SULFUR DIFFUSION IN POLYCRYSTALLINE THIN-FILM CdTe SOLAR CELLS

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ABSTRACT

X-ray diffraction and photoluminescence measurements have been used to characterize the diffusion of S into CdTe during post growth annealing of CdTe solar cells. For anneals at 410°C in the presence of $CdCl_2$, evidence that both a $CdTe_{1-x}S_x$ phase and nearly-pure CdTe are present near the back contact is observed. The ternary phase becomes more prominent and the S concentration increases with depth reaching roughly 4-5% near the CdS interface. Much less diffusion is observed at 350°C while for a 460°C anneal, $CdTe_{1-x}S_x$ with a S concentration near 5% is found throughout the layer. The presence of $CdCl_2$ during the anneal enhances the interdiffusion.

INTRODUCTION

Solar Cells based on polycrystalline CdTe thin films are under intense investigation as potential candidates for low cost, high efficiency photovoltaic applications. In the typical cell structure shown in Fig. 1, the active junction is formed at the interface between an n-type CdS layer and a p-type CdTe layer. Most processes for producing high efficiency cells involve annealing the structure after the CdTe layer is deposited onto the CdS. Annealing temperatures are near 400°C and treatment of the CdTe with $CdCl_2$ is often part of the annealing process. Interdiffusion of the CdTe and CdS with the formation of $CdTe_{1-x}S_x$ ternary phases occurs as a result of the anneal.[1-6] For CdTe deposition techniques which involve deposition temperatures in excess of 400°C, interdiffusion is also observed as a result of the growth process itself.[3] This interdiffusion has profound and complicated effects on the ultimate performance of the resulting device.

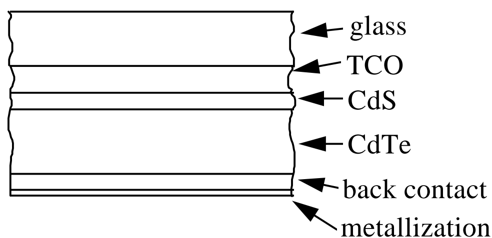

Figure 1: Schematic diagram of a CdS/CdTe solar cell

For example, light enters the device structure in Fig. 1 through the glass. Since CdS absorbs in the blue, the CdS layer thickness is minimized to enhance the optical intensity reaching the CdTe layer and, thus, the short circuit photocurrent (J_{sc}). Interdiffusion consumes the CdS layer making it difficult to optimize thickness and, for the thinnest CdS layers, reducing the open circuit voltage (V_{oc}), presumably through the formation of pinholes. For sulfur content less than roughly 20%, the bandgap of the $CdTe_{1-x}S_x$ alloy decreases as S concentration increases.[7,8] The lowered bandgap extends the wavelength response of the cell which increases J_{sc}. Passivation of defects in the CdTe by the S has also been suggested to occur.[6] It is clearly important to be able to characterize, and ultimately control, this interdiffusion process.

EXPERIMENTAL PROCEDURES

CdTe layers investigated in this study were prepared by electrodeposition. Samples were fabricated by chemical bath deposition of CdS onto SnO_2:F-coated soda-lime glass substrates (Nippon Sheet Glass). CdS layer thicknesses were typically near 200 nm. Following deposition the CdS layers were treated with $CdCl_2$ and annealed at 450°C for approximately 50 minutes in N_2. A CdTe layer from 2-5 μm thick was then electrodeposited onto the CdS. A $CdCl_2$ treatment was then applied to the CdTe surface and the sample was annealed in dry air. Interdiffusion of the CdTe and CdS occurs during this anneal. For optimal cell performance, an anneal temperature of 410°C is typically used. In the present study, the anneal temperature was varied from 350°C to 460°C to explore the effect of temperature on interdiffusion. To fabricate a cell, the next step would be deposition of a back contact onto the CdTe. No contact was deposited in this work and measurements were made on the exposed CdTe surface. A more complete description of the deposition and annealing procedures can be found in Refs. 1 and 9.

