October 2001 • NREL/CP-520-31031

Conference Paper

Effect of Heating, Ion-Beam Milling, and ZnTe:Cu Deposition on the Spectroscopic Cathodoluminescence of Polycrystalline CdTe

Preprint

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To be presented at the NCPV Program Review Meeting
Lakewood, Colorado
14-17 October 2001

National Renewable Energy Laboratory

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Contract No. DE-AC36-99-GO10337

Effect of Heating, Ion-Beam Milling, and ZnTe:Cu Deposition on the Spectroscopic Cathodoluminescence of Polycrystalline CdTe

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ABSTRACT

Cathodoluminescence (CL) is used to study the evolution of the electro-optical properties of the back surface of CdS/CdTe PV device material during the initial process steps of fabricating the NREL ZnTe:Cu contact. Results show that both heating and ion-beam milling lead to generation of defects at the location that will become the CdTe/ZnTe interface. CL can also identify effects due to Cu diffusion into the CdTe following deposition of the ZnTe:Cu layer.

1. Introduction

A process to contact CdS/CdTe PV devices has been developed at NREL that uses a sequence of high-temperature, vacuum-processing steps. These steps include: pre-deposition heating, ion-beam milling the CdTe surface, sputter deposition of a ZnTe:Cu interface layer, and sputter deposition of a Ti outer metallization. Although this contact has demonstrated fill factors approaching 77% [1], and good stability, the mechanism of current transport from the ZnTe:Cu contact interface into the CdTe remains unverified. It has been suggested that low-resistance transport of holes between the CdTe and ZnTe:Cu proceeds via valence-band alignment at the interface. However, it is also known that ion-beam milling tends to disrupt CdTe surfaces, and therefore this interface may be highly defected [2]. Initial efforts to assess the nature of the CdTe surface have included small-spot compositional analysis [3]. These studies have detailed effects that heating and ion-beam milling have on residuals resulting from various $CdCl_2$ treatments. However, the effect of these same heating and milling processes on the electro-optical properties of the near surface remains largely unexplored.

In this study, variable-energy, spectroscopic cathodoluminescence (CL) has been used to study recombination in the near-surface region of CdTe devices following various stages of the ZnTe:Cu contact process. This analysis indicates that both pre-deposition heating and ion-beam milling produce defect complexes that will likely affect interfacial current transport.

2. Experimental

The CdS/CdTe material used in this study was produced at First Solar LLC. The CdS and CdTe layers are deposited on 3-mm soda-lime glass by the vapor-transport deposition (VTD) process to thicknesses of ~300 nm and ~4.5 µm, respectively. Following active layer deposition, a vapor $CdCl_2$ treatment was performed at First Solar. All material used in this study was cut from the same 4"x4" sample plate (#A98082446B2).

ZnTe contacting is performed by cutting a small sample (~4 cm^2) from the larger sample plate, rinsing it with methanol, and placing it into a multi-source vacuum deposition system. The system is pumped to ~$5x10^{-8}$ torr, after which the substrate heater (boron-nitride element) is energized to a constant voltage of 26 V. This voltage produces a substrate temperature of ~360°C, determined by placing a 0.32 cm thick Al block with an imbedded thermocouple at the substrate position, and allowing the block to equilibrate for 2 hours.

One device with a "standard contact" was fabricated for this study. The contact was produced using a sequential process involving 2-hr temperature equilibration, ion-beam milling the CdTe surface to a depth of ~100 nm, r.f.-sputter deposition of ~0.5 µm of ZnTe:Cu (~6 at.% Cu), and d.c.-sputter deposition of ~0.5 µm Ti. To allow CL analysis, the Ti layer from one part of this sample was chemically etched. Measurements from the same device (with the Ti intact) demonstrated performance of 806 mV and a fill factor of 74%. Other samples were prepared in separate deposition runs to study the effect of the pre-deposition heating (0, 2, and 5 hours) and ion-beam milling (0, ~100-nm, and ~200-nm in depth) on the CdTe near-surface region. Preparation of these samples excluded ZnTe:Cu or Ti layer deposition, and thus, device performance could not be assessed.

CL measurements were performed in a JEOL 5800 scanning electron microscope at a sample temperature of 77K. A faraday cup was used to measure the beam current, and an Oxford MonoCL2 monochrometer equipped with a Ge detector was used to collect CL spectrum. This detector examined the entire CL spectral range from 0.7 to 1.7 eV.

3. Results and Discussion

Figure 1 shows the CL spectra of an as-received sample (no heating or ion-beam milling). The spectra is dominated by a free-exciton emission (FE) at 1.58 eV and several donor-acceptor pair (DAP) transitions at 1.3-1.5 eV. This type of spectra is consistent with Te-rich films because the acceptor of the DAP has been related to cadmium vacancies [4]. Monochromatic images of the FE and DAP peaks identified in Figure 1 are shown in Figure 2a and 2b, respectively. Figure 2a shows that the FE emission is located primarily within the grains while grain boundaries act as non-radiative recombination centers for this emission. Figure 2b indicates that, although the distribution of the donors and acceptors of the DAP transition are more diffuse than the FE emission, the centers of large grains and grain boundaries are the most luminescent regions.

