Surface Analysis of CdTe after Various Pre-Contact Treatments


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SURFACE ANALYSIS OF CdTe AFTER VARIOUS PRE-CONTACT TREATMENTS

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ABSTRACT: We present surface analysis of close-spaced sublimated (CSS) CdTe after various pre-contact treatments. Our methods include Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and grazing-incidence x-ray diffraction (GI-XRD). XPS and GI-XRD analyses of the surface residue left by our solution-based CdCl₂ treatment do not indicate the presence of a significant amount of CdCl₂. In addition, the solubility properties and relatively high thermal stability of the residue suggest the presence of the oxychloride Cd₂Cl₂O₂ rather than CdCl₂ as the major chlorine-containing component. Of the methods tested for their effectiveness in removing the residue, only HNO₃ etches removed all detectable traces of chlorine from the surface.

Keywords: CdTe - 1: PV Materials - 2: Characterization - 3

1. INTRODUCTION

CdTe is a good choice of absorber material for photovoltaic devices due to its near-ideal bandgap (1.5 eV) and high absorption coefficient (6×10⁴ cm⁻¹ at 0.6 µm). Solar cell efficiencies as high as 15.8% have been achieved with CSS CdTe as the absorber layer and a CdS window layer [1].

Treating CdTe with chlorine prior to making the back contact is known to dramatically improve the performance of CdTe/CdS solar cells. However, the mechanisms of this treatment are not fully understood and are likely functions of the CdTe microstructure. The promotion of CdTe recrystallization (resulting in larger grains) [2, 3], enhanced CdS/CdTe interdiffusion [3], a reduction in the number of defect states throughout the CdTe layer [2], and low resistance p-type conductivity [4] have been attributed to the action of chlorine in CdTe.

Chlorine can be introduced either during the formation of the CdTe layer or after by diffusion through the exposed CdTe surface. Our solution-based CdCl₂ treatment, which employs the latter method, leaves a significant amount of chlorine-rich residue on the CdTe surface.

An etch with nitric and phosphoric acids (n-p etch) after the CdCl₂ treatment is commonly used to form a Te-rich layer at the CdTe surface by preferentially removing chlorine, cadmium, and oxides. This layer is thought to be beneficial because excess Te can promote p-type conductivity in CdTe [5, 6]. The results of Valdman et al. suggest that the removal of excess chlorine by the n-p etch may also play an important role in establishing p-type conductivity at the CdTe surface [7].

In light of the availability of techniques that can be used to form a Te-rich surface layer in lieu of n-p etching (e.g., evaporating or sputtering Te), it seems reasonable to seek out complementary means for removing the chlorine-rich surface residue. We used AES to study the effects of various treatments intended to remove the residue and found that it was surprisingly resistant to our methods. Further investigation into the matter using XPS and GI-XRD revealed some interesting compositional characteristics of the residue.

2. EXPERIMENTAL

The CdTe material used for this study was deposited by CSS on CdS in an ambient of 0.5-torr O₂ and 14.5-torr He at 620°C. The CdTe layer is 8-9 µm thick and has a surface roughness of approximately 120 nm. The CdS layer (80 nm) was deposited on SnO₂-coated glass by chemical bath deposition.

The solution CdCl₂ treatment begins with soaking the samples for 15 min in a boiling bath of 11.3-g/L anhydrous CdCl₂ in methanol. The samples are then quickly dried with N₂ (g) and annealed at atmospheric pressure in a flow-through furnace at 400°C for 40 min. A continuous gas flow of 100 sccm He and 25 sccm O₂ is used for the duration of the anneal. An additional 5-sccm flow of He is used until the temperature rises to 100°C. It takes 5 to 10 min for the sample temperature to rise from room temperature to 400°C and approximately 30 min to cool down to 100°C.

For the solubility tests, samples were taken directly from the CdCl₂-treatment annealing furnace and were rinsed either for 1 min with deionized water or for 20 sec with methanol, and then dried with nitrogen.