X-ray diffraction (XRD) and photoluminescence (PL) measurements were used to characterize S diffusion into the CdTe layers. XRD was performed on a Rigaku X-ray diffractometer using Cu-Kα radiation. PL measurements were performed at low temperature (15 K) under CW excitation using the 458 nm line of an argon ion laser. The luminescence was dispersed through a double pass grating spectrometer and detected at the exit slit using a cooled GaAs photocathode photomultiplier tube.

Profiles of the S concentration as a function of depth were obtained by sequentially removing the CdTe layer using a Br-methanol etch (0.025-0.1%). For PL measurements, a sequence of steps of various heights were etched into a single sample. A surface profiler was used to determine the step heights. Spectra were then obtained as function of depth. Since XRD measurements require a larger area than PL, profiling was accomplished by thinning the entire CdTe layer between XRD measurements. AFM measurements of the CdTe surface topography were made to confirm that the etching process thinned the sample without preferentially etching grain boundaries or creating pinholes which might expose material deeper in the CdTe layer than the average etch depth. Figure 2a shows an AFM image of the unetched CdTe surface. Figure 2b shows an image obtained after etching close to the CdS interface. It is clear that the etch smoothes the surface without creating pinholes.

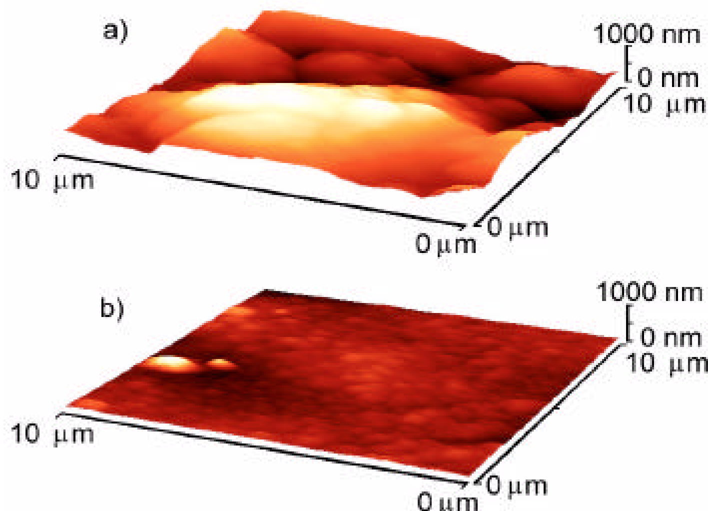

Figure 2. a) AFM image of an unetched CdTe surface.
b) Topograph after etching into the region near the CdS interface.

RESULTS

X-ray Diffraction

The lattice constant of CdTe (0.6481 nm) is larger than that of CdS (cubic, 0.5818 nm). This allows the formation of a $CdTe_{1-x}S_x$ ternary phase as S diffuses into CdTe to be directly observed in XRD as a shift of the XRD pattern to higher diffraction angle. We have previously used XRD measurements to detect the presence of $CdTe_{1-x}S_x$ in the CdTe layer and to show that anneal temperature and $CdCl_2$ treatment have a strong influence on the degree of interdiffusion.[1] Here we use XRD in conjunction with sequential etching to profile the S concentration across the CdTe layer. Figure 3 shows a series of XRD patterns taken on an 5.3μm thick CdTe film which was annealed at 410°C. A high angle diffraction peak of CdTe (531) was chosen to improve resolution and minimize alignment effects. The etch times of 5 and 10 minutes correspond to regions in the middle of the CdTe layer while 20 minutes of etching exposes CdTe very near the CdS interface.

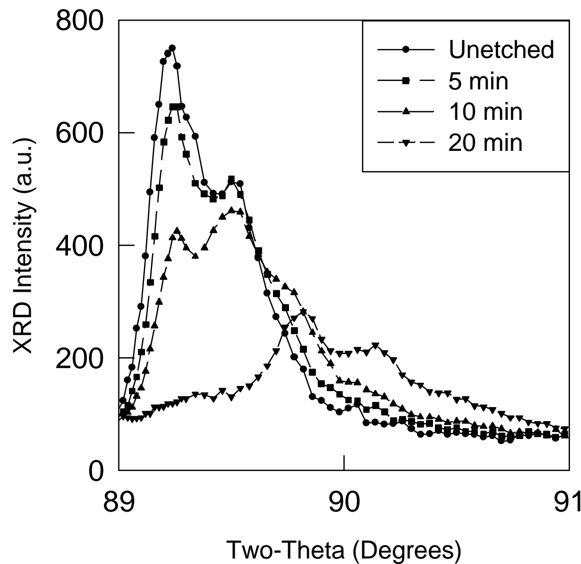

Figure 3 XRD pattern of the CdTe 531 peak as a function of etch time.

