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Conference Paper

# Formation and Characterization of $CdS_xTe_{1-x}$ Alloys Prepared from Thin Film Couples of CdS and CdTe

## Preprint

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# FORMATION AND CHARACTERIZATION OF $CdS_xTe_{1-x}$ ALLOYS PREPARED FROM THIN FILM COUPLES OF CdS AND CdTe

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## ABSTRACT

Alloying between CdS and CdTe at the CdS/CdTe interface is a function of the growth temperature and post-deposition $CdCl_2$ heat treatment (HT). In devices prepared by different techniques, Te-rich $CdS_xTe_{1-x}$ alloys with x = 0.04 to 0.08 have been identified. We present our work on thin-film couples of CdS and CdTe, which can withstand higher level of $CdCl_2$ treatment without the adhesion problems typically encountered in the regular device structure. CdS films with a thickness of ~100 nm were deposited by chemical-bath deposition on glass/$SnO_2$ substrates, and CdTe films with a thickness of 300 and 800 nm were deposited by close-spaced sublimation. The samples were treated in the presence of vapor $CdCl_2$ at 400°-450° C for 5 min. X-ray diffraction and optical analysis of the samples showed that S content in the $CdS_xTe_{1-x}$ alloy increased systematically with the $CdCl_2$ HT temperature. $CdS_xTe_{1-x}$ alloy with x = 0.14 was identified for the samples treated at 430°C, which is much higher than expected from the miscibility gap at 430°C.

## INTRODUCTION

The CdTe based solar cell has attracted considerable attention from the beginning based on its optimal bandgap match to the solar spectrum. After the initial attempts with homojunction devices, most of the attention has focused on heterojunction devices. A number of window layers, such as ZnSe, ZnS, CdS, and CdZnS, have been tried. Even though higher bandgap semiconductors are the most desired window layers for better device performance, the most successful window layer to date has been CdS. There is 10% lattice mismatch between CdS and CdTe, which should generate a large density of defects at the CdS/CdTe interface. Intermixing at the CdS/CdTe interface is considered crucial for device performance, as it is expected to reduce the effect of lattice mismatch by forming a graded layer at the interface. The miscibility gap in CdS-CdTe system limits the range of alloy compositions in the intermixed region [1]. The best device performance is obtained in cells prepared by high-temperature processes (in which the higher temperature processing results in alloy compositions with higher S content). In conventional devices, the interdiffusion takes place during high-temperature deposition of CdTe and post-deposition $CdCl_2$ heat treatment [2]. Our previous work on interface studies has shown that a range of mixed alloys are formed at the interface, and their composition is a function of the level of $CdCl_2$ treatment [2]. In our baseline devices with a glass/$SnO_2$/CdS (100 nm)/CdTe (8 µm) structure, we use vapor $CdCl_2$ treatment at 400°C for 5 min [3]. Treatment at higher temperatures, or for times longer than 10 min. can result in adhesion problems, although high temperatures are desirable for improving device performance. In these devices, the CdS/CdTe interface is not easily accessible for detailed characterization because it is buried under 8 µm of CdTe.

Here we present our results on the $CdCl_2$ HT of thin couples of CdS (100 nm) and CdTe (300-800 nm), and its effect on the formation of intermixed alloy.

## EXPERIMENTAL

A thin film of CdS (80-100 nm) was deposited on glass/$SnO_2$ substrates by chemical-bath deposition (CBD) at 90°C using an acetate recipe [3]. CdTe films were deposited by close-spaced sublimation (CSS) in $O_2$/He ambient at a pressure of 16 torr. Substrate temperature for the CSS deposition was 580°C, and two sets of films were deposited with CdTe thickness of 0.3 and 0.8 µm. Samples were treated in vapor $CdCl_2$ for 5 min, with source and substrate temperature varied from 400° to 450°C. Optical properties were derived from measured values of reflectance and transmittance using a spectrophotometer. Structural properties of the samples were characterized by glancing incidence X-ray diffraction (GIXRD). Atomic force microscopy (AFM) was used to study morphological features of the samples. Compositional information on the samples was determined by Auger electron spectroscopy (AES) depth profiling.

