

Spectroscopic Cathodoluminescence Studies of the ZnTe:Cu Contact Process for CdS/CdTe Solar Cells

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SPECTROSCOPIC CATHODOLUMINESCENCE STUDIES OF THE ZnTe:Cu CONTACT PROCESS FOR CdS/CdTe SOLAR CELLS

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ABSTRACT

Spectroscopic cathodoluminescence (CL), electron-beam induced current (EBIC), and capacitance-Voltage (C-V) measurements are used to study the formation of CdS/CdTe devices processed using ion-beam milling and a ZnTe:Cu/Ti contact. Results show heating in vacuum at $\sim 360^\circ\text{C}$ and ion-beam milling lead to observable changes in the CL emission from the CdCl₂-treated CdTe surface. Changes in the CL spectrum are also observed as ZnTe:Cu layer thickness increases. These changes are correlated to published studies of defect levels and shown to be due, possibly, to an n-type region existing between the ZnTe:Cu contact interface and the p-CdTe layers. This n-type region is eliminated once a sufficiently thick ZnTe:Cu layer is produced.

INTRODUCTION

CdS/CdTe devices demonstrating good stability and fill factors approaching 77% have been produced using a Cu-doped ZnTe (ZnTe:Cu) contact interface layer between the CdTe absorber and a Ti metallization. This contacting process uses ion-beam milling, instead of wet-chemical etching, to prepare the CdTe surface and, therefore, may provide manufacturing advantages [1]. Previous studies focused on understanding how the constituents of the contact diffuse into the CdTe and CdS layers. These studies revealed that a significant amount of Cu can enter the CdTe layer during the 400°C CdCl₂ treatment, followed by additional Cu diffusion during the 360°C ZnTe:Cu/Ti contact process [1,2]. Although it is generally believed that too much Cu diffusion from the contact is related to reduced device stability, it is also believed that the level of acceptor activation in CdTe required for high-performance devices is also linked to Cu diffusion.

In the present work, variable-energy, spectroscopic CL is used to study the evolution of the electrical nature of the CdTe during the Cu diffusion associated with contact formation. This powerful technique allows for depth-resolved analysis of radiative recombination occurring near the CdTe/ZnTe:Cu interface following various stages of the contact process. EBIC and C-V is also used to examine changes in the ability of the CdTe layer to collect current as the parameters of the ZnTe:Cu contact process are systematically changed.

EXPERIMENTAL

The CdS/CdTe material used in this study was produced and CdCl₂ treated at First Solar, LLC. Two types of materials were used. For the close-space sublimated (CSS) material, the CdS and CdTe layers are deposited at $\sim 580^\circ\text{C}$ onto 5-mm-thick soda-lime glass to nominal thicknesses of ~ 300 nm and ~ 4.5 μm , followed by a wet CdCl₂ treatment. For the vapor-transport deposited

(VTD) material, deposition temperature and layer thickness are similar to the CSS, but the substrate is 3 mm thick and a vapor-CdCl₂ process is used. The CSS and VTD materials used for this study were cut from sample plates #20746E5 and #A98082446B2, respectively.

ZnTe:Cu contact formation begins by placing a sample of methanol-rinsed CdS/CdTe material into a multisource vacuum deposition system and heating it to $\sim 360^\circ\text{C}$. Samples are maintained at the substrate temperatures throughout the contacting process (~ 2 h at 360°C + 3 h preheating and cooling). Ion-beam milling is performed with a 3-cm Kaufman-type ion gun, operating at a beam energy and current of 500 eV and 6 mA, respectively. The ion gun is mounted at 45° and is operated using UHP-grade Ar at a chamber pressure of 2×10^{-5} torr. This results in a peak beam current density at the CdTe surface of ~ 0.2 mA cm⁻², and a peak mill rate of ~ 2000 Å min⁻¹. The substrate is automatically rotated under the beam at several off-center positions such that uniform erosion of ~ 100 nm is achieved over a circular region ~ 7.6 cm in diameter for the standard contact process. A ZnTe:Cu (~ 6 at.% Cu, measured with electron microprobe) layer is deposited by r.f. sputter deposition, followed immediately by d.c. sputter deposition of ~ 0.5 μm Ti. To ensure that the parameters linked to Cu diffusion are comparable for samples with different ZnTe:Cu layer thicknesses, the deposition rate of the ZnTe:Cu and the time interval between initiation of ZnTe:Cu and Ti deposition were held constant. Following deposition and sample cooling, a pattern of individual 0.25-cm^2 cells are defined photolithographically on each sample. Cell definition is by two-step chemical etching, first using TFT Ti Etchant (Transene Co. Inc., Rowley, MA) to remove the Ti, followed by an aqueous solution containing 39% FeCl₃ to remove the ZnTe:Cu and CdTe. Following photoresist removal, unwanted areas are mechanically removed, and contact to the SnO₂ layer is ultrasonically formed with a perimeter of In solder around the entire array of cells.

