Te-rich CdTe Surface by Pulsed UV Laser Treatment for Ohmic Back Contact Formation

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***Abstract* — Pulsed UV laser treatments have recently been applied to polycrystalline CdTe solar cells to create an ohmic back contact. In this work, we investigate the surface stoichiometry variations produced by pulsed laser excitation using X-ray photoelectron spectroscopy (XPS). These results reveal surfaces that are becoming more Cd-rich, counter to what is expected from calculations and what has been measured by others. To understand this apparent disagreement, we have constructed a geometric model of the sample surface considering surface topography and a segregation of phases at the surface. From this, we infer that the laser treatments do produce a Te enrichment as expected, but that this enrichment is localized near the grain boundaries. Furthermore, the apparent Cd-enrichment occurs because the Te-rich region's contribution to the XPS intensity is lessened by topographic and surface sensitivity effects as well as a sub-monolayer of Cd found elsewhere on the film surface.**

***Index Terms* — CdTe, laser annealing, surface analysis, surface treatment, thin films.**

I. INTRODUCTION

Recently, we have developed a novel means of using ultraviolet (UV) laser pulses to create an back contact for CdTe solar cells [1]. This method resulted in increased solar cell performance and the disappearing of the "rollover" seen in the current-voltage measurements that is indicative of non-ohmic contacts. The pulsed UV laser treatment (LT) creates a Te-rich surface by exploiting the differences in vapor pressures at high temperatures between Cd and Te, with Cd being the more volatile species [2][3]. The UV laser pulse is absorbed in a very shallow surface region (~10 nm) that quickly heats to very high temperatures. As the temperature rises, Te and Cd are evaporated from the surfaces at unequal rates even at temperatures well below the melting point. Thermal simulations of this process have shown that a single 25 ns pulse of 248 nm light of only 40 mJ/cm^2 is enough to evolve an order of magnitude more Cd than Te from the surface [1][4].

In the work presented here, we study the resulting surface chemistry of LT polycrystalline CdTe surfaces using X-ray photoemission spectroscopy (XPS). Quantitative analysis of our XPS data showed LT enhanced the Cd concentration at the surface, counter to what was expected from works on LT crystalline CdTe [2], [3], [5]. In order to resolve this apparent disagreement, we calculated XPS signal intensities using a computational model that considers surface roughness and incorporates the experimental findings of Nelson *et al.* [6] who showed that pulsed UV LT of polycrystalline CdTe creates regions of Te enrichment near grain boundaries (GBs) with slight Cd enrichment elsewhere. These considerations account for the calculated overall Cd-enrichment as the spot size of our XPS is too large to resolve the segregated regions individually. This analysis also points to what could be a common source of error when using XPS to calculate surface compositions of rough surfaces that may have spatial composition segregation.

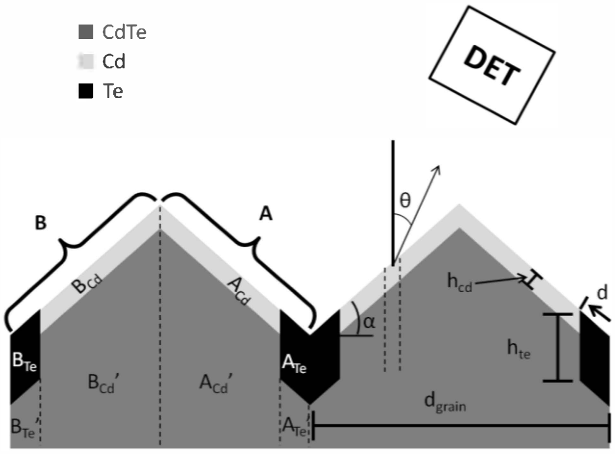

Fig. 1. Geometric model for calculating XPS intensities that includes surface roughness and Cd and Te overlayer effects. See text for details.

II. EXPERIMENTAL DETAILS

The CdTe films used in this study were prepared by close-spaced sublimation of CdTe precursors onto alumina substrates [7] with film thicknesses of about 5 μm. Laser annealing was accomplished with a KrF excimer laser with 25 ns laser pulses of wavelength 248 nm. The LT samples were exposed to 600 pulses at a 10 Hz repetition rate. XPS was performed on a Kratos Axis Ultra DLD system using a monochromatic x-ray source.

