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Processing Effects on Junction Interdiffusion in CdS/CdTe Polycrystalline Devices

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ABSTRACT

The performance of CdS/CdTe solar cells is strongly impacted by the process used to grow the CdS layer. CdS films grown by chemical-bath deposition (CBD) exhibit lower optical absorption than similar films grown by close-spaced sublimation (CSS). CBD-CdS films also form in a cubic phase structure while CSS-CdS films show a strong degree of hexagonality. During the initial growth by CSS, the CdTe structure is influenced by the CdS structure. Hexagonal CdS nucleates hexagonal CdTe. Similarly, cubic CdS favors the formation of cubic CdTe. Both polytypes show similar optical bandgaps. Alloying is not detectable during the initial stages of growth in either case. Auger Electron Spectroscopy (AES) depth profiles through the CdS/CdTe interface in finished CdTe devices, grazing-incidence x-ray diffraction (GIXRD) of the CdTe alloy region, transmission electron microscopy (TEM) with energy-dispersive x-ray (EDS) analysis, and scanning electron microscopy (SEM), are combined to show how CdS type impacts interdiffusion at the CdS/CdTe interface.

1. Introduction

Previously, we observed that changing the process used to grow CdS films (either CSS or CBD processes) had a serious impact on device performance [1]. Replacing CBD-CdS films with CSS-grown CdS resulted in open-circuit voltage, V_{oc} , drops of 100 - 150 mV. Because of the magnitude of this effect, it was believed that further CdS/CdTe interfacial studies using these types of CdS were warranted in understanding how V_{oc} at the interface was affected.

In this paper, we combine previous results with new data obtained by TEM to arrive at a model for how interdiffusion occurs at the CdS/CdTe interface. These differences may explain differences in V_{oc} observed with these types of CdS.

2. Experimental Procedure

CBD CdS films of variable thickness were grown by a standard process involving the titration of Cd-acetate solutions with a thiourea base [2]. CSS-CdS films of similar thickness were grown by CSS in a helium ambient using a process previously described [1].

CdTe films were then deposited by CSS on 800-Å-thick CdS samples, using oxygen ambients of 0, 1, and 1.5 torr in 16 torr total ambients with He as the balance. CdTe source temperatures of 660°C and substrate temperatures of 620°C were used. *Thin-Layer* CdTe samples (100-400 nm) were made by decreasing deposition time to 1-5 seconds, depending upon oxygen level used. Higher oxygen concentrations required longer deposition times due to the growth-moderating effects of oxygen [3].

GIXRD measurements were performed on both as-grown CdS films and *thin-layer* samples to ascertain the CdS

structure effects on CdTe growth. XRD scans were performed at angles near the critical angle (0.291° for CdTe) for total reflection as well as at higher angles up to 2.0° to probe structure as a function of depth. Optical reflection and transmission measurements were also performed on these samples to determine the optical gap of the deposited CdTe layer, and therefore the alloy composition that forms during initial film growth.

Device-representative thick samples (~8 microns; process terminated *before* the backcontact) were prepared for both lift-off analysis and TEM analysis. The lift-off technique involves epoxying a glass plate on top of the CdTe/CdS/TCO/7059 glass structures and then separating the glass layers. Such a method reveals the alloy region and CdS layers for direct analysis.

Finally, *device-representative* samples were prepared for electron microscopy by first mechanical polishing them to ~100 μm thickness, then dimpling the central portion of the specimens down to ~5 μm . The samples were subsequently thinned by using a 4 kV Ar ion-beam at 14° inclination. A liquid-N₂ cooling stage was used in order to minimize milling damage. TEM images were taken on a Philips CM30 microscope operating at 300 kV. The probe size was approximately 60 nm.

3. Results and Discussion

Significant differences were observed in the optical and structural properties of as-grown CBD and CSS-CdS films. XRD data show only low intensity, broad peaks corresponding to the cubic phase of CBD-CdS. In contrast, CSS-CdS reflections are sharper, and show peaks corresponding to the hexagonal phase of CdS. Optical absorption in CSS-CdS films is higher. While the bandgap of CBD-CdS films decreases from 2.5 to less than 2.4 eV as film thickness increases, the bandgap for CSS-CdS films remains constant at about 2.42 eV. The grain size of CSS-CdS films was also found to be much greater (100 - 500 nm depending upon thickness) than CBD films (limited to ~30 - 50 nm).

GIXRD analysis of *thin-layer* CdTe deposited on different CdS substrates shows clearly that hexagonal CdTe nucleates when CSS-CdS is used, and cubic CdTe nucleates when CBD-CdS is used. The tendency for hexagonal CdTe to nucleate increases as oxygen in the growth environment increases. The dependence of CdTe nucleation on CdS type is intriguing in two regards. Recently, it has been predicted that differences in both valence and conduction band offsets can occur at CdS/CdTe interfaces depending upon which phase of CdS is present [4]. Also, if crystal field splitting is significant, so as to minimize thermalization effects, V_{oc} could be perturbed through differences in valence-band density of states which might exist between cubic and hexagonal CdTe.

XRD peak positions of *thin-layer* CdTe on different CdS films did not reveal either differences in initial alloying

behavior (i.e., contrasting CSS and CBD CdS) nor any alloying whatsoever. The optical bandgap of the *thin-layer* CdTe was determined to vary from 1.48 to 1.50 eV using $(\hbar\nu)^2$ vs energy plots, again suggesting little initial alloying. No correlation between structure, oxygen, CdS type and bandgap was observed.