Electrical analysis included light current-voltage (IV) measurements using an XT-10 solar simulator that had been adjusted to approximate Global AM1.5 current from a CdS/CdTe reference cell. Capacitance-voltage (C-V) measurements were performed using an HP 4274 LCR meter at a frequency of 100 kHz. EBIC measurements were performed using a state-of-the-art, field-emission scanning electron microscope (FESEM JEOL 6320F). CL measurements were performed in a conventional SEM (JEOL 5800) equipped with two different detector systems: An Oxford monoCL2 monochromator with a North Coast EO-187R Ge photodiode and an Amherst Sci. Corp. 4500 GaAs photomultiplier tube (PMT), and a Princeton LN/CCD-1340/400 cryogenic charge-coupled detector (CCD) spectrograph. A schematic of the apparatus arrangement and device structure is shown in Figure 1. Initial CL analysis used the monochromator and Ge detector to investigate the spectral region between 0.75

and 1.65 eV. These investigations indicated that heating and ion-beam milling lead to the generation of defects related to Cd vacancies (V_{Cd} , 0.8 eV) and Te vacancies (V_{Te} , 1.0 eV) in the CdTe region near the CdTe/ZnTe:Cu interface [3]. Because of the superior data acquisition rate afforded by the CCD spectrograph, the studies reported here use that detector (range 1.2-1.62 eV) exclusively.

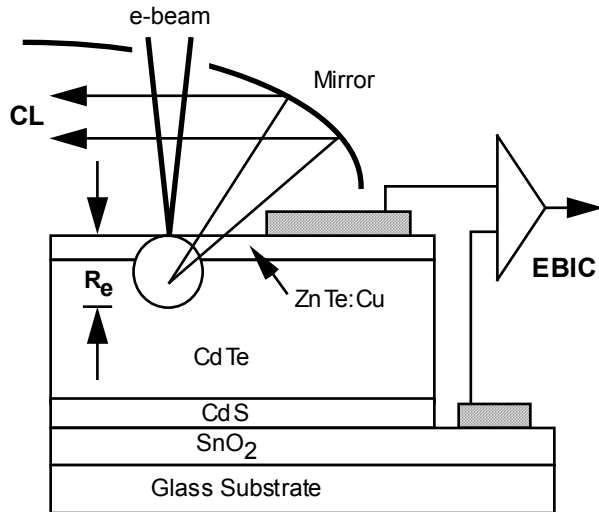


Figure 1. Diagram illustrating device structure and CL and EBIC functional layout.

In both CL and EBIC, energy transferred from the electron beam (1-40 keV) results in the generation of a highly localized source of carriers within the (energy-dependent) penetration range R_e . For EBIC measurement performed in this study, the electron beam is incident on a freshly cleaved cross-section of an otherwise completed device. If the beam generates carriers within the depletion width of the CdTe/CdS junction, the carriers are collected at the contacts and amplified to yield the EBIC signal. In this way, the EBIC signal is used not only to profile the depletion width of the device, but also to determine if secondary junctions exist near the back surface. For the CL measurements performed in this study, the Ti is removed using the TFT etchant, and the electron beam is incident on the back side (through the ZnTe:Cu, if present). Carriers that recombine radiatively supply the CL signal that is focused by a mirror into an optical guide, and directed toward the detector(s) [4]. Because the optical bandgap of ZnTe:Cu is higher than CdTe, absorption of the emergent CL signal is not a concern as it may be for lower-bandgap interface layers.