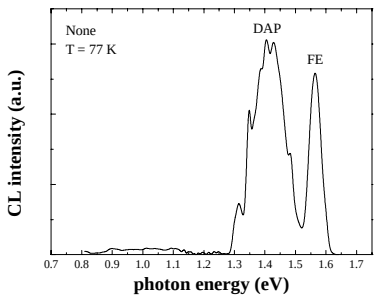

Figure 1. CL spectrum of as-received CdTe material acquired from backside at 20 keV beam energy.

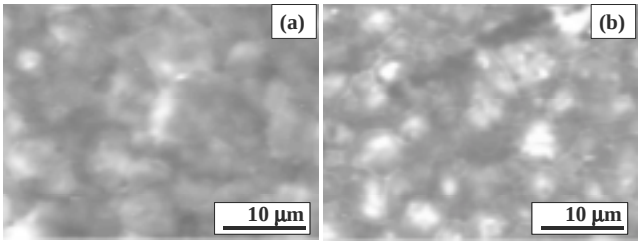

Figure 2. Monochromatic CL images of as-received CdTe at 10 keV for (a) FE at 1.58 eV and (b) DAP emission at 1.3-1.5 eV.

The effect of a 2-hr heat treatment on the CL is shown in Figure 3. Exciting closer to the surface (at 10 keV beam energy, maximum emission intensity at ~200 nm depth), deep level (DL) bands emerge at ~1.1 and ~0.8 eV. The luminescence at ~1.1 eV is associated with Te vacancies (V_{Te}), while the emission at 0.8 eV is related to an acceptor complex involving cadmium vacancies (V_{Cd}) [5]. Therefore, standard heating alone produces both V_{Te} and V_{Cd} in the near surface. Increasing the beam energy to 30 keV (maximum emission intensity at ~700 nm depth), the DL and FE emissions are reduced significantly and the DAP emission dominates, indicating that the defects caused by standard heating occur near the surface and not the bulk. Although not shown, CL of samples heated for 5 hrs reveals the FE emission near the surface is quenched, suggesting that heating in high vacuum yields highly defective surfaces.

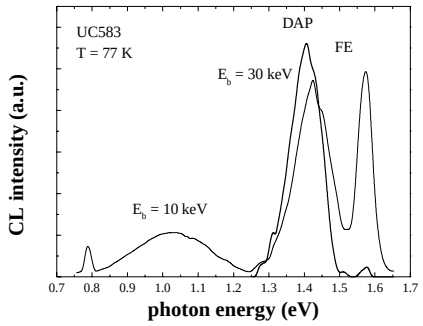

Figure 3. Effect of 2-hr heat treatment in vacuum on CL spectrum of CdTe.

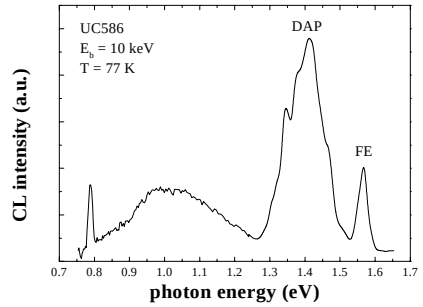

Figure 4. Effect of ion-beam milling on CL spectrum of CdTe.

Figure 4 shows that ion-beam milling increases the ratio of DL to DAP emissions. Further, the DL defects due to Cd vacancies (~0.8 eV) are generated faster than Te vacancies (~1.1 eV). This result is insightful because the earlier compositional analysis indicated that the ratio of surface Cd to Te remained constant after ion-beam milling [3].

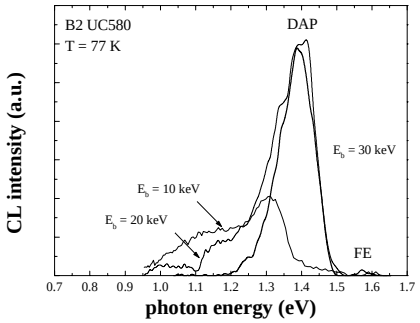

Figure 5. CL spectra of CdTe back surface following standard ZnTe:Cu/Ti deposition (with Ti layer removed).

Figure 5 shows CL analysis of a device with a 0.5-μm thick ZnTe:Cu layer present. The low-energy (10 keV) spectra suggests that Cu diffusion from the ZnTe:Cu (as observed by SIMS analysis) eliminates the DAP emission near the interface and produces a Cu_{Cd} emission [1,4]. Higher energy analysis (30 keV, ~700 nm depth) shows that the DAP complex remains active deeper in the CdTe. This result suggests that electrical activation of Cu, and thus the electrical properties of the CdTe, may change significantly as a function of distance from the ZnTe:Cu/CdTe interface.

3. Conclusions

CL is a powerful tool for probing mechanisms associated with ohmic contact formation to polycrystalline CdTe. These initial studies show that substrate heating and ion-beam milling generate defects in the region that will become the ZnTe:Cu/CdTe interface. Correlation of some of these defect levels to Cu incorporation has already been reported in existing photoluminescence literature. These assignments suggest a V_{Cd} defect is produced near the surface of CdTe by heating and milling. This defect is eliminated following ZnTe:Cu deposition, producing a new defect related to Cu_{Cd}.

4. Acknowledgements

The authors acknowledge D.H. Rose of First Solar LLC for samples and valuable technical discussion. This research was supported by DOE Contract #DE-AC36-99GO10337.

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