Characterization of the metal–semiconductor interface of gold contacts on CdZnTe formed by electroless deposition

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Abstract
Fully spectroscopic x/γ-ray imaging is now possible thanks to advances in the growth of wide-bandgap semiconductors. One of the most promising materials is cadmium zinc telluride (CdZnTe or CZT), which has been demonstrated in homeland security, medical imaging, astrophysics and industrial analysis applications. These applications have demanding energy and spatial resolution requirements that are not always met by the metal contacts deposited on the CdZnTe. To improve the contacts, the interface formed between metal and semiconductor during contact deposition must be better understood. Gold has a work function closely matching that of high resistivity CdZnTe and is a popular choice of contact metal. Gold contacts are often formed by electroless deposition however this forms a complex interface. The prior CdZnTe surface preparation, such as mechanical or chemo-mechanical polishing, and electroless deposition parameters, such as gold chloride solution temperature, play important roles in the formation of the interface and are the subject of the presented work. Techniques such as focused ion beam (FIB) cross section imaging, transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS), x-ray photoelectron spectroscopy (XPS) and current–voltage (I–V) analysis have been used to characterize the interface. It has been found that the electroless reaction depends on the surface preparation and for chemo-mechanically polished (1 1 1) CdZnTe, it also depends on the A/B face identity. Where the deposition occurred at elevated temperature, the deposited contacts were found to produce a greater leakage current and suffered from increased subsurface voiding due to the formation of cadmium chloride.

Keywords: CZT, radiation detection, XPS, PCA, FIB, I–V

(Some figures may appear in colour only in the online journal)
ASICs [7–9]. These detectors have been demonstrated in the fields of medical imaging [10–12], homeland security [13, 14] and materials science [15, 16].

Spectroscopic x-ray imaging is demanding in both energy and spatial resolution requirements. Two of the major factors that affect energy and spatial resolution are material quality and metal contacts. Refinements in the growth process have delivered consistent improvements in both yield and quality of single crystal CdZnTe [17]. For small pixel CdZnTe detectors, the metal contacts are now considered to be the limiting factor in detector performance [18]. It is necessary to deposit metal contacts on the CdZnTe to allow a bias to be applied across the crystal and to allow the charge released during a radiation interaction to be collected and measured by the readout electronics. The work function of the contact metal and the presence of interface states strongly influence the electronic and spectroscopic performance of the detector. Through careful control of the crystal processing and contact deposition processes the concentration of defects in the metal–semiconductor interface may be controlled. Forming a uniform interface between the metal and bulk CdZnTe ensures that the charge transport and counting efficiency is uniform across the detector. This is particularly important for pixellated imaging detectors.

Gold is the most commonly used contact metal for CdZnTe as it is a good conductor and has a work function of 5.1 eV [19], similar to that of high resistivity CdZnTe which is in the order of 5.0 eV. There are several methods of gold deposition; thermal evaporation, sputtering and electroless deposition. Electroless deposition has been observed to result in greater adhesion compared with thermally evaporated contacts [20]. This is explained by the increased chemical bonding and greater incorporation of gold into the metal–semiconductor interface [21, 22]. Electroless deposition of gold has also been shown to produce better spectroscopy compared with sputtered or thermally evaporated contacts [21, 23–25].

The minimum preparation required for a CdZnTe detector prior to contact deposition is mechanical polishing of the top and bottom surfaces with fine-grain alumina or silicon carbide. Further treatments, such as chemo-mechanical polishing with a bromine etchant [26], passivation [27–29] and hydrogen plasma [30] or argon ion [31] etching have been demonstrated to reduce leakage current, modify the surface stoichiometry and work function, and improve detector performance.

