

# XPS and AES Studies of Cu/CdTe(111)-B

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# XPS and AES Studies of Cu/CdTe(111)-B

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## ABSTRACT

Copper is frequently used as a p-type dopant to improve the performance of back contacts in CdTe thin-film solar cells. In this study, surface-analysis techniques are used to probe fundamental interactions between Cu and the CdTe(111)-B surface. The results presented here were facilitated by the newly constructed surface-analysis cluster tool in the Measurements and Characterization Division at NREL; they reveal a host of fundamental phenomena that occur in the Cu/CdTe system.

### 1. Objectives

The objectives of this study are to elucidate the kinetics of Cu absorption into CdTe and to explore changes in surface composition resulting from the addition of Cu that might affect the properties of the back contact, and hence device performance. In addition, this work addresses the Measurements and Characterization goal in the Solar Program Multi-Year Technical Plan to “validate the surface-analysis test platform for process integration.”

### 2. Technical Approach

Single-crystal CdTe(111)-B substrates (1 cm<sup>2</sup> x 1 mm, not intentionally doped, 6/9-purity starting material) were acquired from Keystone Crystal. Prior to introduction into the cluster tool, the samples were etched for 30 s in 0.25% Br/MeOH. The substrate surfaces were further prepared *in vacuo* by sputtering and annealing to produce clean, stoichiometric surfaces. Substrate temperature was monitored with a Type K thermocouple junction clamped to the face of the crystal.

Mass spectrometry, in the form of temperature-programmed desorption (TPD), is a sensitive technique for probing kinetic processes that take place at the surfaces of thin films or single-crystal substrates. In the present study, the reaction rate of Cu with CdTe as a function of temperature is measured by monitoring the desorption rates of Cd and Te from the Cu-dosed CdTe(111)-B substrate during heating.

Auger electron spectroscopy (AES) is a technique in which energetic particles, typically electrons, are directed at a surface and cause atomic core-level transitions in the sample, resulting in the ejection of electrons from the sample with kinetic energies characteristic of the atomic species from which they originate. If the excitation source is a finely focused electron beam, high spatial resolution maps of surface composition may be generated with a technique known as scanning Auger microscopy (SAM).

X-ray photoelectron spectroscopy (XPS) provides information on the elemental composition of a surface by measuring the binding energies of electrons emitted from

the substrate upon irradiation by x-rays. In the present study, XPS measurements are used to quantify the relative amounts of Cu, Cd and Te present at CdTe(111)-B surfaces after various surface treatments.

Each of the measurement techniques described above is part of the NREL surface-analysis cluster tool, which allows *in vacuo* processing, Cu deposition, and measurements without intermediate air exposures.

## 3. Results and Accomplishments

### 3.1 Reaction kinetics of Cu with CdTe

Figure 1 shows the desorption rate of Cd from the CdTe substrate as a function of temperature, for different initial Cu-film thicknesses. As the Cu-film initial thickness is increased, a peak in Cd desorption grows in between 525–575 K. Desorption of Te (not shown) is suppressed during the Cd desorption peak. The leading edges of the Cd desorption traces fall on a common curve, and for each trace the Cd desorption rate abruptly falls to zero as the Cu at the surface is depleted. These features are characteristic of a reaction with zero-order kinetics: the rate is a function of temperature and is independent of the instantaneous amount of elemental Cu at the surface.

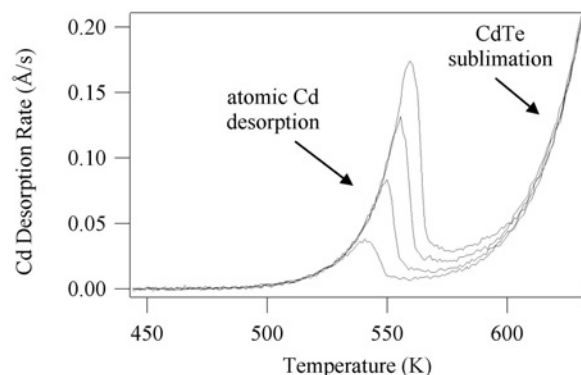


Fig. 1. TPD of Cd from CdTe(111)-B substrate for 5-, 6-, 7- and 8-Å thick Cu films (ramp rate = 0.5 K/s).

The zero-order kinetics for the liberation of Cd by the reaction of Cu with CdTe may be described with a standard rate equation

$$r = \exp(-E_a/k_B T), \quad (1)$$

in which is the exponential prefactor,  $E_a$  is the activation energy,  $k_B$  is Boltzmann's constant, and  $T$  is the temperature in degrees Kelvin. A fit to the leading edge of the Cd desorption peaks in Fig. 1 yields a prefactor in the range  $3.2 \times 10^{14}$  to  $1.4 \times 10^{15} \text{ Å s}^{-1}$  and an activation energy of  $1.73 \pm$

0.05 eV. The uncertainties in the kinetic parameters derive from an estimated uncertainty in the temperature of  $\pm 5$  K.

These measurements demonstrate that Cd is liberated upon the reaction of CdTe with thin films of Cu, implying that Cu either replaces Cd in the CdTe lattice or that a  $\text{Cu}_x\text{Te}$  phase is formed. XPS and SAM measurements reveal that both of these processes occur.