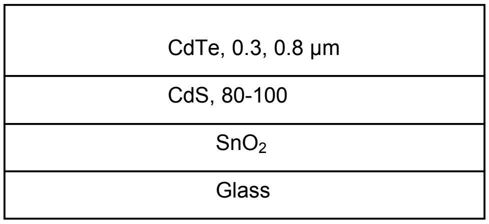

Fig.1. Cross section of a sample.

## RESULTS AND DISCUSSION

Morphology of the samples was analyzed by AFM studies. AFM measurements on the as-deposited and

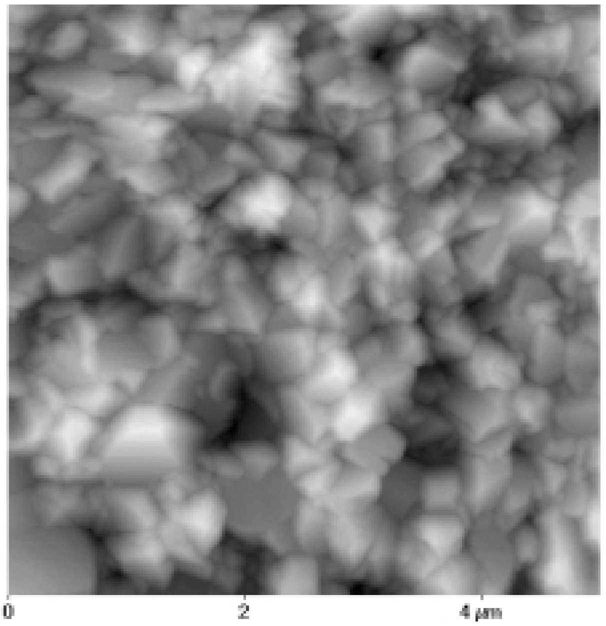

Fig. 2a. AFM image of as-deposited sample with 0.3-µm CdTe layer.

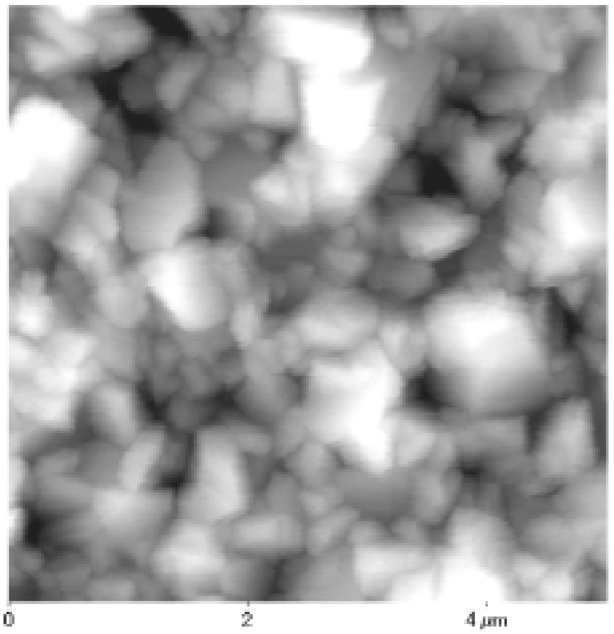

Fig. 2b. AFM image of as-deposited sample with 0.8 µm CdTe layer.

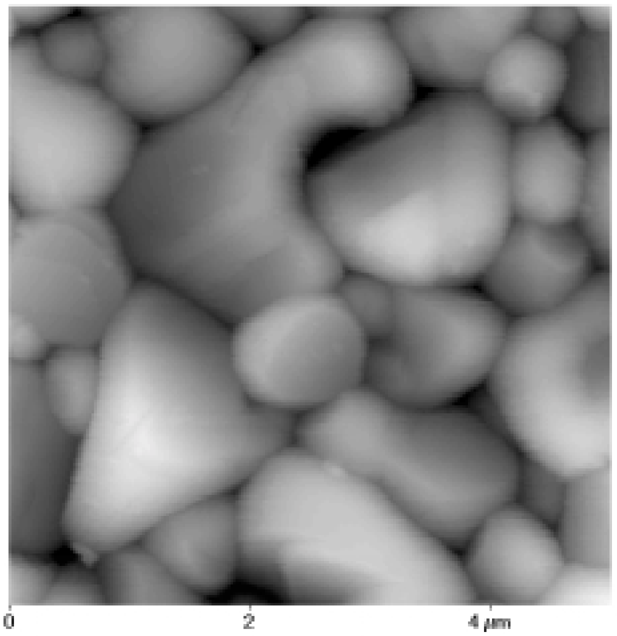

Fig. 2c. AFM image of 0.8-µm CdTe sample treated with $CdCl_2$ at 450°C for 5 min.