The electroless deposition of gold onto CdTe and CdZnTe and the effects of mechanical and chemo-mechanical surface polishing of these materials have previously been investigated. Characterization techniques such as x-ray photoelectron spectroscopy (XPS) [25], Auger electron spectroscopy (AES) [23], Rutherford backscattering spectroscopy (RBS) [22, 32, 33], atomic force microscopy (AFM) [22, 24, 26, 34, 35] and scanning electron microscopy (SEM) [22, 26] have been used in these investigations.

The current work expands on the literature by combining a range of characterization techniques to investigate the effects of gold chloride solution temperature and prior surface preparation on the metal–semiconductor interface. Examples of subsurface damage related to prior surface damage are also discussed. Focused ion beam (FIB) cross section imaging, transmission electron microscopy (TEM), AFM, XPS depth profiling, energy dispersive x-ray spectroscopy (EDS) and current–voltage (I–V) measurements have been used to determine the structural, chemical and electronic properties of the metal–semiconductor interface formed during electroless deposition. This is the first time that the effects of gold chloride solution temperature have been investigated and the first time that such a detailed analysis has been applied to the electroless deposition process on differently prepared CdZnTe surfaces. The results have furthered the understanding of the contact deposition process and allowed improvements to be made in the fabrication of CdZnTe detectors at RAL.

2. Experimental methods

2.1. Sample preparation

The (1 1 1) orientated single-crystal CdZnTe material used in the current study was grown by Redlen Technologies Inc. using the travelling heater method (THM) [17] and supplied with dimensions of 19.5 × 19.5 × 5 mm³. The crystals were diced into sub-samples and reprocessed to remove the original contacts deposited by Redlen. Mechanically polished-only (MP) detectors were prepared by lapping with 3 μm Al2O3 abrasive slurry, followed by a two stage mechanical polish with 0.3 and 0.05 μm Al2O3 abrasive slurry. Chemo-mechanically polished (CMP) detectors were lapped and mechanically polished as above, followed by a 2 min 1% bromine-in-methanol chemomechanical polish.

A tetrachloroauric(III) acid solution with a HAuCl4 to H2O/HCl ratio of 1:25 was used for the electroless deposition [22, 23, 33]. The electroless reaction is dominated by the removal of cadmium rather than tellurium from the CdZnTe surface. This is due to the greater standard potential, ΔE⁰, of the reaction with cadmium. The two competing reactions are stated in equations (1) and (2) [22]. A temperature controlled hot plate or ice bath was used to maintain the solution at the desired temperature, from 0 to 40 °C. Before contact deposition, the detectors were cleaned with acetone and isopropanol and then rinsed with deionized water. The crystal edges were protected with photoresist to stop gold formation before being submerged in the gold chloride solution. Following gold deposition the detectors were annealed at 85 °C for 30 min. The gold layer formed by this process was in the order of 10⁻⁸ nm thick.

\[
2\text{AuCl}_3 + 3\text{Cd}_{\text{surface}} \rightarrow 2\text{Au}_{\text{surface}} + 8\text{Cl}^- + 3\text{Cd}^{2+};
\]

\[\Delta E^0 = +1.40\text{V}\]  

\[
4\text{AuCl}_3 + 3\text{Te}_{\text{surface}} \rightarrow 4\text{Au}_{\text{surface}} + 16\text{Cl}^- + 3\text{Te}^{4+}; \quad \Delta E^0 = +0.43\text{V}.
\]  

(2)

2.2. Atomic force microscopy

An NT-MDT Solver HV-MFM operating in semi-contact mode with a non-conductive Si probe was used to map the
Table 1. The elements, photoelectron peaks and published binding energies considered in the current study [36, 37].

| Element | Peak | Energy (eV) |
|---------|------|-------------|
| Gold    | 4f5/2 | 84.0        |
| Chlorine| 2p3/2 | 198.5       |
| Carbon  | ls   | 285.0       |
| Cadmium | 3d5/2 | 405.1       |
| Oxygen  | ls (oxide) | 529.5–530.6 |
| Oxygen  | ls (contamination) | 532.0–533.1 |
| Tellurium| 3d5/2 (bulk) | 572.2–573.1 |
| Tellurium| 3d5/2 (oxide) | 575.2–576.3 |
| Zinc    | 2p3/2 | 1021.8      |

Surface topography and measure the root mean square (RMS) surface roughness.