Two peaks corresponding to the $CuK\alpha_1$ and $CuK\alpha_2$ lines are visible in the unetched spectrum. As the CdTe layer is thinned, additional structure forms in the XRD pattern at higher angles indicating the presence of a $CdTe_{1-x}S_x$ phase. After the 5 and 10 minute etches this structure is visible as a shoulder on the pure CdTe peak. After 20 minutes the $CdTe_{1-x}S_x$ peak has shifted further (indicating an increase in S concentration) and it has become the dominant feature in the spectrum. Using the lattice constants of CdS and CdTe, peak fitting techniques, and taking into account residual stress in the films as previously discussed[1] we find the S content of the $CdTe_{1-x}S_x$ for the measurement near the CdS interface to be x=0.053.

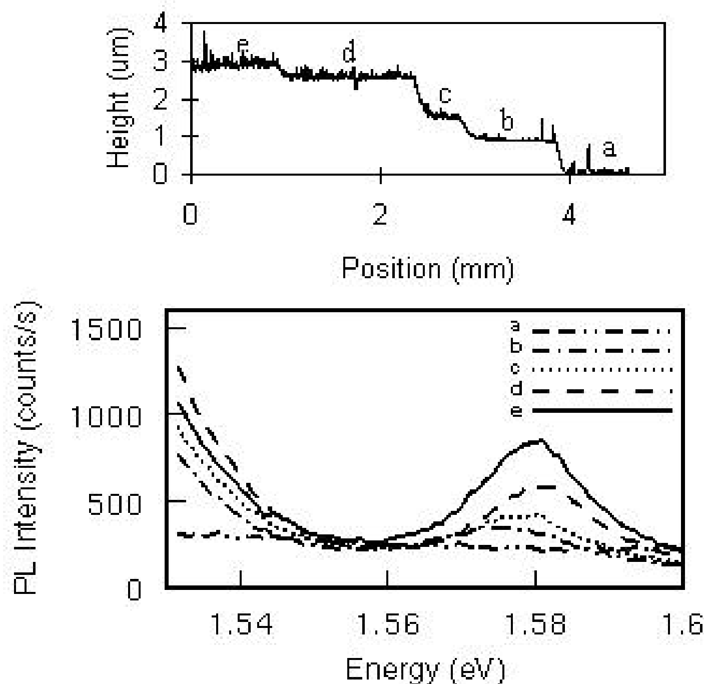

Figure 4 Etch profile and band edge PL spectra for a 350°C anneal.

Photoluminescence

For x < 0.2 the band gap of $CdTe_{1-x}S_x$ decreases as S content increases.[7,8] In this study we use low temperature PL to monitor the shift in the bandgap caused by S diffusion. Using the relationship between energy gap and S content given in Ref. 7 and our PL measurements of the shift in the bandgap as a function of depth, we are able to depth profile S content in the CdTe layer under various annealing conditions.

Figure 4 shows an etch profile for a sample which was annealed at 350°C and the band edge PL spectra obtained at various depths into the layer. The bandgap of CdTe at low temperature (4.2K) is 1.606eV. Excitonic luminescence (free and bound) in crystalline material tends to occur in the range of 1.585 to 1.596eV while donor-acceptor luminescence is typically 30meV or more lower in energy. These are 4.2K values, however, at 15K the band edge is only about 1 meV lower in energy.[10] The PL spectrum obtained from the thickest region of the sample in Fig. 4 (position e) has a peak energy of 1.581eV. There is some sample to sample variation in the position of this peak with it occurring at energies as high as 1.585eV. It is also quite broad as generally observed for polycrystalline material. Based on the excitonic energies given above, we tentatively assign this peak to excitonic luminescence. The presence of a small S content, residual strain, and even internal electric fields can all contribute to variation in the peak position and to a peak energy which is slightly lower than typical of bound excitons in crystalline material. In analyzing the S content, the origin of the band edge luminescence is less critical than its shift in position.