Two etching solutions were used for the acid-etch experiment. For the standard treatment, samples were taken directly from the CdCl₂-treatment annealing furnace and etched with a solution mixture of 350 mL 85% H₃PO₄, 140 mL H₂O, and 4.4 mL 70% HNO₃. They were removed from the etching solution when bubbles appeared across the entire sample surface (approximately 35 sec). The samples were then rinsed thoroughly in deionized water and dried with nitrogen. The other etchant is a dilute solution of nitric acid (0.03 N). The sample was etched for one minute and then rinsed thoroughly with deionized water and dried with nitrogen.

Vacuum anneals were performed in a Phi AES system on samples taken directly from the CdCl₂-treatment annealing furnace. The chamber was evacuated to 5×10⁻⁶ torr, and the sample mount temperature was raised to 400°C in 2.5 min. This temperature was maintained for 45 min. Final spectra were taken once the sample mount had cooled to 100°C and did not differ substantially from spectra taken at 400°C. The AES technique provides an analysis depth of roughly 2 nm. Our system has a spot size diameter on the order of 0.1 mm.

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Because over-exposure to an electron beam can decompose chlorine-containing compounds such as CdCl$_2$ [8], care was taken to minimize beam exposure. A low electron beam energy (3 KeV) was used and the total electron beam exposure time for each sample was limited to 2 min. We confirmed that the decomposition reaction progress was not significant by comparing the chlorine signal from other areas of the sample.

For our XPS experiments, we used a Physical Electronics x-ray photoelectron spectrometer with an energy resolution of 0.2 eV. The XPS technique provides an analysis depth of roughly 3 nm. The system has a spot size diameter of 0.8 mm. Standard sensitivity factors were used to determine atomic concentrations [9].

We used a Scintag polycrystalline texture stress x-ray diffractometer with a thin film (parallel-beam) attachment for grazing incidence diffraction. In this configuration, x-ray penetration is fixed by the incident angle. With our setting of $\Omega = 2^\circ$, the theoretical sampling depth (based on a perfectly smooth surface) is on the order of 500 nm. JCPDS files were used as standards for peak identification.

3. RESULTS AND DISCUSSION

3.1 Solubility Properties of the Residue

Prior to this analysis, we had assumed that a rinse with deionized water or methanol would remove the chlorine-containing component of our solution CdCl$_2$ treatment residue. This was based on our assumption that the residue is primarily CdCl$_2$, which is soluble in both water and methanol. However, we found that much of the residue is insoluble in both water and methanol (Fig. 1), which raised some questions regarding its composition. In addition, because chlorine residues left by vapor CdCl$_2$ treatments are reported to be soluble in both water and methanol [10, 11], we conclude that our solution CdCl$_2$ residue does not have the same composition as these vapor treatment residues.

![Figure 1: The chlorine signal after the solution CdCl$_2$ treatment (dashed line), subsequent water rinse (solid), methanol rinse (bold), and etch with dilute nitric acid (flat, grey line).]

3.2 The Effect of a 400°C Vacuum Anneal on the Residue

Vacuum annealing is a proven method for removing chlorine residue from CdTe following some types of chlorine treatments [7, 10, 11]. However, as can be seen from Fig. 2, a 45-min anneal at 400°C and 10$^{-2}$ torr removes very little chlorine from the solution CdCl$_2$-treated surface. Even after a 17-hour vacuum anneal, a substantial amount of chlorine remains. The relatively high vapor pressure of CdCl$_2$ (10$^{-3}$ torr at 400°C, which is five orders of magnitude higher than the vacuum chamber pressure) suggests that if the residue contained a considerable amount of CdCl$_2$, we would observe a corresponding decrease in the chlorine concentration with vacuum annealing.

![Figure 2: AES spectra of chlorine before (dashed line) and after (solid line) a 45-min anneal at 10$^{-2}$ torr.]