2.3. Focused ion beam cross section imaging

Secondary electron images of cross sections through the metal–semiconductor interface were recorded using three different FIB instruments (FEI Nova Nanolab 600 and two Carl Zeiss XB1540’s). The contact surface was coated with either a dual layer of electron beam deposited platinum/carbon and ion beam deposited tungsten and sputter deposited carbon. These coatings were applied prior to milling to preserve the gold surface and protect from ion damage during alignment. Cross sections through the interface were exposed for imaging by milling a trench with an ion current of 200 pA. A current of 50 pA was used to fine polish the cross section before imaging.

2.4. Transmission electron microscopy and energy dispersive x-ray spectroscopy

Thin cross section foils (~100 nm) were prepared and extracted by an FEI 2500 FIB for imaging in high-angle annular dark field (HAADF) mode with a JOEL TEM. An Oxford Instruments EDS module was used to map the chemical distribution across the interface.

2.5. X-ray photoelectron spectroscopy

A Thermo Scientific Theta Probe spectrometer was used to perform XPS analysis and depth profiling. A monochromated Al Kα characteristic X-ray source (1486.7 eV) with a ~400 μm spot size and a 37° take-off angle were employed. The analyser had a pass energy of 50 eV and the aliphatic carbon contamination peak at 285.0 eV was used to calibrate the measured binding energies. To obtain depth profiles, layers of material were sequentially etched with a 1 μA current of 3 keV Ar+ ions rastered over an area of 2.5 mm², followed by XPS analysis. Peak binding energies of the elements considered in the current study are presented in table 1 [36, 37]. It is well known that the tellurium and oxygen peak positions shift upon oxidation (compared with bulk CdZnTe or OH'/H₂O contamination, respectively) [29, 37] and these modified binding energies have also been considered. Charging of the sample may also lead to a peak shift. This would however affect peaks from all elements. This was not observed at any stage during the XPS depth profile measurements.

Instrument-modified Wagner sensitivity factors were applied to the XPS peak intensities to calculate the atomic composition following a Shirley background subtraction [36]. With the assumption that a linear relationship between sputter rate and etch time existed [38], the depth profiles were normalised to a common etch current of 1 μA. This was necessary to correct for a measured variation in the Ar⁺ ion etch current between measurements. The variation in etch rate of the different materials in the surface layers made it impractical to convert etch time to interface depth.

The mathematical method of principal component analysis (PCA) was applied to the depth profile datasets. This allowed different regions within the depth profile to be identified where a particular photoelectron peak had shifted or broadened, possibly indicating the presence of multiple chemical states of the element of interest. Principal components associated with the elements listed in table 1 were calculated and the intensity of these components were quantified and plotted as a function of etch time. If the intensities of two components from different elements were found to vary in coincidence through a region of the depth profile, it was considered to be an indication that a chemical compound of the two elements existed in that region. The built-in PCA function of the Avantage software of the theta probe instrument was used to complete the PCA data processing. Further information regarding the PCA method can be found in the literature [36, 39].

2.6. Current–voltage measurements

A Keithley pico-ammeter and probe station housed in an electrostatically shielded and light-tight enclosure were used to measure the low voltage (± 1 V in 0.1 V steps) and high voltage (± ± 1 kV in 25 V step) room temperature I–V response of the detectors. The bias was applied to the (1 1 1)B Te-face of the detector and the current read out from the (1 1 1)A Cd-face. The high voltage I–V data was used to assess the scale and mechanism of leakage current in the detectors.

