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Surface Analytical Study of CuInSe$_2$ Treated in Cd-Containing Partial Electrolyte Solution

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Abstract. Junction formation in CuInSe$_2$ (CIS) has been studied by exposing thin films and single-crystal samples to solutions containing NH$_4$OH and CdSO$_4$. The treated samples were analyzed by secondary ion mass spectrometry to determine the amount and distribution of Cd deposited on the surface of the films. Cadmium is found to react with the surface for all the solution exposure times and temperatures studied. The reaction rapidly approaches the endpoint and remains relatively unchanged for subsequent solution exposure. Cadmium in-diffusion, as measured by secondary ion mass spectrometry, is obscured by topography effects in the thin-film samples and by ion-beam mixing and topography in the single-crystal sample.

INTRODUCTION

Alloys of Cu(In,Ga)Se$_2$ in combination with CdS are some of the most promising materials for high-efficiency thin-film photovoltaic devices. The best devices are achieved when the junction is formed by CdS made by chemical bath deposition (CBD). CdS deposited by methods other than CBD has not given rise to devices with as high efficiencies. This has led to interest in the effects of the chemical bath on the CIS surface. Previous work has shown that a significant improvement in device performance is obtained simply by exposing the as-grown CIS film to a solution containing the Cd salt (CdSO$_4$) and NH$_4$OH without the actual deposition of a CdS layer; thiourea is not added to the bath (1,2). The solution lacking thiourea is the partial electrolyte, or PE, bath. It is thus important to understand the processes occurring at the CIS surface during Cd PE bath exposure.

Secondary ion mass spectrometry (SIMS) is the analytical method of choice to study in-depth distributions of trace elements in materials. This technique has been used to study the Cd distribution in CIS reacted with the Cd PE bath (1,2). However, SIMS is somewhat prone to artifacts caused by the ion sputtering process. In this work, we have used SIMS to measure the surface composition CIS thin films and single crystals after exposure to the partial electrolyte solution for varying times and at various temperatures. The goal of this work is to understand the in-depth distribution of Cd in CIS after reaction with the PE bath.

EXPERIMENTAL

Thin films of CuInSe$_2$ were grown by co-evaporation of the elements onto Mo-coated soda-lime glass. The films were treated in an aqueous solution of 0.0015 M CuSO$_4$ and 1.5 M NH$_4$OH. Thiourea was not added to the bath in these experiments. This solution is subsequently referred to as the Cd partial electrolyte (PE) bath. Exposure times for the thin films ranged from 60 seconds to 10 minutes. PE bath

temperatures were varied between room temperature and 85°C. One CIS single-crystal sample was treated in the PE bath at 85°C for 10 minutes.

SIMS measurements were performed on a Cameca IMS-5F. Analyses were performed with 10 kV and 7.5 kV Cs^+ primary ions, corresponding to impact energies of 5.5 kV and 3 kV, respectively. Positive secondary ions were collected at ~300 mass resolution from an area 60 μm in diameter. Molecular species $(M+Cs)^+$ were followed to minimize variations in secondary ion yield of the elements. The In signal was not followed in these analyses, to minimize the cycle time for the mass spectrometer.