The luminescence in Fig. 4 shifts to lower energy as measurements are made closer to the CdS interface, ending up about 7 meV lower in the region closest to the CdS. This shift may indicate increasing S content. Based on the Ref. 7, however, a 7 meV shift would only correspond to an increase in S content of 0.7% which suggests the S concentration is quite low across the entire CdTe layer after a 350°C anneal when compared to anneals at 410°C and 450°C as discussed next.

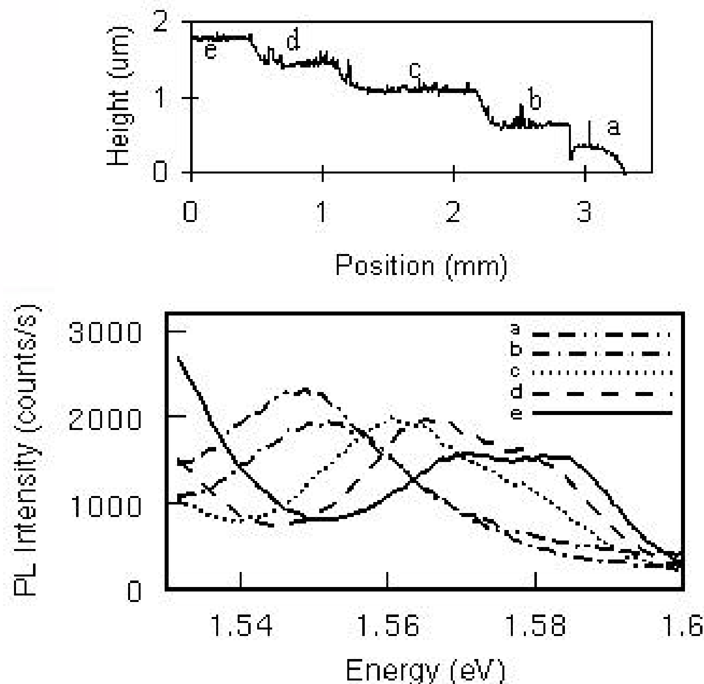

Figure 5 Etch profile and band edge PL spectra for a 410°C anneal.

Figure 5 shows PL spectra for a sample annealed at 410°C. The spectrum obtained from the thickest region of the sample (the unetched surface) shows two distinct peaks. Most measurements we have made on material annealed at 410°C exhibit this two-peak structure. As measurements are made closer to the CdS interface, the higher energy peak drops in amplitude (possibly decreasing slightly in energy), while the second peak shifts to lower energy indicating it arises from a ternary phases with a S concentration which increases with depth. The position of the higher energy peak near 1.584eV is close to the peak energy after the 350°C anneal and to excitonic energies in pure CdTe. We associate this feature with the presence of nearly pure CdTe. The coexistence of CdTe and a ternary $CdTe_{1-x}S_x$ phase is consistent with the XRD observations above, although in PL

coexistence is only observed near the unetched surface, while in XRD it is observed throughout the layer. The energy difference between the CdTe and ternary peaks can be used to estimate the S concentration of the ternary phase as a function of depth. For the curves shown in Fig. 5 we estimate S to vary from 1.5% at the surface to 4% near the CdS interface. PL studies of the unetched CdTe surface were also made as a function of $CdCl_2$ treatment. We find in general that increasing the $CdCl_2$ exposure time increases the amplitude of the ternary peak relative to the CdTe peak in agreement with the view that $CdCl_2$ promotes interdiffusion.[1,4]

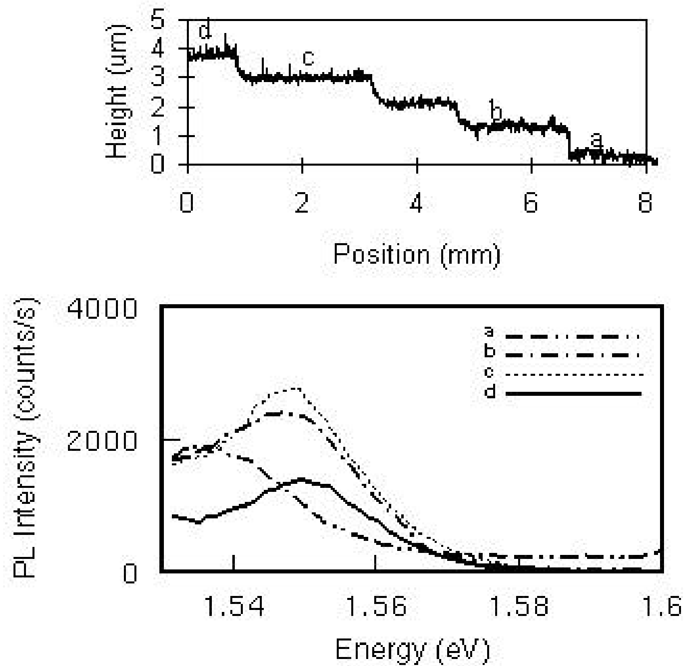

Figure 6 Etch profile and PL spectra for a 460°C anneal.

We have also performed room temperature PL measurements on a sample annealed at 410°C. A shift of the PL to longer wavelength with increasing depth was again observed. The size of the shift was the same as found at low temperature. Room temperature PL arises from band to band transitions rather than bound levels which makes it a more direct measurement of bandgap energy. This supports our conclusion that the decrease in PL energy with depth is associated with a decrease in bandgap and, therefore, with an increase in S concentration. Room temperature lifetime measurements gave a decay time of 300 psec which did not vary significantly with depth.

PL spectra for a sample annealed at 460°C are shown in Fig. 6. The PL peaks occur at an energy corresponding to the highest S content in the 410°C anneal indicating that S has diffused throughout the film. The S concentration near the CdS interface is estimated to be 5%.

DISCUSSION

The agreement between XRD and PL results is really quite good considering some of the differences between the two techniques. For example, the x-ray penetration depth is estimated to be 2.5 μm which indicates XRD measurements, while weighted toward the top of the film, are sampling a large fraction of the film. The optical absorption length for 458nm PL excitation is much smaller (less than 0.5 μm). However, carriers can move distances comparable to the minority carrier diffusion length before recombining to give off light. If a large and small band gap region are within a diffusion length of one another, the PL measurements will be heavily skewed toward the lower bandgap region. In addition, the S compositions estimated from PL are dependent on our choice of the PL peak position in pure CdTe which could lead to an error of up to one percent in composition. With this in mind we obtain the following general conclusions. The amount of S which diffuses into the CdTe layer changes substantially between 350°C and 460°C. After a 410°C anneal, nearly pure CdTe and $CdTe_{1-x}S_x$ coexist. The S content of the $CdTe_{1-x}S_x$ phase varies from 1% or less near the back contact to 4-5% near the CdS interface (for the 2 μm

thick sample used in this study). For all annealing temperatures studied here, the maximum S concentration is observed to be around 5% which is quite close to the S solubility limit at 415°C of 5.8% reported by Jensen et al.[5]

The presence of distinct CdTe and $CdTe_{1-x}S_x$ phases within the film after the 410°C anneal is quite interesting. There is no reported evidence that phase segregation occurs for S compositions less than the 5.8% solubility limit. We might, therefore, expect diffusion to lead to a broad distribution in S compositions and to one broad peak instead of two distinct sets of peaks in PL and XRD. S diffusion into the CdTe layer undoubtedly occurs preferentially along grain boundaries. Diffusion of S into individual crystallites can then occur from the grain boundary as well as from the CdS layer itself. The grain regrowth which occurs during the anneal will also influence the S distribution.[11] Several possibilities then exist for obtaining inhomogeneous S distributions. If S penetration along grain boundaries varies from boundary to boundary, the S concentration within individual crystallites will also vary. S diffusion into the grain from the grain boundary surface will lead to variation in S content across the grain. PL measurements might be more sensitive to grain-to-grain inhomogeneity than to variations in S content across the grain due to minority carrier diffusion as discussed above. Our XRD results in Fig. 3 indicate two phases are present across the entire film thickness, while in PL we really only detect pure CdTe near the unetched surface which would seem to suggest that pure CdTe and $CdTe_{1-x}S_x$ are separated further spatially, perhaps in separate crystallites, near the unetched surface.

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