RESULTS AND DISCUSSION

CL analysis of all CdCl₂-treated CdTe material reveals two main features in the spectral range 1.2–1.6 eV. The first feature is peaks in the range of 1.5-1.6 eV that are associated with free-carrier transitions, exciton transitions, or transitions between relatively shallow donors and acceptors. Analysis of these higher energy transitions can indicate

changes in material quality and the dominance of shallow donors. The second feature is a broad peak between 1.3 eV and 1.5 eV, which is related to deep donor-acceptor pair (DDAP) transitions. Although it is believed that many deep-donor energy levels are associated with this transition, the acceptor is thought to be a single state and related to a cadmium-vacancy complex located at 140-150 meV above the valence band (known as the A center). This broad emission is not observed in crystalline CdTe unless Cu has been diffused [5]. It is also suppressed in polycrystalline CdTe if it has not been CdCl₂ treated [4]. Because previous results show Cu can accompany the CdCl₂ treatment [1,2], identifying the relative importance of Cu or Cl to the origin of this peak will require further investigation.

Figure 2 shows CL analysis of VTD material following various pre-contact treatments. The analysis shows a shift of the exciton emission from the as-received position at 1.580 to 1.565 eV following both heat treatment and ion-beam milling. This would indicate that the as-received surface is dominated by exciton recombination and is relatively free of shallow states. The 1.565 eV emission observed after heat-treatment, and after heat treatment plus ion-beam milling suggests a surface dominated by either free-to-bound exciton recombination, or bound excitons. This indicates that both heating and ion-beam milling lead to the evolution of shallow defects in the region of CdTe that will become the CdTe/ZnTe:Cu interface. Analysis of the overall structure of the DDAP emission reveals a systematic shift of ~15 meV for the two samples that were heated relative to the two samples that were both heated and ion-beam milled. Analysis also shows that the position of the DDAP substructure, following both heating and ion-beam milling, aligns well with the as-received sample. Although efforts to correlate the small shift in the substructure of the DDAP peak with contact performance are ongoing, the shifts suggest that heating and ion-beam milling cause the dominance of deep donors to be altered.

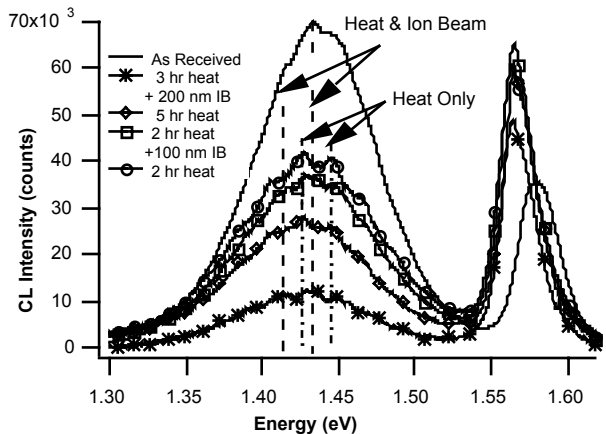


Figure 2. CL spectra showing effect of heating and ion-beam milling on the CdCl₂-treated VTD material.

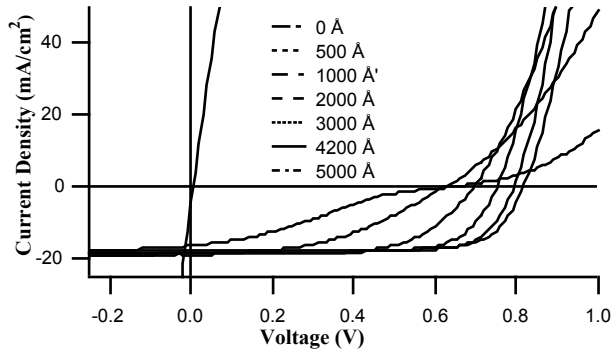


Figure 3. Light I-V curves showing changes in V_{oc} and fill factor as thickness of ZnTe:Cu layer is increased at constant temperature and time.

Figure 3 shows the effect of increasing ZnTe:Cu thickness on the light I-V characteristics of the devices produced with CSS material. The highest performance devices in this set demonstrated open-circuit voltages (V_{oc} 's) of ~ 820 mV, fill factors of 76%. Because the shunt resistance was uniformly high for all devices with a ZnTe:Cu layer (~ 3 Mohm- cm^2), C-V measurements were performed and the results analyzed using a $1/C^2$ fit. As shown in Figure 4, this analysis indicated the maximum depletion width attainable for all devices was ~ 4 μm , which is a value consistent with the known thickness of these structures. It was also determined that the devices produced with 500 Å and 1000 Å of ZnTe:Cu were completely depleted at zero bias, suggesting that the acceptor activation for these devices is very low. For ZnTe:Cu thicknesses of 2000 Å – 5000 Å, the depletion width at zero bias is reduced with increasing ZnTe:Cu thickness, indicating that acceptor activation increases near the contact interface as the thickness of the ZnTe:Cu layer thickness increases.