It is difficult to find a chlorine-containing compound with properties that match those of the residue. The presence of a significant amount of CdCl$_2$ at the surface is unlikely because of its expected volatility under our vacuum anneal conditions and its high solubility in water and methanol. Cadmium chlorates are also soluble in water and alcohol. The tellurium chlorides TeCl$_2$ and TeCl$_4$ are too volatile to remain at the sample surface during the CdCl$_2$ treatment anneal or the vacuum anneal. However, the oxychloride Cd$_3$Cl$_2$O$_2$ has thermal properties consistent with those of the residue and is insoluble in methanol. Perhaps the characteristics of the residue can be explained by the presence of this compound.

If the limited solubility and relatively high thermal stability are due to the formation of oxychlorides, it seems reasonable to assume that vacuum annealing is most effective in removing residue from CdCl$_2$ treatments when exposure to oxygen during the treatment is minimized. Interestingly, although we found that chlorine-bound oxides do not form until the CdCl$_2$ treatment anneal, the results of annealing in He (only) indicated that surface oxides form independent of whether oxygen is provided by the anneal ambient.

3.3 The Effects of Acid Etching on the Residue

Although we were unable to remove the chlorine residue with water, methanol, or a 400°C vacuum anneal, we found that all detectable traces of chlorine can be removed from the sample surface by etching the sample for one minute with dilute nitric acid (0.03 N) and then rinsing it thoroughly with deionized water. Because CdTe is known to decompose in nitric acid, we could not conclude that the chlorine compound also decomposed. Our final composition was slightly Te rich relative to a polycrystalline CdTe standard, indicating that some CdTe decomposition had indeed occurred.

The standard etching step used in our device fabrication employs a concentrated solution of nitric and phosphoric...
acids for the formation of a Te-rich region at the CdTe surface. It is very effective at removing oxides, chlorides, and cadmium, and CdCl solution, all signs of chlorine are eliminated from the surface by the etch.

3.4 Grazing-angle X-ray Diffraction Analysis

We used GI-XRD to further characterize the surface of solution CdCl$_2$-treated CdTe. Two samples were treated in a CdCl$_2$/methanol solution, but only one was given a CdCl$_2$ treatment anneal (Fig. 4).

The most prominent peaks are due to cubic CdTe ($23.76^\circ$ and $39.32^\circ$). CdCl$_2$ is present as orthorhombic CdCl$_2$-H$_2$O ($20 = 12.10^\circ$, $15.06^\circ$, and $34.10^\circ$). Monoclinic CdO is also observed ($\theta = 32.96^\circ$ and $38.24^\circ$). After the CdCl$_2$-treatment anneal, the CdCl$_2$-H$_2$O and CdO peaks are no longer detectable. Anhydrus CdCl$_2$ is not observed either. Thermal desorption could account for the loss of CdCl$_2$, which has a vapor pressure on the order of $10^{-3}$ torr at 400°C [12], but certainly not the loss of CdO, which requires temperatures greater than 1000°C to build up an appreciable vapor pressure [13]. There is a new peak at $30.52^\circ$, which may be due to monoclinic Cd$_2$Cl$_2$O$_2$. We propose that the following reaction may have occurred during the anneal: $2 \text{CdO} + \text{CdCl}_2 \rightarrow \text{Cd}_2\text{Cl}_2\text{O}_2$. Although some weaker peaks support this assignment, their signal-to-noise ratio is poor. Since there is only one distinct peak that matches the standard diffraction spectrum for Cd$_2$Cl$_2$O$_2$, the identification of this compound by GI-XRD is uncertain.

3.5 Properties of Oxychlorides

As mentioned earlier in this paper, the chemical and thermal properties of the residue appear to be consistent with what is known about the oxychloride Cd$_2$Cl$_2$O$_2$. Further, the GI-XRD results seem to support this identification. For these reasons, we include some relevant information from the literature regarding this compound and also another oxychloride, tellurium oxychloride (Te$_2$O$_3$Cl$_2$).

A study of the system CdO-CdCl$_2$ by Walter-Levy and Groult [14] reports that CdO and CdCl$_2$ react to form Cd$_2$Cl$_2$O$_2$ at around 400°C. The dehydration of species that contain hydroxyl groups (e.g., Cd[OH]$_2$ and Cd[OH]Cl) also leads to the formation of Cd$_2$Cl$_2$O$_2$ around 400°C. In the referenced publication, the authors show that CdCl$_2$ is stable up to 600°C and insoluble in alcohol, consistent with the compound in question.

