness was attributed to greater interdiffusion for longer annealing times [23].

Fig. 7(a) shows diffraction scans for the ultra-thin CdTe solar cells after various post-deposition CdCl$_2$ activation treatments together with that for the reference device (no CdCl$_2$ activation treatment). Fig. 7(b) shows the CdTe (111) peak in high resolution. The reference device has a single (111) diffraction peak associated with CdTe. For the activated ultra-thin devices, the CdTe diffraction peak is shifted from that of the reference device and a second peak at a higher 20 value emerges and increases in intensity with longer CdCl$_2$ deposition times. The shift of the main CdTe peak for the ultra-thin devices exposed to CdCl$_2$ treatment compared to the reference device is most probably related to recrystallisation and strain relaxation which occurs upon annealing. The second peak which emerges at higher 20 values is associated with the CdTe$_{1-x}$S$_x$ alloy. This layer typically thickens with increased CdCl$_2$ treatment and the CdTe$_{1-x}$S$_x$ alloy exhibits a lattice parameter, $a$, which is on average 0.4% lower than that for the CdTe alloy in these devices, in good agreement with previous work [23,25]. The thicker CdTe$_{1-x}$S$_x$ layer formed enhances strain relaxation and results in the higher $V_{oc}$ observed in Fig. 6. Increased S diffusion across the Cd$_{1-x}$Zn$_x$S/CdTe interface may also give rise to a greater passivation of defects by Cl and S species [26].

From the XPS data it is clear that the Zn concentration in the Cd$_{1-x}$Zn$_x$S layer decreases following the CdCl$_2$ treatment. Not surprisingly, the loss of Zn from this layer causes a progressive reduction in the lattice parameter, $a$, which is on average 0.4% lower than that for the CdTe alloy in these devices, in good agreement with previous work [23,25]. This layer typically thickens with increased CdCl$_2$ treatment and the CdTe$_{1-x}$S$_x$ alloy exhibits a lattice parameter, $a$, which is on average 0.4% lower than that for the CdTe alloy in these devices, in good agreement with previous work [23,25].

The CdTe (111) peak was employed to determine the average grain size. As this peak is broadened by the presence of the CdTe$_{1-x}$S$_x$ layer, a progressive increase in the average grain size with the CdCl$_2$ deposition time is apparent. However, the average grain sizes are greater than those determined by XRD. A probable explanation for the discrepancy in the XRD and SEM measured average grain size can be described as follows. Competitive grain growth leads to a preferential increase in the size of the faster growing grains, suppressing the development of other grains which initiate in the early stages of layer growth. The XRD analysis will consider all grains present in the layer, whilst any smaller CdTe grains closer to the Cd$_{1-x}$Zn$_x$S/CdTe interface will not be considered in the SEM analysis. Furthermore, SEM measurements consider the grain size parallel to the surface plane whilst XRD measurements determine the grain size perpendicular to the surface plane. Hence, anisotropy in the grain development and growth would also explain the discrepancy in the values measured by the two techniques.

The increase in CdTe grain sizes for longer CdCl$_2$ deposition times is a well-known phenomenon, resulting from recrystallisation of the grains. Grain boundaries act as carrier recombination centres and larger grain sizes reduce the density of such recombination sites and also contribute to an increase in $V_{oc}$ [30]. The rate of grain growth is rapid for a small grain but larger grains do not increase in size as significantly during the CdCl$_2$ anneal [31]. Grain size is not only influenced by the CdCl$_2$ anneal treatment but also the temperature of the deposition process [32].

4. Conclusions

Ultra-thin CdTe solar cells using a 0.5 μm absorber thickness were exposed to CdCl$_2$ activation treatments for varying times and annealing temperatures. The treatments led to changes in layer compositions and diffusion across interfaces which have been studied using XPS and XRD and correlated with the PV properties of the devices. The most evident effect of the CdCl$_2$ treatment was the leaching of Zn from the Cd$_{1-x}$Zn$_x$S window layer. As the degree of CdCl$_2$ treatment was increased, a greater loss of Zn was observed. It is proposed that the CdCl$_2$ treatment caused Zn to be preferentially leached from the Cd$_{1-x}$Zn$_x$S layer enhanced by the chloride concentration gradient. The depletion of Zn in the Cd$_{1-x}$Zn$_x$S
Cd concentration, was observed to diffuse from the CdTe into the with a thicker CdCl2 layer and greater loss of Zn. An increase in device levels of CdCl2 treatment, but with the same 10 minute anneal. The image for the reference alloy was observed, which thickened with CdCl2 treatment time. S was spectral response measurements. led to a progressive increase in the absorption edge wavelength for the spectral response measurements.

S diffusion across the Cd1−xZnxS/CdTe interface occurred, which was more pronounced as the CdCl2 treatment was increased. A CdTe1−xS alloy was observed, which thickened with CdCl2 treatment time. S was found throughout the CdTe layer at an average concentration of 2.0 at.% for a CdCl2 treatment time of 179 s and anneal time of 600 s. A small concentration of Te (1–2 at.%), in addition to a more significant Cd concentration, was observed to diffuse from the CdTe into the Cd1−xZnxS layer. The diffusion of Cd into the Cd1−xZnxS layer coincided with a thicker CdCl2 layer and greater loss of Zn. An increase in device Voc was observed for greater S diffusion across the Cd1−xZnxS/CdTe interface. This was attributed to enhanced strain relaxation and associated reduction of defects in the interface region.

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