RESULTS AND DISCUSSION

Several researchers have studied the effect of the Cd PE solution on CIS films with the finding that Cd reacts with the surface of the CIS during exposure (1-3). Our own x-ray photoelectron spectroscopy results, to be published separately, conclude that Cd reacts with Se and O, and that Cu is depleted from the surface. Figure 1 shows the results of treating a CIS thin film with Cd PE solution under varying exposure conditions. First, it is clear that there is a definite increase in surface Cd between all the treated films and the control sample. The second and third points are tied to the fact that a wide range of temperatures and exposure times are shown in Fig. 1. It is significant that there is very little difference between films treated for 5 minutes at room temperature and 85°C for 10 minutes. From this, we infer that Cd reacts almost instantaneously with the surface and that further exposure does not appreciably change the shape of the profile. Although there appears to be some loss of Cu near the surface, the same Cu signal is seen in the control sample. This may be more a result of Cu grading at the surface during growth.
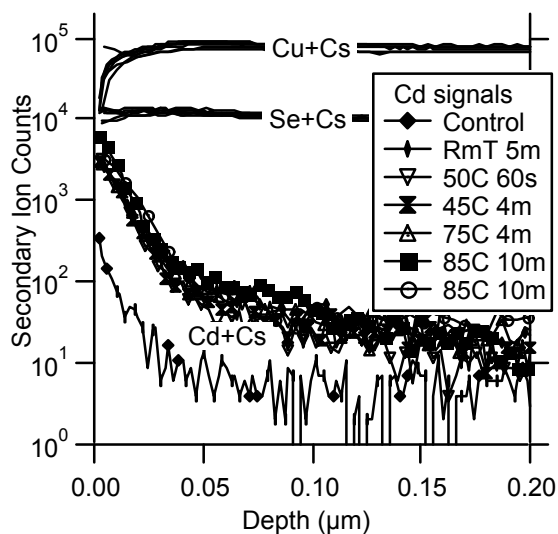

FIGURE 1. SIMS depth profiles for a variety of thin-film Cd PE exposure conditions.
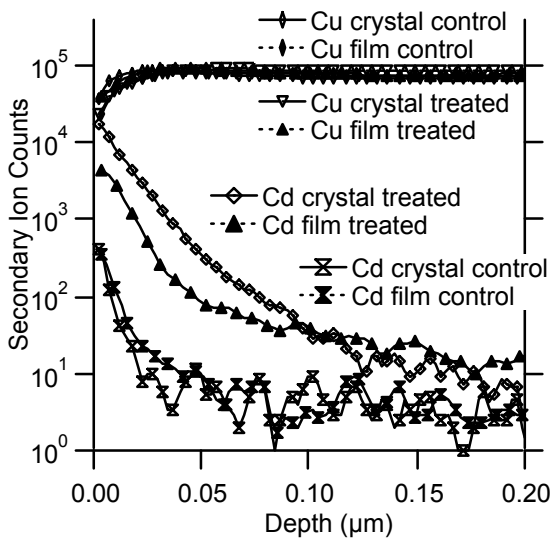
FIGURE 2. SIMS depth profiles from a single crystal and a thin-film exposed to Cd PE solution at 85°C for 10 minutes.

Figure 2 shows the result of treating a p-type CIS single crystal and a polycrystalline thin film in the Cd PE bath at 85°C, 10 min. From the graph, it is apparent that the crystal has a higher level of Cd at the surface and a longer tail that

extends into the crystal almost 120 nm. The Cd background limit for the crystal is equal to the level in the untreated film and crystal, but lower than the Cd background in the treated film. The Cd profile from the control (untreated) crystal shows little difference when compared to the control thin film. There appears to be a depletion of Cu from the surface of the treated crystal relative to the control. From these data, it appears that there is some diffusion of Cd into the crystal and some corresponding loss of Cu from the surface.

These results are not unexpected. The apparent in-diffusion of Cd and depletion of Cu have been observed previously by this and other groups. Nonetheless, it is curious that there is not more of a difference between thin-film samples that had significantly different Cd PE exposures. There is a large difference between the thin films and the crystal. This may be a result of the different process used to make the thin film, which purposely leaves the surface Cu-poor. If the reaction of Cd at the surface involves diffusion, we would expect that changing bath exposure times and temperatures would influence the distribution of Cd. However, this does not appear to be the case. To understand both the similarities and differences between the profiles, we must determine how the SIMS measurement process might be influencing the actual shape of the Cd and Cu profiles.

In a SIMS measurement, there are several possibilities for artifacts in polycrystalline materials and in regions near the surface. The measured profile shape is strongly influenced by several factors: the primary-ion impact energy, the initial surface topography, any subsequent sputter-induced topography, and finally, the properties of the elements and materials themselves. The distortion caused by any of these factors may obscure the actual depth distributions of the elements in the sample.