$CdCl_2$-treated samples showed that the thickness of the CdTe layer and the level of $CdCl_2$ heat treatment had a significant effect on the morphology of the samples. From the AFM images of the as-deposited samples (Figs. 2a and 2b), we see that the grain size increases with thickness of the sample. There was no measurable change in the grain size of the as-deposited films and films treated at 400°C for 5 min.

The grain size increased continuously with increase in the HT temperature from 410° to 450°C. Fig. 2c shows an AFM image of an 0.8-µm CdTe sample treated with $CdCl_2$ at 450°C. Average grain size increased from 0.4 µm to more than 1 µm. Samples with thinner CdTe (0.3 µm) also showed a similar trend. In contrast, our baseline samples with an 8-µm-thick CdTe layer did not withstand a $CdCl_2$ heat treatment beyond 400°C and showed no grain growth [4].

Structural analysis of the samples was carried out using X-ray diffraction analysis. All samples showed peaks corresponding to the cubic Te-rich $CdS_xTe_{1-x}$ alloy phase only. The GIXRD technique was used to examine the structure of the layers at different depths. At glancing incidence angles of 0.5, 1, 2, and 5 degrees, the penetration depth of X-rays in CdTe matrix is 96 nm, 240 nm, 0.5 µm, and 1.275 µm, respectively.

GIXRD patterns for [111] peaks at different incidence angles for a 0.3-µm CdTe sample treated at 430°C are presented in Fig.3a. Peak position does not change appreciably as incidence angle increases, i.e., X-rays penetrate deeper in the sample, indicating that bulk of the sample consists of an intermixed Te-rich $CdS_xTe_{1-x}$ alloy. In CdS-CdTe system, (111) peak of the cubic phase shifts toward higher angles as the lattice constant of the Te-rich $CdS_xTe_{1-x}$ alloy decreases with addition of S. Ohata et al. [5] have reported that $CdS_xTe_{1-x}$ alloy exists in cubic phase for x = 0 to x ~ 0.2 and the lattice constant in this range varies as

$$a \text{ (zincblende)} = 6.477 - 0.657\,x \qquad (1)$$

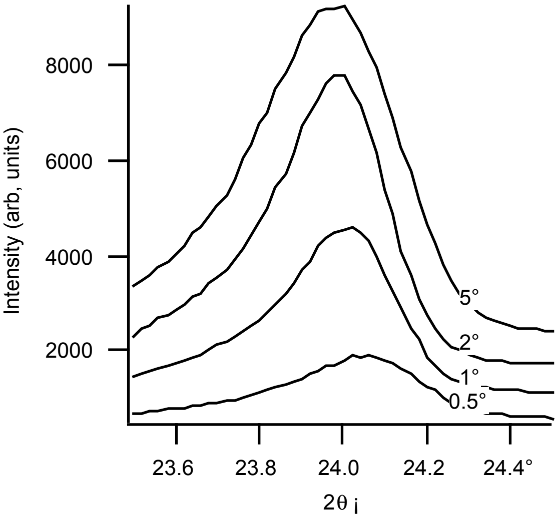

Fig. 3a. XRD Pattern for 0.3-µm CdTe sample $CdCl_2$ treated at 430°C.

