July 1998 ● NREL/CP-530-23876

Surface Analysis of CdTe after Various Pre-Contact Treatments

D.M. Waters, D. Niles, T.A. Gessert, D. Albin,
D.H. Rose, and P. Sheldon

Presented at the 2nd World Conference and Exhibition on
Photovoltaic Solar Energy Conversion; 6-10 July 1998; Vienna, Austria

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
A national laboratory of the
U.S. Department of Energy
Managed by the Midwest Research Institute
For the U.S. Department of Energy
Under Contract No. DE-AC36-83CH10093

SURFACE ANALYSIS OF CdTe AFTER VARIOUS PRE-CONTACT TREATMENTS

D.M. Waters*, D. Niles, T.A. Gessert, D. Albin, D.H. Rose, P. Sheldon
1617 Cole Blvd.
National Renewable Energy Laboratory
Golden, CO 80401, USA

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 $CdCl_2$ treatment do not indicate the presence of a significant amount of $CdCl_2$. In addition, the solubility properties and relatively high thermal stability of the residue suggest the presence of the oxychloride $Cd_3Cl_2O_2$ rather than $CdCl_2$ as the major chlorine-containing component. Of the methods tested for their effectiveness in removing the residue, only HNO_3 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 ($6x10^4$/cm 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 $CdCl_2$ 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 $CdCl_2$ 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 Valdna 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 O_2 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 SnO_2-coated glass by chemical bath deposition.

The solution $CdCl_2$ treatment begins with soaking the samples for 15 min in a boiling bath of 11.3-g/L anhydrous $CdCl_2$ in methanol. The samples are then quickly dried with N_2 (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 O_2 is used for the duration of the anneal. An additional 5-slm 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 $CdCl_2$-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 $CdCl_2$-treatment annealing furnace and etched with a solution mixture of 350 mL 85% H_3PO_4, 140 mL H_2O, and 4.4 mL 70% HNO_3. 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 $CdCl_2$-treatment annealing furnace. The chamber was evacuated to $5x10^{-8}$ 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.

*e-mail: waters@physics.ucsc.edu; Dept. of Physics, University of California, Santa Cruz 95064

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 $\Omega = 2°$, 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.

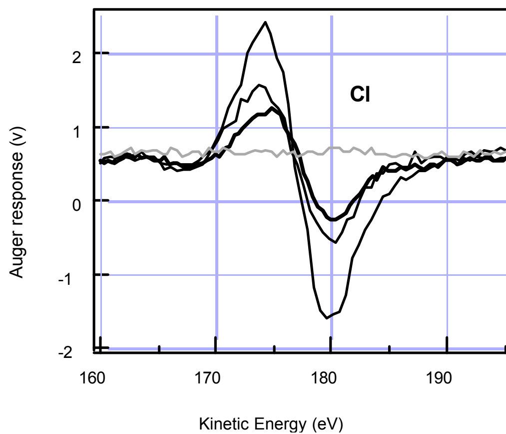

Figure 1: The chlorine signal after the solution $CdCl_2$ treatment (dashed line), subsequent water rinse (solid), methanol rinse (bold), and etch with dilute nitric acid (flat, grey line).

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^{-8} 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.

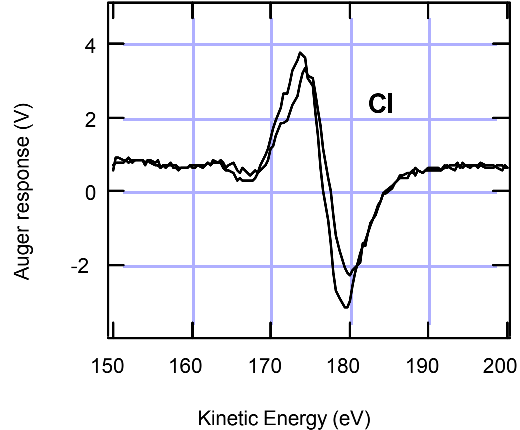

Figure 2: AES spectra of chlorine before (dashed line) and after (solid line) a 45-min anneal at 10^{-8} torr.