One of the possibilities for CIS exposed to a Cd PE bath is that a thin layer of Cd is deposited over the CIS surface. In the case of ion-sputter profiling through an overlayer, the depth profile will show two distinct regions: first, a sharp decrease consistent with sputtering through the overlayer; second, a long tail that is caused by atoms of the overlayer being pushed deeper into the sample by the mixing action of the primary ion beam. The tail region is often characterized by the decay length, λ, specified as the depth for the analytical signal to fall by a factor of $1/e$ (4). The depth profiles shown in Fig. 1 exhibit this type of behavior, a sharp decrease followed by a long exponential tail. However, this is not the behavior shown by the crystal (Fig. 2).

If collisional mixing is the primary contribution to profile broadening, then reducing the impact energy will significantly sharpen the observed profile shape. If other factors such as surface roughness were more important, we would expect to see little or no effect of changing the energy. We chose to perform SIMS depth profiles at two different impact energies to study the effect of collisional mixing on the profiles. Decreasing the impact energy from 5.5 kV (10 kV primary-ion energy) to 3 kV (7.5 kV primary-ion energy) reduces the mixing depth for Cs^+ from 4.3 nm to 2.4 nm, respectively. Shown in Figure 3 and 4 are the results for the thin film and single crystal samples profiled at the lower energy.

For the thin-film case (Fig. 3), any changes in profile shape between the two energies are minimal, although there may be a slight sharpening in the surface feature of Cu at the lower energy. The Cd profiles from the two different energies are

indistinguishable. However, in the case of the crystal (Fig. 4), there is a definite difference between the low- and high-energy profiles. The lower energy definitely sharpens the profile. The initial decrease is steeper, indicating more clearly the presence of the Cd-containing layer at the surface. In addition, the profile for Cu is also sharpened, again indicating that Cd and Cu are linked. The profiles for the control
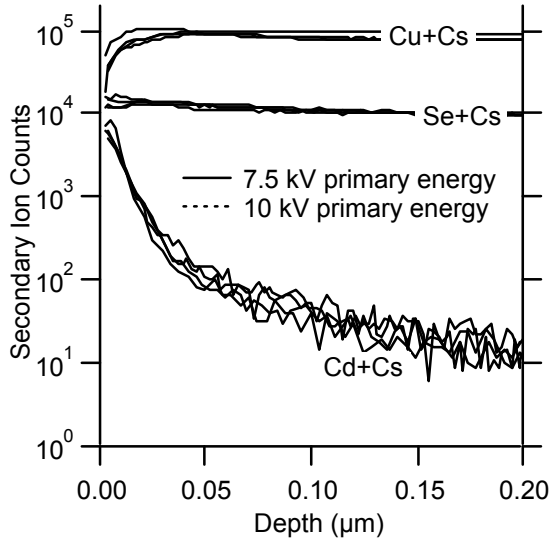

FIGURE 3. Influence of lowering the impact energy from 5.5 kV to 3 kV on the depth profile from the CIS thin film treated with Cd PE solution, 85°C 10 min.
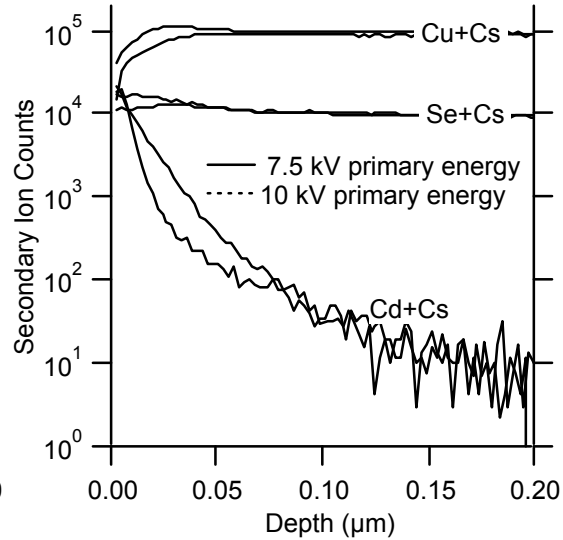
FIGURE 4. Influence of lowering the impact energy from 5.5 kV to 3 kV on the depth profile from the CIS single crystal treated with Cd PE solution.