A common method of measuring CdZnTe bulk resistivity involves fitting equation (4) to the low voltage I–V data [40], where V is the applied bias, A the contact area, I the leakage current and d the detector thickness. This method assumes that the contacts are not contributing to the series resistance of the detector and that the resistance measured is purely due to the bulk CdZnTe. This is not the case for electroless contacts on CdZnTe where the contacts contribute to the series resistance. To demonstrate this, the detector resistance has been calculated by fitting equation (4) to the low voltage I–V data, averaging across both positive and negative bias.

\[ \rho = \frac{VA}{Id} \] (3)

\[ R = \frac{V}{I} \] (4)
3. Results and discussion

3.1. Effects of gold chloride solution temperature

The effects of varying the temperature of the gold chloride solution on the physical and electronic properties of gold contacts formed by electroless deposition have been investigated and are discussed in the following section. The CdZnTe crystals were mechanically and chemo-mechanically polished before being immersed in a gold chloride solution for 1 min to deposit the gold contacts.

3.1.1. $I–V$ measurements. The $I–V$ measurements taken from detectors contacted with increasing gold chloride solution temperature are presented in figure 1. The detector labels refer to the deposition temperature. It was observed that the $I–V$ response deteriorated with increasing solution temperature, with leakage currents increasing from 5.1 to 55.0 nA cm$^{-2}$ at 1500 V cm$^{-1}$. This would be equivalent to 3.2 to 34.4 pA per pixel for a 250 $\mu$m pitch pixellated detector, well within the required specification for the HEXITEC ASIC tolerance of 50 pA per channel and comparable with the performance of detectors fabricated directly by Redlen Technologies [41]. The back-to-back blocking $I–V$ response of all five detectors was characteristic of a metal–semiconductor–metal system with two Schottky barriers. This was evident from the subtle ‘S-bend’ in the low voltage $I–V$ data [42]. The back-to-back blocking response extended up to $\pm$2000 V cm$^{-1}$ for detector 0C and $\pm$1500 V cm$^{-1}$ for detectors 10–30C. The blocking response of detector 40C was limited to low field strengths with elevated leakage currents measured at both positive and negative bias.

3.1.2. Voltage dependency of leakage current. A closer inspection of the voltage dependency of the leakage current for three of the detectors is shown in figure 2. Three distinct leakage current regions were observed. The first region had a $V^{1/2}$ dependency. The depletion width of a semiconductor increases with $V^{1/2}$ before full completion of the bulk is reached [43, 44]. This suggests that the thermal generation of carriers in the depletion region of the partially depleted detector was the dominant leakage current mechanism in this first region. The second region, where the detector had become fully depleted, had a quasi-Ohmic linear voltage dependency indicative of diffusion-limited current and the presence of a Schottky barrier [42]. A quasi-Ohmic voltage dependency is one where $I$ is linearly proportional, but not equal to $V/R$. The final region, at the largest bias, had a quadratic voltage dependency indicative of space-charge limited (SCL) injection at the contacts [44–48].

The detectors with contacts deposited at 0–30$^\circ$C all produced a similar response, with full depletion and quasi-Ohmic behaviour beginning at $\sim$300 V cm$^{-1}$ for negative bias. For positive bias, depletion occurred later and the quasi-Ohmic behaviour was only observed from $\sim$400–600 V cm$^{-1}$. SCL current was observed above a field strength of $\sim$1200 V cm$^{-1}$ for detectors 10C and 20C for positive bias. The SCL current region was not reached during the negative bias ramp of detectors 0–20C but it was measured above a field strength of $\sim$1100 V cm$^{-1}$ for detector 30C. Detector 0C did not exhibit any SCL current under either polarity of bias.

The voltage dependency of the leakage current for detector 40C was distinctly different from the other detectors. Detector 40C exhibited space-charge limited current at a relatively low field strength of $\sim$200 V cm$^{-1}$ for positive bias and $\sim$800 V cm$^{-1}$ for negative bias. This indicated that injection was occurring at the contacts of detector 40C at much lower field strengths compared with the other detectors.