### 3.2 Metastable $\text{Cu}_x\text{Te}$ phase formation on $\text{CdTe}(111)\text{-B}$

Figure 2 shows a secondary-electron image (SEI) and the corresponding SAM image of Cu concentration for a  $\text{CdTe}(111)\text{-B}$  surface exposed to a total dose of 150  $\text{\AA}$  Cu, with brief anneals to 623 K, in the course of a TPD measurement similar to the one described above. The surface was sputtered briefly (on the order of 10  $\text{\AA}$  were removed) to increase contrast in the SAM image. Roughly triangular depressions on the order of 1  $\mu\text{m}$  across are visible in the SEI, which correspond to the Cu-rich features (bright areas) seen in the SAM image. Also visible are smaller triangular features ranging in size from 50–250 nm.

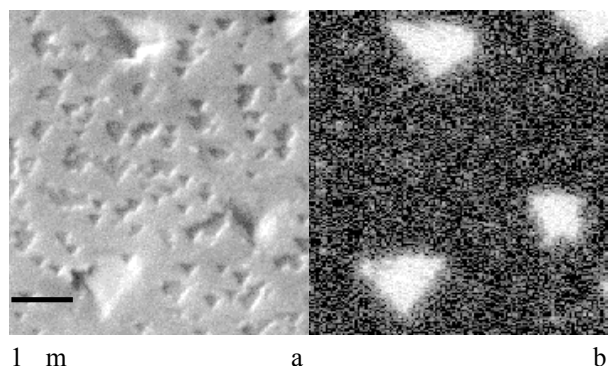


Fig. 2. SEI (panel a) and SAM image of Cu concentration (panel b) for the same area of a  $\text{CdTe}(111)\text{-B}$  surface with triangular  $\text{Cu}_x\text{Te}$  features.

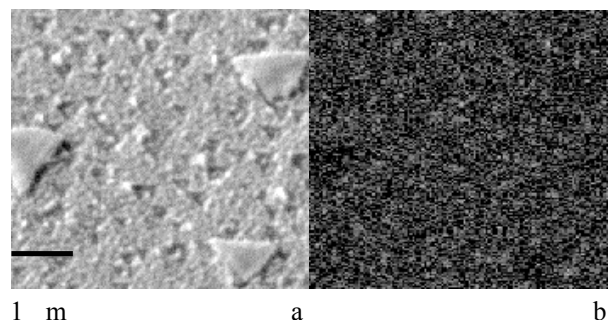


Fig. 3. SEM image (panel a) and SAM image of Cu concentration (panel b) for the  $\text{CdTe}(111)\text{-B}$  substrate in the previous figure, after additional annealing.

Figure 3 shows a different region of the same surface after additional annealing (588 K for 3 hours). While the micron-scale triangular features are still visible, AES survey spectra reveal that Cu is present at only trace levels, and the SAM image shows no Cu-rich features. As we detect no Cu desorption from CdTe, these

observations lead to the conclusion that the Cu has diffused into the bulk, and therefore that the  $\text{Cu}_x\text{Te}$  phase is metastable. After annealing, the triangular depressions have become flat protrusions from the surface. This is understood by considering sublimation of the substrate during annealing: Cu-telluride phases have lower vapor pressures than CdTe, so the  $\text{Cu}_x\text{Te}$  features have remained at roughly the same height, while the level of the surrounding CdTe has decreased due to sublimation.

### 3.3 Temperature-reversible surface segregation of Cu at $\text{CdTe}(111)\text{-B}$

Temperature-programmed XPS measurements are used to study the surface segregation of Cu in Cu-doped  $\text{CdTe}(111)\text{-B}$  substrates. Figure 4 shows a typical series of measurements in which the temperature is alternately ramped between 473 and 588 K while the surface composition is monitored with XPS. Cu segregates at the surface at low temperature and diffuses into the bulk at high temperature. XPS depth profiles of the Cu-segregated surface show that Cu is concentrated within 5–10  $\text{\AA}$  of the surface, implying that the segregated Cu resides in the topmost unit cell. This is in contrast to the formation of bulk  $\text{Cu}_x\text{Te}$  features discussed in the previous section. The bulk  $\text{Cu}_x\text{Te}$  features extend much deeper into the substrate (on the order of 100–1000 nm) than the surface-segregated Cu phase. Also, the bulk  $\text{Cu}_x\text{Te}$  phase is metastable, and does not lead to a temperature-reversible surface Cu concentration.

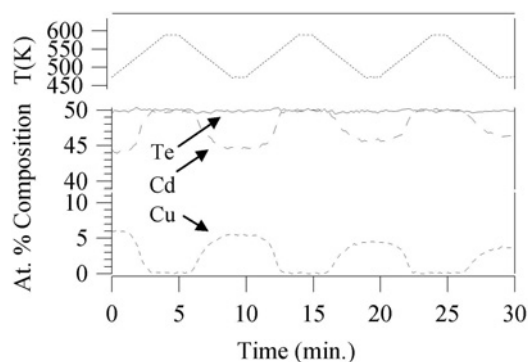


Fig. 4. Plot of surface composition of Cu-doped  $\text{CdTe}(111)\text{-B}$  substrate vs. time as substrate temperature varies from 473–588 K.

## 4. Conclusions

The kinetic parameters for the reaction of Cu with the  $\text{CdTe}(111)\text{-B}$  surface have been extracted from TPD measurements of Cu-dosed  $\text{CdTe}(111)\text{-B}$  substrates. A metastable  $\text{Cu}_x\text{Te}$  phase has been observed that forms upon the reaction of Cu with CdTe. Finally, a temperature-reversible, surface-segregated Cu phase has been observed in Cu-doped  $\text{CdTe}(111)\text{-B}$  substrates.

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