GIXRD analysis of lift-off samples prepared from both vapor CdCl₂ and non-CdCl₂ treated cells could not detect the presence of any hexagonal CdTe at the CdS/CdTe interface. It therefore appears that the initial hexagonal CdTe phase is transitory during growth.

TEM cross-sections of both types of interfaces did reveal a very unique difference between CSS and CBD-CdS films. As shown in Figure 1, the presence of the 80 nm (pre-CdTe measured) CBD CdS layer is clearly visible as a discrete layer between the SnO₂ and CdTe layers. However, the 70 nm (pre-CdTe measured) of CSS-CdS appears to be absent.

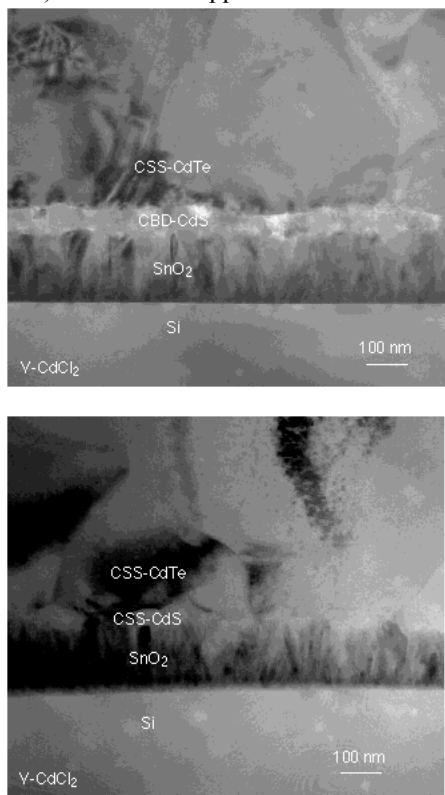


Fig. 1 TEM cross-sections of CBD CdS/CdTe (top) and CSS CdS/CdTe (bottom) devices.

This is a very interesting observation. Previous reports would support enhanced diffusion in smaller grained CBD CdS [1,5]. GIXRD data of lift-off samples clearly show, for example, that the degree of alloying at the CBD CdS/CdTe interface is much greater (~12 at.% S) than in the CSS CdS/CdTe case (~2-3 at.% S) [1]. However, recent AES depth profiles shown in Figure 2 seem to indicate much greater penetration of S into the CdTe layer when CSS-CdS films are used [6]. Surface S levels of only 3 at.% (identified by GIXRD) and long-penetrating S "tails" identified by AES strongly suggest enhanced grain boundary diffusion for the CSS-CdS samples. This has now been substantiated by the TEM data. The penetration of S (and similar, albeit smaller, penetration of Te into CdS) is also a strong function of the

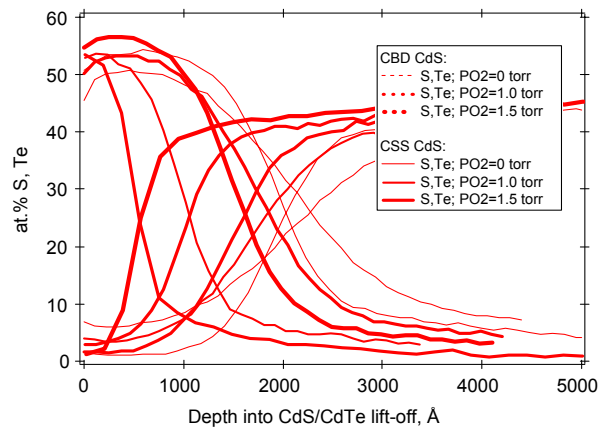


Fig. 2 AES depth profiling data through CBD-CdS/CdTe (dotted lines), and CSS-CdS/CdTe (solid lines) interfaces (lift-off samples)

oxygen present during the CSS growth of CdTe (as indicated in Figure 2). Increasing oxygen minimizes interdiffusion of

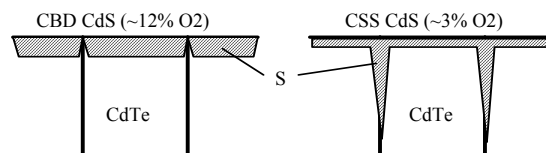


Fig. 3 Interdiffusion Models for CBD and CSS CdS/CdTe interfaces

both species. The reason why interdiffusion for CBD CdS is less than CSS CdS (in Fig. 2) may be that CBD CdS has much more residual oxygen (12 vs. 3 at.%) prior to CdTe deposition.

Combining data from GIXRD results [1], AES studies [6] and TEM (this study) suggests two consistent but different modes (dependent upon CdS type) for interdiffusion as shown in Figure 3.

In the case of CBD CdS, alloying is limited by bulk diffusion across the CdS/CdTe interface parallel to the substrate, possibly due to grain boundary oxides. In the CSS CdS case, less oxygen makes grain boundary diffusion the more favorable path, such that the same bulk diffusion is limited to only 3-4 at.% at the CdS/CdTe planar interface. The impact on V_{oc} will be different in both cases. In particular, total consumption of the CSS-CdS layer is problematic since TCO/CdTe interfaces are believed to be electrically inferior to TCO/CdS/CdTe interfaces.

4. References

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