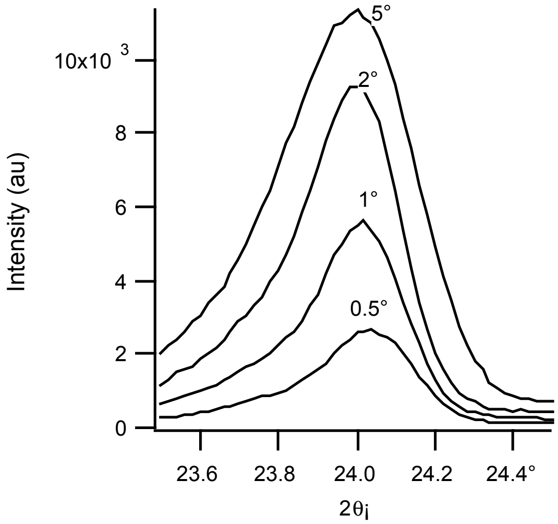

Fig. 3b. XRD Pattern for 0.8 µm CdTe sample $CdCl_2$ treated at 450°C

From the peak positions of the (111) peak, lattice constants at the given glancing angle were calculated. For this sample, lattice constant ranged from 6.422 Å at surface to 6.44 Å in the bulk. All of these peaks also showed considerable broadening due to a range of alloys present in the film. The peak corresponding to 0.5° glancing angle shows the most broadening, which is possibly due to poor crystallinity of the surface region rather than compositional variation at the surface. For the as-deposited samples of both types, the peak shift was lowest and corresponded to lattice constant of 6.475 Å, close to the value of 6.477 Å for CdTe.

XRD analysis results for 0.8-µm-thick CdTe samples were similar to 0.3-µm CdTe samples. The peak shifts were smaller for thicker films compared to 0.3-µm CdTe films for a treatment at same temperature, indicating a lower amount of S in the alloy. Results for 0.8-µm CdTe sample $CdCl_2$ treated at 450°C are presented in Fig. 3b. These patterns are similar to the 0.3-µm sample results for 430°C treatment shown in Fig. 3a. Lattice constants for the thicker samples vary from 6.424 Å at the surface (0.5°) to 6.437 Å in the bulk of the sample.

AES depth profiling analysis also supports these data, and shows that the intermixing for thinner samples is much higher than for thicker samples.

Optical analysis was carried out using measured reflectance (R) and transmittance (T) of the samples. Absorption coefficient ($\alpha$) was calculated using the relationship

$$\alpha = -\frac{1}{d}\ln\frac{T}{(1-R)} \qquad (2)$$

where d = thickness of the film.

Optical bandgaps of the samples were determined from the intercept of $(\alpha h\nu)^2$ versus $h\nu$ plots. As-deposited samples had bandgaps of 1.49 eV, which was the same as $SnO_2$/CdTe samples. Thus, CdTe absorption is dominant in these samples. From our earlier work on CdS/CdTe interfaces, we know that there is appreciable intermixing for samples deposited at high substrate temperatures. Similar alloying should be present in the samples used in this study. The reason for the dominance of the CdTe phase is that the alloyed region is not optically thick enough to influence the optical measurements. XRD data presented earlier for the same samples also showed the dominance of the CdTe phase in the bulk of the sample and, correspondingly, a lattice constant close to CdTe for higher glancing-angle measurements where X-rays penetrate deeper in the sample.

Ohata et al. [5] have shown that the bandgap of $CdS_xTe_{1-x}$ alloy decreases with addition of S in the Te-rich region for values of x up to 0.25. Optical analysis of the films $CdCl_2$ treated at different temperatures showed that the bandgaps of the films decreased due to the formation of Te rich $CdS_xTe_{1-x}$ alloy. The lowest bandgap of 1.43 eV was seen for a 0.3-µm thick CdTe sample treated at 440°C for 5 min. The 0.8-µm-thick samples treated at identical temperatures had lower shifts in the bandgap, indicating lesser intermixing for these samples.

Plots of optical bandgap vs. $CdCl_2$ temperature for samples with two thicknesses are presented in the Fig. 4. For the same treatment temperature, the 0.3-µm-thick sample results in a lower-gap alloy, indicating that the effect of the treatment for this sample is greater due to thinner CdTe. This effect is clearly seen from the data presented in Fig.4. Shapes of the curves for these plots are similar. The curve for thinner samples shows a shift toward lower bandgap values resulting from the formation of Te-rich $CdS_xTe_{1-x}$ alloy with higher S content.