samples (thin-film and single-crystal) were unaffected by changing the primary-ion energy. It is obvious from these two figures that there are other factors that are affecting the depth profile shape besides the primary-beam energy.

The surface topography can have a significant effect on the measured depth-profile shape. In an ideal depth profile, the signal at each point in the profile is generated from the same depth in the sample. However, if the surface is rough, the analytical signal arises from multiple depths in the sample. This causes the broadening of the real depth distribution in the measured profile shape. This kind of distortion will be present in depth profiles made by any technique using ion-sputtering.

To study surface roughness in more detail, we used atomic force microscopy (AFM) to examine the crystal and thin-film surfaces before and after sputtering. Figure 5 shows AFM micrographs of the thin-film surface before and after sputtering. The average roughness is about equal, 49 nm before and 54 nm after. It is clear from the micrographs that although the sputtering process changed the surface, the roughness is dominated by the initial topography of the thin film. The surface roughness of the thin film is an order of magnitude greater than the primary-ion mixing depth at 10 kV, which is 4.3 nm. In the case of the thin film, the effect of primary-ion mixing is insignificant compared to the surface topography. From this, we see that differences in Cd diffusion lengths that are less than the magnitude of the topography will be lost in the depth profile.
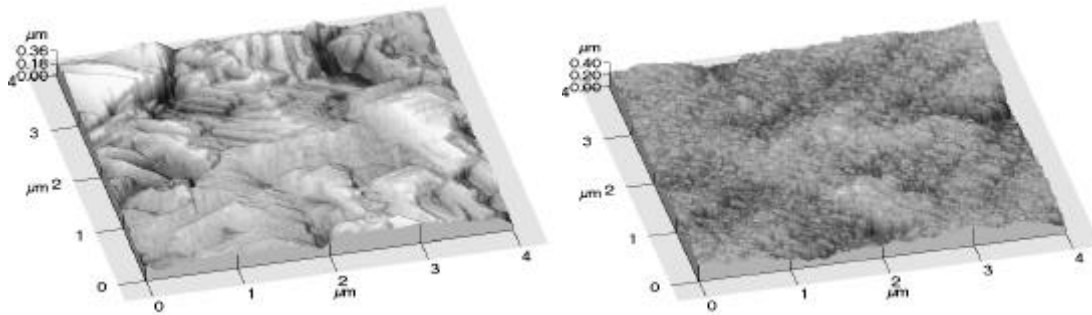
FIGURE 5. AFM micrographs of the CIS thin-film surface treated with Cd PE solution, 85°C 10 min, before (left) and after (right) sputtering. Average roughness of 49 nm before and 54 nm after sputtering.
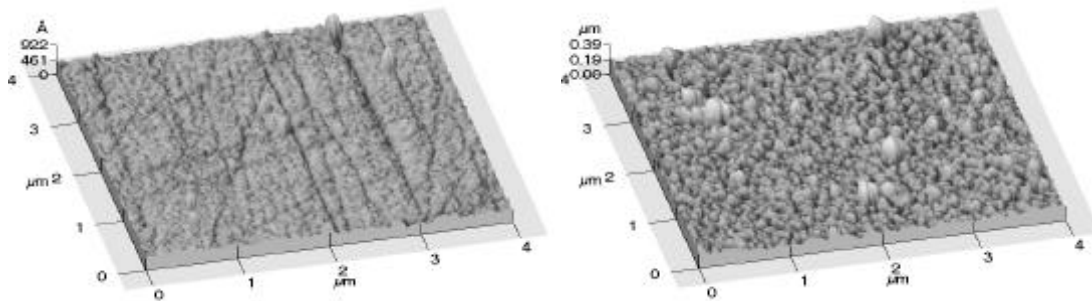

FIGURE 6. AFM micrographs of CIS single-crystal surface treated with Cd PE solution, 85°C 10 min, before (left) and after (right) sputtering. Average roughness of 5.0 nm before and 29 nm after sputtering.