A cross section of the geometric model used in this study for calculating XPS intensities is shown in Fig. 1. The model assumes triangular prisms that create parallel ridges where the valleys are at a GB. Surface roughness is incorporated through the angle, α, which is the average angle a surface facet makes

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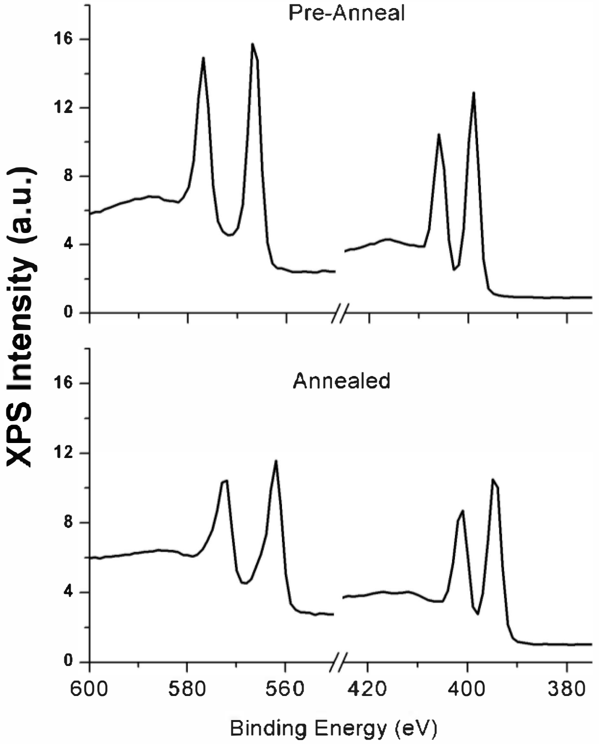
with the horizontal plane. For our model, this was calculated from optical profilometry data and was 3.2°. Non-uniformity at the surface is accounted for by including two different overlayers: one of elemental Cd over the grain interiors and one of elemental Te at the GB surfaces. These are characterized by their respective thicknesses h_{Cd} and h_{Te}. These thicknesses are exaggerated in Fig. 1 for illustrative purposes as the actual thicknesses modeled are typically sub-monolayer for Cd and nanometers for Te. This choice of surface configuration was influenced by the experimental findings of Nelson *et al.* who showed evidence of this from x-ray photoelectron microscopy of laser treated CdTe [6]. The extent to which the Te layer extends from the GB is parameterized by the distance, d. The width of each grain, d_{grain}, was 1µm in good agreement with SEM images of the surface.

Calculation of the XPS intensity is achieved by segmenting the surface into *j* regions and calculating the signal strength as a function of depth in each segment [8]. The contributions from all segments are then summed together for the total signal intensity. One such segment is drawn in Fig. 1 with its surface at an angle θ to the electron detector (DET). For each facet, A and B, 200 segments were used. The intensities of Cd and Te are determined by considering 100% of the signal from the overlayers to contribute to either Cd or Te depending on its location in either the Cd or Te overlayer regions. The sub-surface regions are considered to be stoichiometric CdTe so the contribution here is half from Cd and half from Te. This method extends from a method derived for inhomogeneous solids with buried surface layers [9], but instead of a single overlayer, we consider two different, spatially separated, overlayers as shown in Fig. 1.

III. RESULTS AND ANALYSIS

Fig. 2 shows the XPS results both before and after laser treatment. The two doublets seen are from Te 3d at higher binding energies and Cd 3d at lower binding energies. Following annealing, both doublets make an obvious shift towards lower binding energy. This is a result of the surface becoming more conductive [1]. Also there is a slight asymmetrical broadening which is due to two effects. The first is because of a small amount of oxidation that occurs during LT. Since the films were annealed and transferred to the ultrahigh vacuum XPS chamber in an inert (Ar) environment it is believed that this is from oxygen diffusing to the surface from the film bulk during LT (a small amount of oxygen was present during film deposition). The second reason for the broadening of the Te 3d peak is from the inclusion of elemental Te at the surface resulting from LT [1], whose peak is 0.8 eV higher than the main Te-Cd peaks. Elemental Cd is much more difficult to measure conclusively as it only has a peak separation of 0.1 eV [10].

The stoichiometry of the surface can be calculated from these spectra by integrating the peaks for Cd and Te and taking the ratio. This was done for a number of angles, θ, that the XPS detector makes with the sample surface. These results are shown in Fig. 3. It is seen that the unannealed sample begins slightly Cd-rich (Cd:Te > 1). Although this would not be inconsistent with other reports in literature [11], it could also easily be accounted for in errors in the instrument response functions used to quantify the concentrations of Cd and Te. What is surprising, however, is the apparent relative increase of the Cd:Te ratio of the laser annealed film by 13.1% over the pre-LT sample. This is the opposite result expected based on previously published literature and thermodynamic modeling.