Te$_2$O$_3$Cl$_2$ is also worth mentioning because it is formed at 400°C and is stable up to 650°C [15], which appears consistent with the thermal characteristics of the residue. However this compound is typically formed from TeCl$_4$(g) and TeO$_2$. As will be explained in the next section, we have reason to believe that CdTeO$_3$ is the primary surface oxide, rather than TeO$_2$. In addition, we are not aware of any free Te at the surface (needed to form TeCl$_4$). The Te-containing compounds that we have detected (CdTe and CdTeO$_3$) are probably too stable to form the tellurium chloride. Further, if CdCl$_2$ was present during the anneal as a solid or gas, it probably would not remain at the surface long enough for Te$_2$O$_3$Cl$_2$ to form. Therefore, of the two oxychlorides we have discussed, Cd$_2$Cl$_2$O$_2$ appears the more likely constituent of the residue, not only based on the GI-XRD result, but also on the greater assumed availability of the reactants required to form it as compared to the assumed availability of reactants to form Te$_2$O$_3$Cl$_2$.

3.6 X-ray Photoelectron Spectroscopy of the Residue

When discussing XPS results, it is common to identify compounds by the characteristic electron binding energies of elements in those compounds. However, we present our data in terms of differences between characteristic binding energies for elements in a given compound. This lessens the contribution to energy shifts from sample charging.

The signal from chlorine persists 13 nm into the material and accounts for 10 atomic % of the surface composition (neglecting carbon). The difference in binding energies between cadmium and chlorine at the surface is 206.7 eV. The corresponding reference value for CdCl$_2$ is 207.1 eV. We would expect to observe an asymmetry in the Cd peak if CdCl$_2$ were present. However, the peak is relatively symmetrical and centered at an energy relative to Te that is consistent with the presence of CdTe (within 0.1 eV).

The oxygen peak (not shown) does not indicate the presence of Cl-O bonds. Oxychlorides such as Cd$_2$Cl$_2$O$_2$ have no Cl-O bonds, and may explain the presence of a Cl peak in the absence of CdCl$_2$ and chlorates.
The difference in binding energies between the two Te peaks at the surface is 3.57 eV (Fig. 6), which more strongly suggests the presence of CdTeO$_3$ (3.5 eV) [16] than TeO$_2$ (3.2 eV) [16]. After removal of the first few nanometers of material the oxide signal is very small (the dotted line). At 13 nm, the Te-oxide is no longer present and the difference between the binding energies of Cd and Te is 167.4 eV, characteristic of CdTe [9].

Our XPS results seem to suggest the presence of oxychloride(s). However, because we have no Cd$_3$Cl$_2$O$_2$ and Te$_6$O$_{11}$Cl$_2$ standards, we cannot determine where the peaks would lie for these compounds and thus, cannot use our XPS results to confirm or disprove their presence.

4. CONCLUSIONS

We investigated the surface composition of CSS CdTe after a solution CdCl$_2$-treatment using AES, XPS, and GI-XRD. Our results indicate that residue remaining after the CdCl$_2$ treatment does not contain a significant amount of CdCl$_2$. Rather, it contains chlorine compound(s) much more chemically and thermally stable than CdCl$_2$. It appears likely that Cd$_3$Cl$_2$O$_2$ formed from CdCl$_2$ and CdO during the annealing step of the CdCl$_2$ treatment process and has a strong influence on the properties of the residue.

The relatively high stability of the residue makes it difficult to remove from the CdTe surface. Of the methods we investigated, only acid-etching removes the Cl-rich surface residue. Rinsing with deionized water, rinsing with methanol, and vacuum annealing, which have been reported as effective means for removing residue from samples treated by other CdCl$_2$ methods, are not effective in removing the thicker, more oxide rich layer that is left by the solution-CdCl$_2$ treatment.

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