3.1.3. Detector resistance. The detector resistance, as defined by equation (4), was measured to decrease with increasing deposition temperature (see figure 3). The measured resistance was not purely an intrinsic property of the bulk, as assumed by equation (3) [40], but instead was modified by the series resistance of the contacts and interface states shifting the Fermi level in the vicinity of the contacts. A similar
variation in resistivity of a factor of two has previously been reported for contactless CdZnTe prepared with different surface treatments [49].

3.1.4. Role of subsurface voids. Cross section FIB images are presented in Figure 4 of the interface through gold contacts deposited at (a) 0°C and (b) 40°C. A previous study by Bell et al [41] has been used to help identify the features of the FIB images. The current FIB images show subsurface voids in the CdZnTe crystal below the contact. The presence of voids and degradation of crystal quality has been attributed to the precipitation of CdCl2 [50–53]. Voids and local deformations form due to stress from lattice mismatches and the solubility of chloride salts. An increase in subsurface voiding was observed for the contacts deposited at 40°C compared with those deposited 0°C. This was attributed to the increased reaction rate and increased precipitation of CdCl2 for the electroless process occurring at elevated temperatures. The precipitation of CdCl2 within the interface occurs during electroless deposition as the concentration of Cd²⁺ and Cl⁻ reach supersaturation levels within the solution. Chloride species have previously been observed in the interface following electroless deposition [50–53] and PCA analysis of XPS measurements [41] have confirmed that the depth distribution of metal chloride correlates with that of a compound of cadmium other than CdZnTe.

The deterioration of the subsurface structure of the contact and associated increase in crystalline defects with increasing deposition temperature was thought to be the cause of the increase in leakage current and decrease in detector resistance. These measurements have shown that a reduced gold chloride solution temperature improves interface uniformity by controlling the reaction rate and reduces detector leakage current. The measurements presented were made after the contacts had returned to room temperature. It is unlikely that any significant thermodynamically-driven diffusion through

![Figure 2. Log–log (a) positive and (b) negative bias I–V data for detectors contacted with gold chloride solution at 0, 30 and 40 °C. Measurements made at room temperature. Three distinct regions are identified where different leakage current mechanisms dominate. The V¹/² region is dominated by the thermal generation of carriers in the partially depleted bulk. The V¹ region is diffusion limited (quasi-Ohmic) and the V² region is dominated by space-charge limited injection from the contacts.](image-url)
Figure 3. Resistance of detectors contacted with gold chloride solution at 0–40°C. Measurements made at room temperature.

Figure 4. FIB cross section images of contacts deposited with gold chloride solution at (a) 0°C and (b) 40°C showing subsurface voids.
the interface would occur after contact deposition as CdZnTe detectors are typically operated at room temperature or below.

3.2. Effects of surface preparation

The effects of varying the CdZnTe surface preparation on the physical and chemical structure of gold contacts formed by electroless deposition have been investigated and are discussed in the following section. The CdZnTe surfaces were either mechanically polished-only (MP) or both mechanically and chemically polished (CMP).

3.2.1. Interface depth measurements. XPS depth profiles through contacts deposited on the Te- and Cd-faces of MP and CMP CdZnTe crystals are shown in figure 5. These profiles are representative of the four MP and eight CMP crystals investigated. The chemistry of the four presented profiles were similar, with a surface gold layer on top of a mixed interface of gold/tellurium oxide and finally bulk CdZnTe. The time taken to etch through and reach the bulk CdZnTe was recorded during the XPS analysis giving an indication of the depth of the metal–semiconductor interface from the surface (the interface depth represents the gold layer plus oxide region). The bulk was considered to have been reached once the tellurium concentration reached 95% of its maximum value. It was consistently found that for the eight CMP detectors tested, the interface formed on the (1 1 1)A Cd-face penetrated deeper into the CdZnTe crystal than the interface formed on the (1 1 1)B Te-face. On average, the time taken to etch through the interface formed on the Cd-face was 23 ± 4% longer than that through the interface on the Te-face. No such asymmetry was found between the interfaces formed on the two (1 1 1) faces of the four detectors tested with MP surfaces. The time taken to etch through the interface formed on the Te-face of MP detectors was found to be longer than the time taken to etch through the same face of CMP detectors. This difference can also be seen in the example FIB cross section images shown in figure 6, where the average total interface depth was measured to be 137 ± 2 nm on the MP Te-face and 77 ± 2 nm on the CMP Te-face. Other than surface preparation, the deposition conditions were identical. For the Cd-face, the difference in etch time between MP and CMP surfaces was negligible and within the uncertainty.