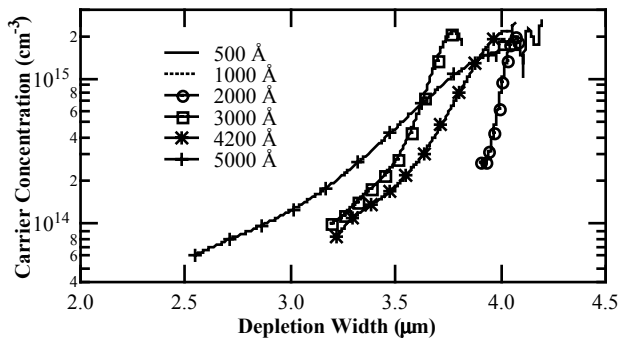


Figure 4. C-V measurements of samples produced with various thickness of ZnTe:Cu, and fitted using $1/C^2$ analysis.

The roll-under characteristic observed for the device shown in Figure 3 produced with 500 Å of ZnTe:Cu is similar to characteristics in modeled devices if a 100-nm-thick layer of n-type ($1 \times 10^{17} \text{ cm}^{-3}$) is placed between a contact and a p-layer ($1 \times 10^{16} \text{ cm}^{-3}$) that is ~ 4 μm thick [6]. To investigate further the possibility of an n-type layer being present near the contact interface, EBIC was performed on four CSS samples with ZnTe:Cu thicknesses of 500 Å to 4200 Å. Figure 5 shows that the samples with thick ZnTe:Cu (4200

Å) demonstrated high response, but only near the CdS/CdTe interface, and very little response near the back surface. This is typical and necessary for good CdS/CdTe devices. Although the sample with 500 Å of ZnTe:Cu also indicated significant response near the CdS/CdTe junction, it also indicated significant response near the CdTe/ZnTe:Cu interface. Although not shown, devices with ZnTe:Cu thicknesses of 1000 Å and 2500 Å indicated relatively uniform EBIC response throughout the CdTe. This analysis supports the above suggestion that an n-type layer is present at the back surface for samples with 500 Å ZnTe:Cu.

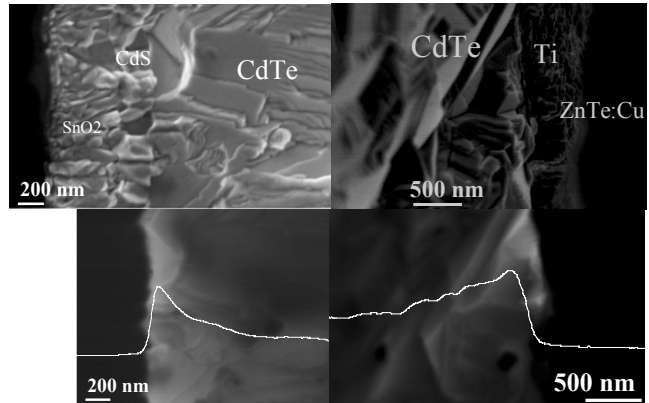


Figure 5. SEM (top) and EBIC (bottom) images of CSS samples with 4200 Å (left side) and 500 Å (right side) of ZnTe:Cu. For each sample, the interfaces have been aligned to correlate roughly EBIC response to the respective features indicated on the SEM image.

Figure 6 shows the effect of increasing ZnTe:Cu thickness on the CL spectra for CSS CdS/CdTe material that was wet- $CdCl_2$ processed. Comparing Figure 6 and Figure 2 shows that ZnTe:Cu contact diffusion into the CdTe reduces the energy positions of both the high-energy and DDAP emission by ~ 0.5 eV. The reduction of the DDAP energy position with Cu incorporation is consistent with PL observations for Cu diffusion into crystalline CdTe [5]. However, the shift of the higher energy peaks following even a small amount of ZnTe:Cu deposition is still being investigated. Analysis of the DDAP substructure at all thicknesses and both beam energies shows that, unlike the effect of heating and ion-beam milling, the positions of the DDAP substructure remain unchanged as the thickness of the ZnTe:Cu layer is increased. However, the position of the high-energy peak for 500-Å ZnTe:Cu thickness at a 20-keV beam energy shows a shift from 1.53 to 1.51 eV.