It is difficult to find a chorine-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 $Cd_3Cl_2O_2$ 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 occured.

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 (Fig. 3). As with the less concentrated nitric acid solution, all signs of chlorine are eliminated from the surface by the etch.

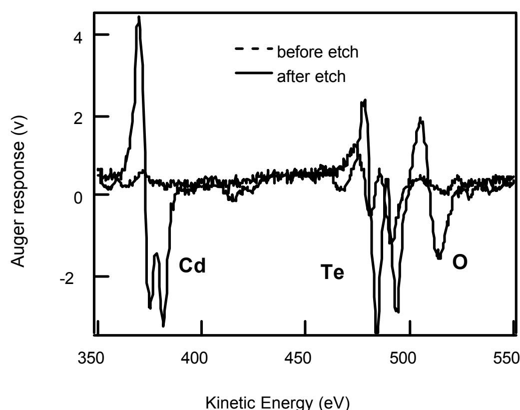

Figure 3: Auger analysis of solution $CdCl_2$-treated CdTe after an etch with a concentrated solution of nitric and phosphoric acids.

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).

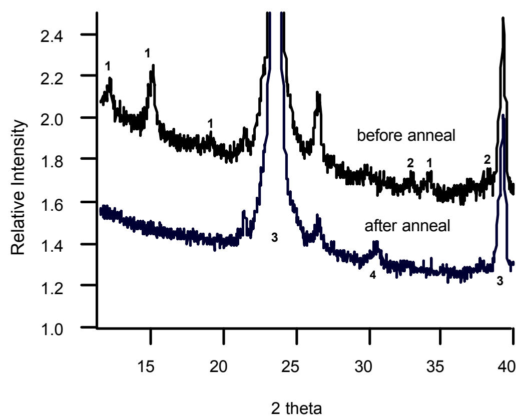

Figure 4: Preliminary GI-XRD results from samples before and after the $CdCl_2$-treatment anneal indicating the peak identification by number: 1- $CdCl_2$-H_2O; 2- CdO; 3- CdTe; 4- $Cd_3Cl_2O_2$.

The most prominent peaks are due to cubic CdTe (23.76° and 39.32°). $CdCl_2$ is present as orthorhombic $CdCl_2$-H_2O (2θ = 12.10°, 15.06°, and 34.10°). Monoclinic CdO is also observed (2θ = 32.96° and 38.24). After the $CdCl_2$-treatment anneal, the $CdCl_2$-H_2O and CdO peaks are no longer detectable. Anhydrous $CdCl_2$ 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°, which may be due to monoclinic $Cd_3Cl_2O_2$. We propose that the following reaction may have occured during the anneal: 2 CdO + $CdCl_2$ --> $Cd_3Cl_2O_2$. 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 $Cd_3Cl_2O_2$, 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 $Cd_3Cl_2O_2$. 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 ($Te_6O_{11}Cl_2$).

A study of the system CdO-$CdCl_2$ by Walter-Levy and Groult [14] reports that CdO and $CdCl_2$ react to form $Cd_3Cl_2O_2$ 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 $Cd_3Cl_2O_2$ around 400°C. In the referenced publication, the authors show that $Cd_3Cl_2O_2$ is stable up to 600°C and insoluble in alcohol, consistent with the compound in question.

$Te_6O_{11}Cl_2$ 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. Futher, if $TeCl_4$ was present during the anneal as a solid or gas, it probably would not remain at the surface long enough for $Te_6O_{11}Cl_2$ to form. Therefore, of the two oxychlorides we have discussed, $Cd_3Cl_2O_2$ 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 $Te_6O_{11}Cl_2$.

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 $Cd_3Cl_2O_2$ have no Cl-O bonds, and may explain the presence of a Cl peak in the absence of $CdCl_2$ and chlorates.