3.2.2. Role of (1 1 1) face identity. Mechanical polishing of CdZnTe is an abrasive process that introduces damage to the crystal surface that penetrates into the bulk material [54]. This mechanical damage is likely to degrade the definition of the (1 1 1) Te- and Cd-faces. However this does not explain why electroless contacts on MP surfaces produce a symmetric $I$–$V$ response when sputtered contacts on a similar surface produce an asymmetric $I$–$V$ response (see Figure 7). It can be concluded that the innate polarity of the (1 1 1) crystal orientation is preserved during mechanical polishing. Instead, the corrosive nature of the electroless process roughens the interface and degrades the (1 1 1) face definition, which weakens

Figure 5. Example XPS depth profiles through contacts deposited on (a) MP Te-face, (b) MP Cd-face, (c) CMP Te-face and (d) CMP Cd-face.
the crystal polarity and results in the symmetric I–V response of electroless contacts on MP CdZnTe.

However, the asymmetric interface depth of electroless contacts on the CMP detectors indicates that the electroless reaction does not completely degrade the (1 1 1) face definition of bromine treated CdZnTe. It is known that the bromine treatment preferentially removes cadmium, leaving a tellurium rich surface [55–57]. The electroless gold chloride reaction with cadmium is also energetically favoured over the reaction with tellurium [22]. The result is that the Cd-face of the (1 1 1) aligned crystal is preferentially etched twice during the fabrication of a CMP detector with electroless contacts, which leads to a difference in total interface depths for (1 1 1) CMP CdZnTe.

3.2.3. Interface uniformity. The interface formed during electroless deposition was observed to be more uniform for MP surfaces compared with CMP surfaces (see figure 6). The difference in interface uniformity after electroless deposition is thought to be due to differences in surface roughness prior to contact deposition. Bare MP CdZnTe was measured by AFM to have an RMS surface roughness of 2.9 ± 0.6 nm, compared with 8 ± 1 nm for bare CMP CdZnTe. The CMP surface also presented an undulating morphology, as shown in the AFM map of figure 8(b), where the height of the crystal surface was observed to change by ~±50 nm over distances of ~20 μm. This was attributed to be the ‘orange peel’ effect which is commonly observed following bromine-in-methanol etching [58, 59]. The MP surface, shown in figure 8(a), presented a flat morphology in comparison.

3.2.4. Subsurface damage. Cross section images of the interface formed by electroless deposition were taken using a FIB. A number of samples were found with deep subsurface features present within the interface. Of the six MP and six CMP interfaces investigated in this manner, all six of the later and only one of the former contained these features. A TEM foil was extracted from one of the interfaces for further TEM and EDS analysis (see figure 9). The features were characterized by a region of bright grains dispersed throughout the darker subsurface layer. An EDS line scan across one of the affected interfaces confirmed that these regions were dominated by the presence of gold, tellurium and oxygen.