Photoluminescence (PL) analysis of similar material at 10 K and 77 K has indicated that the CL peaks observed at 1.53 and 1.51 eV can be correlated with peaks observed in crystalline CdTe. These peaks have been assigned to transitions between a free electron and an acceptor (F-A, 1.53 eV peak) and a shallow donor and acceptor (D-A, 1.51 eV peak) [7]. The fact that an emission signature related to a shallow donor is observed only for the sample that demonstrated light I-V characteristics consistent with a thin n-type layer near the contact interface supports further the

suggestion that an n-type region exists for these contacts with thin ZnTe:Cu layers. Furthermore, the fact that the D-A emission is only observed at higher electron-beam energy suggests that the n-type layer may not be immediately adjacent to the ZnTe:Cu, but located deeper into the CdTe (i.e., depth of maximum CL emission for a 20-keV electron beam is ~400 nm, whereas at 10 keV it is ~200 nm).

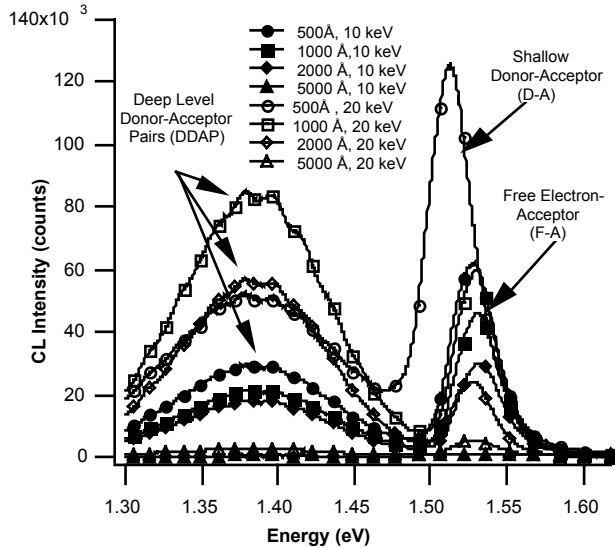


Figure 6. CL spectra showing effect of ZnTe:Cu layer thickness on DDAP and higher energy recombination.

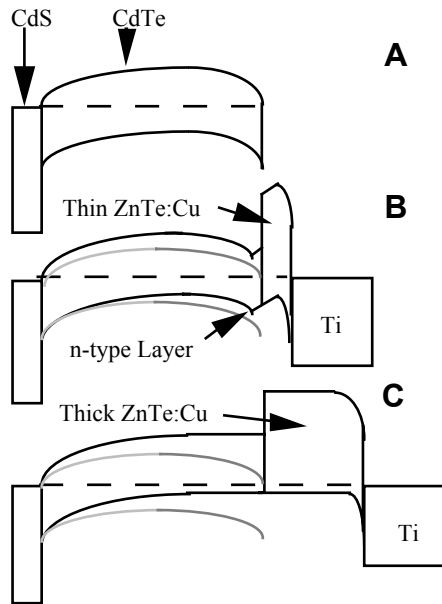


Figure 7. Model for band evolution in ZnTe:Cu contacted CdS/CdTe devices. A – Possible band structure prior to back contact formation. B – Thin ZnTe:Cu contact interface layer (~500 Å). C – Thick ZnTe:Cu contact interface layer (>3000Å).

Based on these observations, Figure 7 shows a series of band diagrams that illustrate the main points of contact formation for this ZnTe:Cu contact discussed above.

CONCLUSIONS

This study has shown that a CdS/CdTe PV device undergoes significant changes during formation of a ZnTe:Cu contact. These changes not only involve formation of low-resistance barriers at the CdTe/ZnTe:Cu and ZnTe:Cu/metal interfaces, but also considerable acceptor activation in the CdTe near the contact interface and within the CdTe bulk. It is likely that this activation is, in part, responsible for the increase in V_{oc} observed with increasing ZnTe:Cu thickness. For thin layers of ZnTe:Cu (~500 Å), roll-under is observed in the LIV behavior. CL and PL analyses indicate that this artifact is likely due to an n-type CdTe region existing between the ZnTe:Cu interface and p-CdTe. This is consistent with numerical modeling results and suggests that the back surface of the CdTe may be n-type prior to contacting. Efforts are ongoing to determine what part of the pre-contact processing may form and/or enhance the electrical properties of this layer.

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