The angle-resolved XPS measurements were simulated using the model depicted in Fig. 1 and the results are shown in Fig 3. As the laser annealed sample is tilted with respect to the electron detector, the measured Cd:Te ratio increases. This behavior is simulated by our model by including a Te overlayer that is 100 times thicker than a sub-monolayer Cd overlayer and is highly localized to the regions near the GB (h_{Te} = 100 Å, h_{Cd} = 1 Å, d = 14 nm). It is important to note that if a uniform Te-layer is modeled, as is believed to be the result of LT of single-crystalline CdTe, the trend reverses and a decrease in Cd:Te is shown. It was only with the inclusion of the very thin Cd overlayer that the trend matching our experimental observation is observed. The agreement of the model calculations with our observations leads to the conclusion that pulsed UV LT causes a Te-enrichment near the

GBs with much thinner layers of Cd elsewhere. It is cautioned that the exact thicknesses of the Cd and Te overlayers used in the model are not necessarily representative of actual thicknesses in the films due to the physical differences between the actual surfaces and the geometry used in the model. However, the qualitative interpretation of the results are valid in that a single Te overlayer would be inconsistent with our experiments.

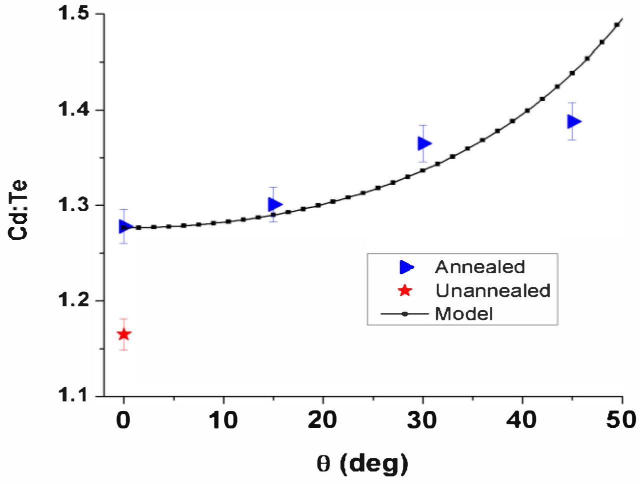


Fig. 2. Angle resolved XPS data. The data is simulated with h_{Te}=100 Å, h_{Cd}=1 Å, and d=14 nm.

In order to understand these results more fully, Fig. 4 shows a breakdown of the intensity contributions from different regions of the model, which are labeled in Fig. 1. Fig. 4a. shows the contributions from the Te regions near the GB surfaces, 4b. from the Cd surface regions and 4c. from the sub regions of presumed stoichiometric CdTe. For this region, it is important to remember that half of the intensity is ascribed to Cd and half to Te. It is immediately seen that the largest intensity contribution is from the Cd overlayer regions (4b.), which are also relatively constant with respect to angle. This is easily explained by the inherent surface sensitivity of the XPS measurement. The surface area of the Cd regions is much greater than the surface area of the Te regions, even though the volume of the Te region is much larger, which leads to preferential weighting of the Cd-rich overlayer. The relative insensitivity of Cd counts versus that of the Te counts is also a result of this effect and is why the apparent Cd:Te ratio increases with angle. Also of note in Fig. 4c. is the negligible degree to which the regions under the Te overlayers contribute to the calculated XPS intensity. This again reflects XPS's surface sensitivity and is the main reason that the value of h_{Te} = 100 Å should be viewed as qualitative. Essentially, one could increase the thickness of h_{Te} beyond this amount and have little to no effect on the overall signal as photoelectrons from beyond this depth do not escape to the film's surface.

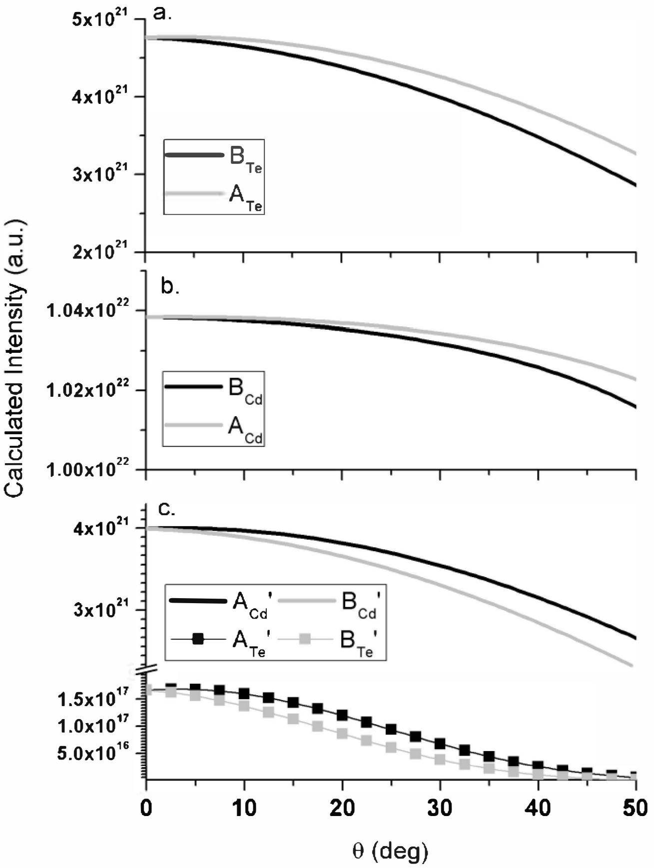


Fig. 3. A breakdown of the XPS intensity contributions from specific regions in the model: a. from the Te-rich surface regions at GBs, b. from the Cd-rich grain interiors, and c. from the stoichiometric CdTe subsurface regions. A and B refer to the facets from Fig. 1.