Principal component analysis was applied to the XPS depth profile shown in figure 5(c), which was measured through one of the contacts possessing a subsurface feature. A FIB cross section image of the contact showing a subsurface feature is presented in figure 10(a) and the XPS–PCA depth profile though the contact is shown in figure 10(b). Two PCA components for the gold 4f peak and three for tellurium 3d_{5/2} peak were identified and are shown in figures 10(c) and (d) respectively. The binding energy (83.8 eV) and distribution through the interface of the first gold 4f component was consistent with that of elemental gold. The second gold component was broadened and shifted by 0.4 eV to higher energies, indicating that some of the gold present was bound in a different chemical state. The first tellurium component was consistent with bulk CdZnTe and the second consistent with tellurium oxide. The third tellurium component was broadened and shifted by 0.3 eV to higher energies compared with the CdZnTe component and the distribution of this component through the interface appeared to track that of the second gold component, indicative of a gold telluride phase in this region. A localized increase in the concentration of gold and tellurium was also found within the EDS line scan of figure 9(b), between 200–250 nm. The photoelectron spectra for the gold 4f and tellurium 3d_{5/2} peaks are presented in figures 10(e) and (f) for comparison with the PCA components presented in figures 10(c) and (d). The binding energy of the gold 4f_{7/2} peak was measured to increase by 0.4 eV from its value of 83.8 eV in the surface gold layer (after etching for 250 s) to its values in the interface of 84.2 eV (after etching for 1250 s). The tellurium 3d_{5/2} was also measured to increase by 0.4 eV from its bulk value of 572.3 eV (after etching for 6000 s) to a value of 572.7 eV at the peak of the gold telluride component (after etching for 2250 s). The gold telluride peak binding energy value of 572.7 eV is lower than that of elemental tellurium, which is 572.9 eV [37]. The positive shift of the gold binding energy and the negative shift of the tellurium binding energy, both relative to their pure elemental values, is indicative of (partial) electron transfer from gold to tellurium.
This is consistent with the core level binding energy shifts for other metal tellurides [37].

During XPS measurements a sample may become charged as electrons are ejected from the surface. This can result in a positive shift in the apparent binding energy of a photoelectron. If charging had been responsible for the binding energy shift observed during the current XPS measurements, the photoelectron peaks of all the elements would have been shifted. This was not observed, hence the components observed in the PCA analysis can be considered to be real changes in the chemical state of the elements.

Subsurface gold features similar to the ones presented above have been observed before in FIB images of gold contacts on CdZnTe. Based on PCA analysis of XPS data these were attributed to the presence of Au/AuTe particulates [41]. It is proposed that the bright grains, observed in the deep subsurface features within the TEM/FIB cross section images of figures 9 and 10, are gold particulates with an internal composition of elemental gold and a surface composition of gold telluride. In the previous study, the gold particulates were dispersed throughout the interface suggesting a uniform deposition process. The features observed in the current study are believed to originate from a non-uniform deposition process across the CdZnTe surface. The electroless deposition reaction rate will vary at locations with surface scratches and defects. Such features are introduced during crystal processing and handling. This effect will be more pronounced for CMP detectors due to the non-uniform bromine etching of these features [49, 60]. This is why the localized subsurface damage and deep penetration of Au/AuTe particulates, as exemplified in figure 9(a), was more often found in CMP detectors compared with MP detectors.

Further evidence of possible subsurface damage was found in the depth profile through the CMP detector shown in figure 5(c). Oxygen present within the interface of electroless contacts has generally been found to be in the form of oxide, with an O1s binding energy of ~530.5 eV. In figure 4(c), between ~1000–2500 s, the O1s peak was split with a significant shoulder-peak at a binding energy 532.3 eV. This was consistent with a high concentration of OH⁻/H₂O within the

Figure 7. A comparison of the I–V response of MP and CMP CdZnTe detectors with contacts formed by electroless deposition at 0°C. The CMP detector exhibits slightly increased asymmetry compared with the MP detector. The MP detector with sputtered contacts is highly asymmetric indicating that mechanical polishing alone does not explain the symmetry of the electroless contacts on MP detectors. Sputtering was performed with an Emitech K575X magnetron sputter coater with a target current of 100 mA for 2 min without heating or cooling the substrate. The deposition conditions were identical for both faces of the sputter contacted detector.