The single crystal is expected to have a smoother surface. The AFM micrographs in Figure 6 show the crystal surface before-sputtering roughness to be only 5.0 nm. The after-sputtering roughness is 29 nm. In this case, there are two effects at work in the profile. In the beginning, the ion mixing depth is on the order of the surface roughness. Lowering the energy results in a smaller mixing depth and the profile shape sharpens. As the analysis progresses, topography develops in the analysis area. This tends to broaden the profile, making the diffusion tails look longer than they are and reducing the positive effects of lowering the primary-ion energy.

It is clear from the SIMS profiles that there is Cd remaining on the surface of the CIS after treatment in the Cd PE solution. Figure 7 shows an expanded region of the low-energy profiles from the control and treated single-crystal samples. Again, there is correspondence between the Cd and Cu profiles, with no detectable difference in the Se profile. Although the lower-energy profile will more accurately reflect the depth
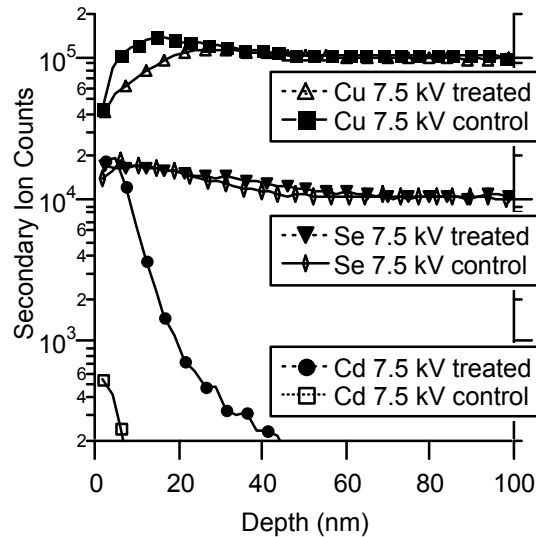

Figure 7. Surface region of 7.5 kV depth profile, for control and 85°C 10 min treated single crystal.

distribution of Cd, surface roughness and sputter mixing will still affect the profile. The apparent depth of Cd diffusion and Cu depletion are <20 nm. This is within the experimental limits of the profile shape expected for a Cd-reacted surface layer with no Cd diffusion into the crystal. This possibility cannot be excluded based on the SIMS data. Regardless, we find any Cd diffusion to be shallow.

CONCLUSIONS

The SIMS depth profiles show that Cd is definitely added to the surface of both the CIS thin film and single crystal for treatment in the Cd PE solution. The reaction goes rapidly to completion, and subsequent exposure does not significantly change the amount of Cd at the surface of CIS thin films. However, the profile data must be interpreted carefully because of artifacts from surface topography and ion-beam mixing effects. In the CIS thin-film case, the dominant artifact is profile broadening caused by the native surface topography of the polycrystalline material. The native roughness obscures most of the diffusion information in the thin films. In the case of the single crystal, both ion-beam mixing and sputter-induced topography have an effect on the shape of the depth profile. Reducing the primary-ion impact energy sharpens the profile in the surface regions and gives a truer picture of the Cd distribution. The SIMS data cannot exclude the possibility that the Cd reaction occurs in a layer at the surface and does not diffuse into the material. Study of epitaxial CIS layers on smooth substrates will minimize the effects of surface roughness and may allow study with other surface-sensitive techniques such as ion-scattering spectrometry.

ACKNOWLEDGEMENTS

REFERENCES

1. Ramanathan, K., Wiesner, H., