

Investigation of CdZnTe for Thin-Film Tandem Solar Cell Applications

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ABSTRACT

Modeling of two-junction tandem devices shows that for optimal device performance, the bandgap of the top cell should be around 1.6-1.8 eV. CdZnTe alloys can be tailored to yield bandgaps in the desired range. In this study, we considered were used to fabricate these films, using close-spaced sublimation (CSS) and radio-frequency sputtering (RFS) techniques. In the first approach, we used mixed powders of CdTe and ZnTe as the source for film deposition by CSS. Even for the ZnTe/CdTe (95:5 ratio) source material, the deposited films were entirely CdTe due to higher vapor pressure of CdTe. In the second approach, we used pre-alloyed CdZnTe powders (CERAC, Inc.) as the source. Due to the lower sticking coefficient of Zn, even for the source composition of 75% Zn, these films contained very low quantities of Zn (~5%). We tried unsuccessfully to increase the Zn content in the films by confining Zn vapor by enclosing the region between the source and substrate, reducing the substrate temperature to 400°C, and adjusting the source/substance distance. Finally, we used thin-film couples consisting of 300-nm-thick CdTe deposited by CSS and 300-nm-thick ZnTe deposited by RFS; the samples were then heat-treated in cadmium chloride vapor. Compositional analysis of the samples showed extensive interdiffusion of Cd and Zn for the annealed samples. We will present the data on the various stack configurations of CdTe and ZnTe, the effect of different post-deposition anneals, the effect of oxygen on the interdiffusion and alloy formation and its possible correlation to the device performance degradation.

INTRODUCTION

Polycrystalline thin-film solar cells based on II-VI and I-III-VI compounds have been quite successful, with efficiencies of laboratory devices reaching 16.5% for CdTe [1] and 19.2% for CIGS [2] single-junction solar cells. For further improvement, one needs to look at the tandem device option. Device modeling of two-junction tandem devices shows that the optimal bandgap of the top cell should be around 1.6-1.8 eV [3]. Ternary alloy CdZnTe is a good candidate as it is a well-behaved system and is based on CdTe.

In this paper, we use three key approaches that have been responsible for improved performance of CdTe devices: 1) CSS technique for the deposition of alloy layers because the best-performing CdTe devices have resulted from the films prepared by CSS at high deposition temperatures. 2) CdCl₂ heat treatment, which is a crucial step for the fabrication of high efficiency CdTe devices. 3) We explored the use of oxygen during different stages on film properties because it is another essential component of high-efficiency CdTe device fabrication. One of the objectives of this work is to investigate the differences in CdTe and CdZnTe systems that could explain vast difference in the device performance of solar cells fabricated from these materials [4,5].

EXPERIMENTAL DETAILS

All the samples in this study were prepared on borosilicate glass/SnO₂/CdS substrates. F-doped SnO₂ films with a thickness of 0.5 μm were deposited by chemical vapor deposition. CdS films (85 nm thick) were deposited by chemical-bath deposition at 90° C. Films with a thickness of around 500 nm were deposited from a mixed powder source of CdTe and ZnTe and pre-reacted Cd_xZn_{1-x}Te alloys with x values in the range of 0.25 to 0.75 (Cerac, Inc.) by CSS at substrate temperatures in the range of 400° to 580° C in He/O₂ ambient. ZnTe films (~ 300 nm thick) were deposited by RF sputtering at 350° C. Figure 1 is a cross-section of the samples used for the interdiffusion experiments.

CdTe (CSS)
ZnTe (CSS, RF)
CdTe (CSS)
Substrate

Figure 1. Cross-section of the samples used for interdiffusion studies

Post-deposition heat treatment of the samples was carried out at temperatures in the range of 400°-440°C in the presence of CdCl₂ vapor in He/O₂ ambient. Samples were analyzed using the following techniques: X-ray diffraction (XRD), atomic force microscopy (AFM), auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS).

RESULTS

Films deposited from CdTe/ZnTe powders and CdZnTe alloys

Films deposited using mixed powders of CdTe and ZnTe for different deposition parameters mentioned below did not show the presence of Zn, as measured by AES. This could be explained by the two factors: First, vapor pressure of ZnTe is almost an order of magnitude lower than CdTe in the source temperature range of 650°-700°C; second, both CdTe and ZnTe decompose in elemental form, and the sticking coefficient of Zn is considerably lower than Cd at substrate temperatures over 400°C. We varied the source composition from a ZnTe:CdTe ratio of 1: 1 to 20:1 with no success in incorporating Zn.

To circumvent the problem due to the vapor pressure difference between CdTe and ZnTe, we fabricated films using pre-alloyed CdZnTe powder sources. These alloys were prepared by Cerac, Inc., by sintering the powders of CdTe and ZnTe at temperatures above 1000°C. We confirmed that these alloys were single phase by XRD analysis. Although we have not measured the vapor composition, the deposition of a considerable amount of Zn on the cooler parts of the reactor during deposition indicates that the preformed alloys may be evaporating almost congruently. We did not see similar deposits when we used mixed powders of CdTe and ZnTe with similar Zn content in the source and identical deposition conditions.

We varied the source temperature in the range of 640° to 700°C and the substrate temperature from 400° to 580°C and found out that the Zn content in the resulting films was always less than 5%. Because there was a considerable amount of Zn evaporating from the CdZnTe alloy sources, we tried to confine the vapor by placing spacers on all four sides between the source and substrate. We did not see a noticeable increase in Zn content in the film. In the future, we will try to increase the partial pressure of Zn during deposition to increase Zn content in the films.

Thin film couples of CdTe and ZnTe

We attempted to form a CdZnTe alloy by interdiffusion of CdTe and ZnTe layers. We used the structure shown in Figure 1 for these experiments, where the substrate was borosilicate glass coated with SnO₂ and CdS. Here, we present results on two types of samples: In the first, the top layers of CdTe were deposited at 580°C (HT sample) whereas in second sample, top layer of CdTe was deposited at 400°C (LT sample). In both cases, the bottom CdTe layer was deposited at 580°C. We analyzed both as-deposited and CdCl₂-treated samples. We show representative AFM images of as-deposited and CdCl₂-treated samples in Figure 2.

As-deposited samples, grown at 580°C, show the presence of boulders on the surface that disappear after CdCl₂ heat treatment. We did not observe these structures on samples deposited at lower temperatures. The samples after CdCl₂ heat treatment also showed a gradual increase in the grain size with increase in the temperature from 400° to 440°C for both sets of samples.

AES depth profile spectra of HT samples before and after CdCl₂ treatment are presented in Figures 3 and 4. Even though the top layer of the structure is CdTe, we see intermixing of Cd and Zn, as a result of high temperature deposition at 580°C. We also see considerable concentration of oxygen in this sample, which is comparable to the quantity of Zn in the sample. Another interesting fact is that the profiles of Zn and O and of Cd and Te track each other. We also find diffusion of Zn and Te in the CdS layer, with slight diffusion of S in the CdTe layer. We do not see the distinct CdTe/ZnTe/CdTe structure for the as deposited sample in Figure 3.

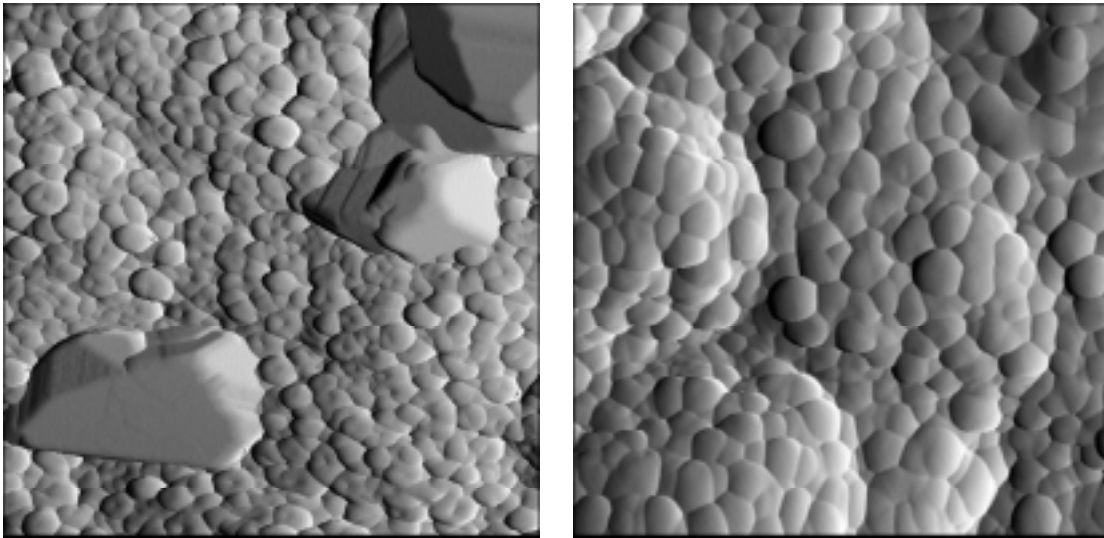


Figure 2. AFM (1µm) of as deposited (left) and CdCl₂-treated (440°C) samples.

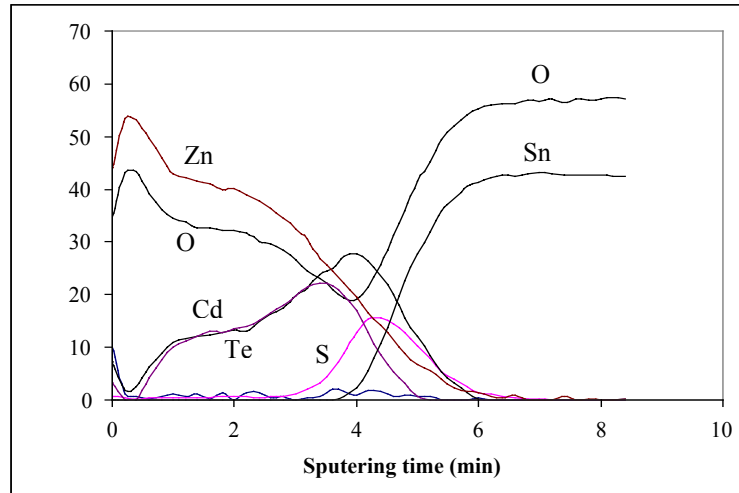


Figure 3. AES data for as-deposited HT sample.

After CdCl_2 heat treatment (Figure 4), there is further interdiffusion, with Zn moving toward the front surface and the spreading of Cd and Te toward the center of the sample. We still see high concentration of O_2 and the profiles of Zn tracking that of O. We also see significant Cl concentration toward the front of the sample.

AES data for the LT samples are presented in Figures 5 and 6. Data for the as-deposited sample (Figure 5) shows a distinct 3-layer structure, which is completely different than the data for the HT sample (Figure 3).

In addition, the Cd spectra in the top and bottom layer exhibit different binding energies, implying different chemical bonding for CdTe deposited at 580°C (bottom layer) and 400°C (top layer). We see similar differences for Te in top CdTe layer and in ZnTe and bottom CdTe layers. The Zn spectra in the middle ZnTe layer have different binding energies compared to the interdiffused Zn in the top and bottom CdTe layers. AES data for the CdCl_2 -treated sample (figure 6) show extensive interdiffusion, with no signs of distinct layers. There is an

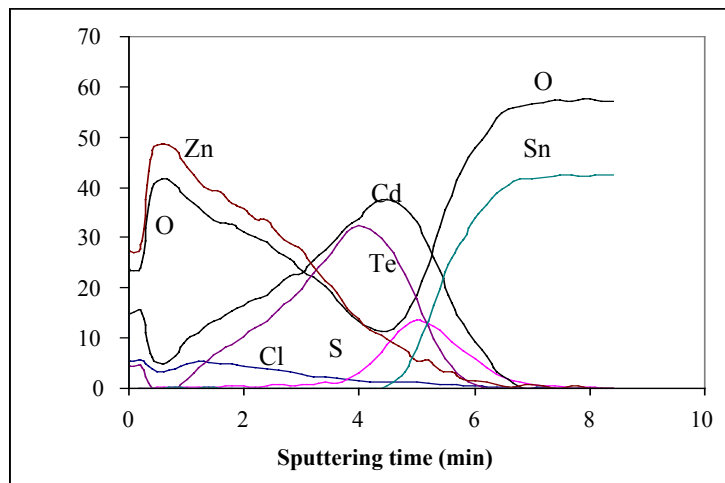


Figure 4. AES data for 420°C CdCl_2 -treated HT sample.

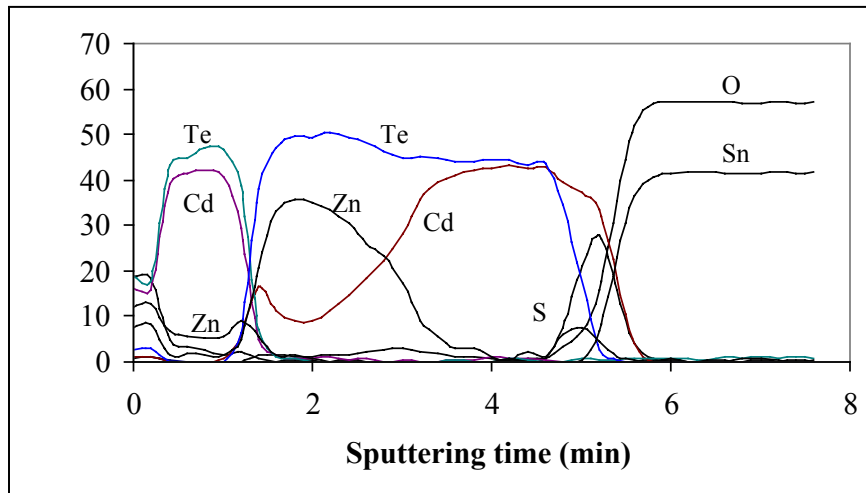


Figure 5. AES data for as-deposited LT sample.

accumulation of Zn in the front with a gradual decrease in the bulk of the film, tailing off at the CdS layer. This sample also shows behavior similar to samples deposited at higher temperature; the amount of oxygen in the layer is comparable to Zn, and profiles of Zn and O have the same shape. In all the samples, we find S confined within the CdS layer in the substrate.