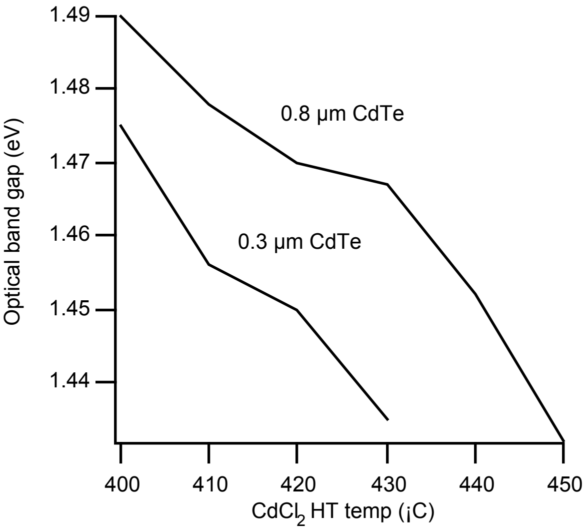

Fig. 4. Optical bandgap vs. $CdCl_2$ HT temperature for 0.3-µm and 0.8-µm CdTe samples.

Composition of the $CdS_xTe_{1-x}$ alloy can be determined from the lattice constant determined by XRD measurements and from the bandgap from optical analysis. For the 0.3-µm CdTe sample $CdCl_2$ treated at 430°C, the lattice constant at the (111) peak position is found to be 6.422 to 6.44 Å, which corresponds to x=0.07 to 0.09 in $CdS_xTe_{1-x}$ alloy using equation (1). The same sample gives optical bandgap value of 1.435 eV. Using the analysis of Ohata et al. [5], the bandgap for x=0.25 $CdS_xTe_{1-x}$ alloy is 0.1 eV below the bandgap of CdTe. In our optical analysis, the bandgap of CdTe (for $SnO_2$/CdTe sample) was determined to be 1.49 eV. Using that value and approximating linear change in bandgap between x=0 to x=0.25, the bandgap of 1.435 eV corresponds to 14% S in the $CdS_xTe_{1-x}$ alloy. The reason for the difference in the composition calculated by these two methods is related to the techniques. XRD signal is dominated by the layer composition closest to the surface as well as the crystallinity of the phase. Optical measurements mainly determine the phase with the lowest optical bandgap and phases that are optically thick. The composition determined by the XRD measurements corresponds to just peak position. As mentioned earlier, the peaks in the XRD patterns for the samples are broad resulting from the range of alloys present in the sample, and the 9% S composition corresponds to the surface region. Fourteen percent S composition determined by optical technique represents the optically dominant phase within the bulk of the sample and is expected to be a better indicator of the composition of the sample.

From the work of Nunoue et al. [7], a composition of 14% S $CdS_xTe_{1-x}$ alloy in a CdS-CdTe system is expected for processing temperatures of 650°-700°C. Formation of such an alloy at 430°C indicates that the presence of $CdCl_2$ during the heat-treatment process acts as a catalyst to reduce the miscibility gap in the system.

## CONCLUSIONS

Thin couples of CdS and CdTe can withstand very high levels of $CdCl_2$ HT without adhesion problems. In addition, the higher level of HT on these couples leads to formation of Te-rich $CdS_xTe_{1-x}$ alloys with larger S content. S levels as high as 14% were detected in the $CdS_xTe_{1-x}$ alloy for higher levels of $CdCl_2$ treatment. Thin films of CdTe deposited at 580°C showed recrystallization and grain growth after $CdCl_2$ HT, and the grain size increased from 0.3-µm to almost 1 µm for an 0.8-µm CdTe film after $CdCl_2$ HT at 450°C. Adhesion problems typically encountered during $CdCl_2$ HT of polycrystalline CdTe/CdS devices can be a significant problem for device performance optimization. The highest-performing polycrystalline CdS/CdTe devices have resulted from high-temperature processes such as CSS [1] that promote formation of $CdS_xTe_{1-x}$ alloys with higher x values. Use of the thin-film couples can allow systematic variation of the interface composition in the device to study the correlation between $CdS_xTe_{1-x}$ alloy composition and device parameters. Results on the devices prepared incorporating thin CdS/CdTe couples at the interface will be published elsewhere.

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