Figure 8. AFM measurements of (a) bare MP and (b) CMP CdZnTe surfaces. The fine peaks are dust particulates on the crystal surface.
interface. The binding energy of an OH\textsuperscript{−} species is typically ~1.5 eV higher than the oxide binding energy. The \text{H}_2\text{O} binding energy is in turn ~1.5 eV higher than the OH\textsuperscript{−} peak. It was not possible to resolve the two peaks within the shoulder-peak so only a single, combined OH\textsuperscript{−}/\text{H}_2\text{O} peak has been fitted and quantified. It is proposed that OH\textsuperscript{−}/\text{H}_2\text{O} was incorporated in a subsurface region of damage, possibly similar to that shown in figure 9. The O1s spectrum measured at 1600 s, where the OH\textsuperscript{−}/\text{H}_2\text{O} peak was most intense, is shown in figure 11.

4. Conclusions and summary

The effects of prior surface preparation and gold chloride solution temperature on the formation of gold contacts by electroless deposition on (111) orientated single-crystal CdZnTe have been investigated. The structure, chemistry and electronic response of the contacts have been studied using a range of characterization techniques, including $I$–$V$, FIB, XPS, AFM, TEM and EDS.

Increasing gold chloride solution temperature was found to detrimentally affect the $I$–$V$ response of the contacts formed by electroless deposition due to the formation of voids. The operating bias of detectors with contacts deposited at higher temperatures is limited by current injection through these contacts. It was concluded that a low temperature deposition was preferable. This simple modification of the fabrication process has the potential to improve both detector performance and yield.

![Figure 9](image_url)
Figure 10. (a) FIB cross section image through an electroless gold contact on a CMP surface. Deep subsurface features are observed, along with damage to the surface gold layer associated with the failure to develop a continuous film over the subsurface feature. (b) XPS depth profile showing the distribution of the two gold and three tellurium PCA components, which are shown in (c) and (d) respectively. Au_PCA_1 (83.8 eV) and Au_PCA_2 (84.2 eV) are associated with elemental gold and gold telluride, respectively. Te_PCA_1 (572.3 eV), Te_PCA_2 (576.0 eV) and Te_PCA_3 (572.6 eV) are associated with bulk tellurium, tellurium oxide and gold telluride, respectively. (e) Gold 4f photoelectron spectra measured within the surface gold layer (250 s) and at peak of gold telluride component (1250 s). (f) Tellurium 3d5/2 photoelectron spectra measured within the CdZnTe bulk (6000 s, 572.3 eV), at the peak of the gold telluride component (2250 s, 572.7 eV) and at the peak of the oxide component (1750 s, 576.2 eV).
The interfaces formed on the Te- and Cd-faces of mechanically polished-only CdZnTe are identical and detectors fabricated this way produce a symmetric $I$–$V$ response. This is because the electroless deposition process degrades the definition of the mechanically polished-only (1 1 1) face. The interfaces formed on the Te- and Cd-faces of chemo-mechanically polished CdZnTe are not identical, however the $I$–$V$ response is broadly symmetric with a deviation from symmetry only observed at elevated field strengths. It is proposed that the preferential removal of cadmium by both bromine and the gold chloride solution results in a deeper interface at the (1 1 1)A Cd-face. The frequency and extent of subsurface damage was also found to increase following chemo-mechanical polishing with bromine-in-methanol. Eliminating the chemo-mechanical polish stage from the fabrication process is desirable from a time, cost and safety perspective. The current work has shown that it would also be desirable from a fabrication yield perspective.

Understanding the contact deposition process is of vital importance to understanding how a CdZnTe detector will perform. The presented results build on and complement the previous literature regarding the electroless deposition of gold contacts on CdZnTe and will ultimately lead to improvements in the fabrication of these detectors.

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