DISCUSSION

AES data presented here shows the effects of three factors: deposition temperature, CdCl_2 heat treatment, and oxygen. The as-deposited LT sample shows limited interdiffusion, with clear demarcation of individual layers. The bonding energy of Zn in the ZnTe layer, deposited by RF sputtering in argon atmosphere, may be representative of Zn to Te bonding. The change of the bonding energy of Zn in the top and bottom CdTe layers, both of which are deposited in O_2 -containing atmosphere, may be due to Zn bonded to oxygen. The LT sample after CdCl_2

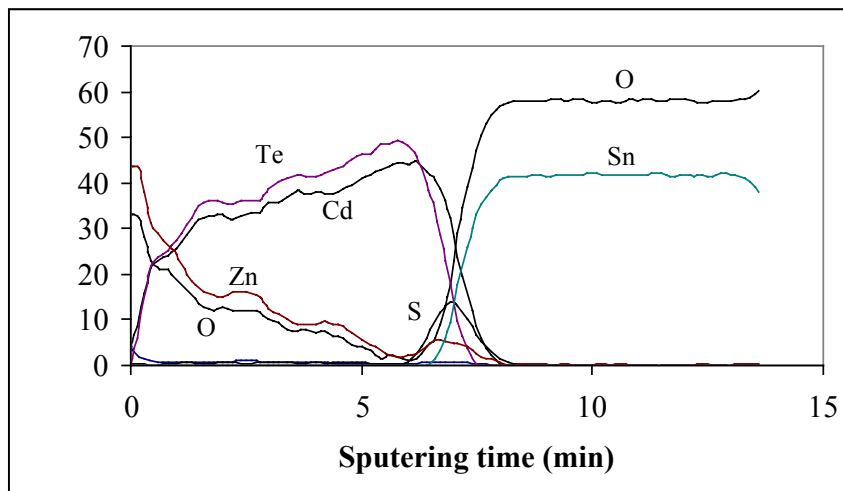


Figure 6. AES data for 420°C CdCl_2 -treated LT sample.

treatment in He/O₂ ambient at 400°C has similar Zn and O profiles indicating that all the Zn in this layer is bonded to O forming ZnO. We also see Cd and Te profiles to be similar and the concentrations comparable to each other. This indicates that these are present as a CdTe compound. For the samples treated at higher temperatures, we find a gradual decrease in Zn concentration, with Zn and O having similar features. This may be due to the reaction between Cl₂ and ZnO, leading to the formation of ZnCl₂, thereby losing Zn from the film. The HT sample shows the oxidation phenomena more distinctly. Here, even for as-deposited samples, we find an accumulation of Zn in front. Thus, during the high-temperature growth of CdTe on the ZnTe surface in oxygen ambient (1 torr O₂/15 torr He), oxygen reacts with ZnTe at 580°C, forming ZnO. After CdCl₂ heat treatment, we see further movement of Zn toward the front, as well as reduction in Zn/O concentrations, again indicating the loss of Zn by ZnCl₂ formation.

The results show that due to high affinity of Zn to oxygen, the presence of O₂ during the deposition and/or postdeposition CdCl₂ heat treatment results in the oxidation of Zn. Even the small amount of oxygen during deposition (1 torr) is sufficient to oxidize all the Zn, particularly at high temperature. Thus, the attempt to form the CdZnTe alloy is in fact producing a two-phase mixture of CdTe and ZnO. XRD results show the presence of two phases for the samples where we have seen significant Zn accumulation at the surface.

One can explain performance degradation of CdZnTe devices as compared to CdTe devices processed under identical conditions. During CdCl₂ heat treatment in oxygen atmosphere, Zn is oxidized, resulting in a mixed layer of p-type CdTe mixed with n-type ZnO in the bulk. In addition, there may be an accumulation of n-type ZnO at the surface, forming a junction at the back contact that is opposing the main junction at the CdS interface.

CONCLUSIONS

Use of oxygen in any processing step of CdZnTe based devices results in oxidation of Zn, thereby decomposing the alloy or preventing the of the alloy. The oxidation process is enhanced by high processing temperatures and CdCl₂ ambient. CdCl₂ vapor also leaches out Zn by the reaction with Cl. The principal reason for the poor performance of present-day CdZnTe solar cells may be the result of using processing steps that work well for CdTe devices, but are inadequate for CdZnTe devices. The presence of ZnO in the absorber and at the back contact of these devices can explain severe performance degradation. We need to develop oxygen-free device processing to improve device performance of CdZnTe devices.

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