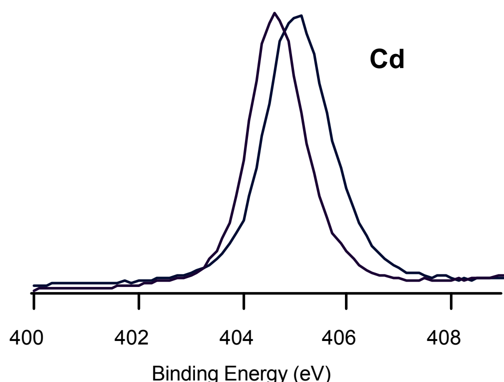

Figure 5: XPS spectra of Cd, at the surface (dashed line) and at 13 nm (solid line).

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].

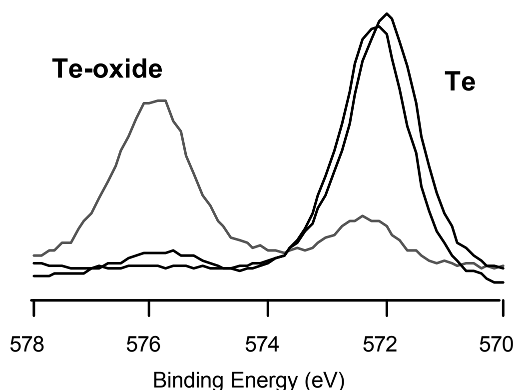

Figure 6: XPS spectra of Te, showing the presence of Te oxide(s) at the surface (dashed line), and its diminution deeper in the material: at 4 nm (dotted line) and at 13 nm (solid line).

Our XPS results seem to suggest the presence of oxychloride(s). However, because we have no $Cd_3Cl_2O_2$ and $Te_6O_{11}Cl_2$ 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 $Cd_3Cl_2O_2$ 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.

5. ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy under contract No. DE-AC36-83CH10093 and a GAANN grant from the Department of Education and UCSC. The authors would like to express their gratitude to A. Mason, Y. Mahathongdy, and R. Ribelin for their contributions to this project. D. Waters would also like to thank her academic advisor, D. Belanger, for his continued support and encouragement.

REFERENCES

[1] J. Britt, C. Ferekides, Appl. Phys. Lett. **62** (1993) 2851-2.
[2] S.A. Ringel, A.W. Smith, M.H. MacDougal, A. Rohatgi, J. Appl. Phys. **70** (1991) 881-889.
[3] B.E. McCandless, L.V. Moulton, R.W. Birkmire, Prog. Photovolt. Res. Appl., **5** (1997) 249-260.
[4] V. Valdna, Mat. Res. Soc. Symp. Proc. **442** (1997) 585-591.
[5] D.W. Niles, X. Li, P. Sheldon, J. Appl. Phys. **77** 9 (1995) 4489-4493.
[6] A.J. Ricco, H.S. White, M.S. Wrighton, J. Vac. Sci. Technol., **A2** (1984) 910-915.
[7] V. Valdna, J. Crys. Growth, **161** (1996) 164-167.
[8] C.J. Aidinis, M. Green, J. Appl. Phys. **63** 9 (1988) 4397-4405.
[9] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy (Perkin-Elmer Corp., 1992).
[10] T.X. Zhou, N. Reiter, R.C. Powell, R. Sasala, P.V. Meyers, IEEE Proceedings of the 1st WCPEC (1994) 103-106.
[11] B.E. McCandless, H. Hichri, G. Hanket, R.W. Birkmire, IEEE Proceedings of the 25th PVSC, (1996) 781-784.
[12] D.R. Stull, Ind. Eng. Chem. **39** (1947) 517.
[13] R.C. Weast, M.J. Astle, CRC Handbook of Chemistry and Physics, 63rd ed. (CRC Press, 1982).
[14] L. Walter-Levy, D. Groult, Bull. Soc. Chim. Fr. **11** (1970) 3868-78.
[15] G.I. Novikov, V.V. Zvezdina, V.P. Bochin, Russian Journal of Physical Chemistry, 52 **4** (1978) 608-609.
[16] F. Wang, A. Schwartzman, A.L. Fahrenbruch, R. Sinclair, R.H. Bube, J. Appl. Phys. 62 **4** (1987) 1469-1476.