IV. DISCUSSION

The analysis presented here is valuable in two respects. First, it allows one to infer a lateral distribution of Te and Cd that results from pulsed LT with the Te enrichment occurring near the GB. This realization is particularly interesting when one considers the charge separation that is believed to occur at the GBs within the bulk. The space charge region that exists there is believed to push holes towards the grain interiors and electrons to the GBs where they conduct readily to the pn-junction in a solar cell device [12]. This then leaves the surfaces of the grain interior to allow hole conduction at the back contact. In our model, these regions are covered with a thin layer of Cd, which would ultimately impede hole flow and make for a less ohmic junction. However, we have empirically shown that an ohmic contact results from LT [1]. Possible explanations are 1) that the Te-rich regions in our model (A_{Te} and B_{Te}) are wider than the depletion region established at the GBs in the bulk therefore allowing for a region of hole conduction through the Te-rich region at the surface, 2) that there are other islands of Te-enrichment besides those at the GB surfaces that allow for hole conduction, or 3) some GBs conduct holes rather than electrons as has been suggested in the literature [13] and that is where the ohmic contact is formed. Further experiments could distinguish between these possibilities.

Second, this work reveals a possible large source of error when using XPS to calculate stoichiometry of non-planar surfaces if they exhibit spatial inhomogeneities. Indeed, Fig. 5 shows an illustration of this point for a hypothetical binary system with constituents A and B that is supposedly 1:1 stoichiometric. The A:B ratio calculated using our model is shown plotted versus the distance d that segregated regions extend from the GB. This shows that if there are surface distributions, even ones less than 1 Å, it is highly unlikely that XPS will return a value of A:B = 1:1 even when the vast underlying region is exactly 1:1. As XPS is often used to investigate changes to stoichiometry due to different surface treatments, care should be given to interpretation. This could be particularly important when XPS is used to study chemical etching effects on surfaces if the etches preferentially attack GBs as is often the case.

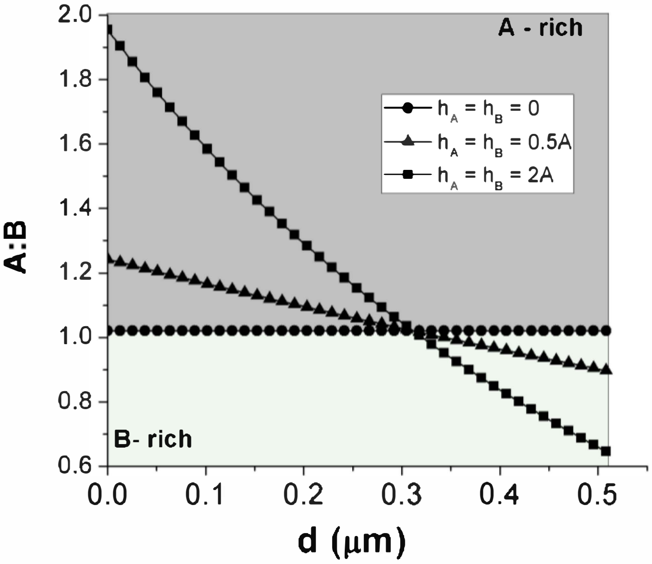


Fig. 5. Calculations for a hypothetical binary system AB based on the model presented here. The ratio A:B is plotted versus the distance d for different thicknesses of overlayers.

V. CONCLUSIONS

XPS data are presented that shows a Cd-enrichment at the surface of polycrystalline CdTe as a result of pulsed UV laser treatment, which is contradictory to the expected result from the literature. To explain this discrepancy, a model has been developed that combines the effects of surface roughness with nonuniform overlayers. The apparent Cd enrichment can be explained by including elemental Te regions localized near grain boundaries with submonolayer elemental Cd overlayers in grain interiors. Additionally, we have shown that a single uniform layer of Te resulting from UV laser treatment is inconsistent with our observations from angle-resolved XPS, giving further evidence to our interpretation. It is only through the inclusion of a sub-monolayer Cd overlayer that we find good qualitative agreement with our results.

ACKNOWLEDGMENTS

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