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Micro-PL Studies of Polycrystalline CdS/CdTe Interfaces

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ABSTRACT

We describe a technique of photoluminescence measurements with a resolution of microns. This technique is applied to examine the CdS/CdTe interface of CdTe solar cells. The devices were made using chemical-bath deposited CdS on SnO2/glass substrates. The CdTe was deposited by close spaced sublimation and subsequently CdCl2 treated and annealed. Micro-photoluminescence (micro-PL) analysis reveals sulfur accumulation at the grain boundaries and a graded CdSxTe1-x alloy at the interface. We have compared these results with measurements from a SnO2/CdTe interface to make sure that the features observed in CdS/CdTe interface analysis are the result of CdSTe alloy and not other factors such as grain size or stress.

INTRODUCTION

Polycrystalline semiconductors are used in a number of device applications. Due to the inherent advantages of lower cost and ease of fabrication, polycrystalline thin film solar cells are prime candidates for commercialization. CdS/CdTe solar cells have demonstrated efficiencies of 15.8% in laboratory devices [1]. Due to its good stability and ease of fabrication, a number of groups are involved in development of this technology. There are however many issues that still need to be understood for successful scaling-up. In the case of polycrystalline semiconductors, grain boundaries can influence the properties of the material considerably. There has been extensive work done on the structural characterization of grain boundaries using microscopic techniques such as scanning and transmission electron microscopy. In the case of electronic devices, the effect of the grain boundaries on the electro-optical properties can be substantial and development of processing techniques to mitigate damaging effects are crucial for enhancing the performance of these devices. Most electro-optical analysis techniques give information on a macroscopic scale and the effect of grain boundaries can only be speculative based on comparison with equivalent single crystal samples. So far only Electron Beam Induced Current (EBIC) measurements have provided useful information on the properties of grain boundaries in CdTe based devices. In this paper, we describe a micro-PL technique, which can resolve the electrical properties of the grains and grain boundaries. CdS/CdTe samples are used as a test case to demonstrate the capabilities of this technique. The effect of grain boundaries and intra-grain structural defects on electro-optical properties is studied by micro-PL measurements.

EXPERIMENTAL DETAILS

Micro-PL measurements were performed at 4.2 K using a confocal spectroscopy setup. (Figure 1) About 130 W of the 514.5 nm excitation laser beam was focused onto the sample inside an Oxford Microstat He cryostat using a long-working distance reflective microscope objective. The objective lens has a capability to compensate for the spherical aberration due to the 500 µm-thick window of the cryostat. The spot size on the sample is estimated to be 1–2 µm in diameter. The PL signal was collected and collimated by the same objective, and then focused onto the input slit of a Spex 0.6µm triple spectrometer. A charge-coupled-device (CCD) detector array was used to collect the spectra. The resolution of the system is estimated to be approximately 0.5 meV. In order to investigate the spatial variation of the PL spectra, the sample (and cryostat) was scanned in 1µm steps using an optically decoded translation stage. Although the spectrum changes significantly as a function of position, it varied little as a function of time at a given position. This indicates that the spatial stability of the sample was adequate. Details of the fabrication of CdS/CdTe samples are described elsewhere [2].

RESULTS AND DISCUSSION

Figure 2 shows the PL intensity as a function of position for a film that was released from the substrate, directly exposing the CdS/CdTe interface. The sample was
deposited at 610°C with a subsequent CdCl₂ heat treatment. In Figure 2, the peaks correspond to the center of the grains, and the valleys to the grain boundaries. The numbers above the arrows indicate the approximate distance between grain boundaries. PL intensity analysis from the CdTe side also shows similar behavior. PL spectra measured from the CdTe side and the CdS/CdTe interface side (for selected points in Figure 2 closer and away from grain boundaries) are presented in Figure 3. The PL spectra for measurements on the CdTe side show that, even though the intensity changes considerably from the center of the grain to the grain boundary, the peak position of the spectra remains at the same position (1.581 eV), corresponding to the CdTe bandgap. On the other hand, the PL spectra from the CdS/CdTe side show changes both in the intensity and the peak position. All of these spectra are shifted to lower energy and their bandwidth is much larger than that of the CdTe spectra seen from the backside. These spectra correspond to the alloyed region at the interface, which explains the peak shift to lower energies (expected for Te-rich CdS₃Teₓ₋ₓ alloys) [3]. Peak broadening is due to the superposition of spectra corresponding to the range of alloy compositions present in the alloyed layer. To substantiate this hypothesis, we also did these measurements on similar samples with SnO₂/CdTe structure from SnO₂ side. The spectra of PL intensity as a function of position for these samples were similar to spectra from CdTe side for CdS/CdTe samples. Peak position of these spectra also remained closer to CdTe bandgap (1.581 eV) and there was no peak broadening (Figure 4). Therefore the peak position shift and peak broadening seen for PL spectra of CdS/CdTe samples can be uniquely assigned to the formation of CdS₃Teₓ₋ₓ alloying. The spectra corresponding to the positions in the center of the larger grains (~9 µm) have higher intensities, with a peak position at 1.543 eV and symmetrical peak broadening in the range of 1.524 eV and 1.569 eV, corresponding to alloy composition range of x = 0.024 to 0.114. The spectra corresponding to the center position of a small grain (~2 µm) has a peak position at 1.535 eV and is asymmetrical, indicating the contribution predominantly from the lower gap alloys between 1.52 eV and 1.545 eV (x = 0.072 to 0.122). The peaks corresponding to the grain boundaries (lowest intensity peaks in the spectrum) have peak positions at 1.538 eV and also show predominant contribution from lower gap alloys. Previous work on Te-rich CdS₃Teₓ₋ₓ alloys [3], indicates that the bandgap decreases as x increases from 0 to 0.25. Therefore, grain boundaries and heavily faulted small grains contain alloys with higher sulfur compositions as compared to the middle of the larger grains.

Figure 4. PL spectra from SnO₂ side of SnO₂/CdTe sample at 4.2 K at different positions.

CONCLUSIONS

Micro-PL technique can determine electro-optical properties with microscopic resolution and give relevant information for the properties of grain boundaries in polycrystalline semiconductor device structures.

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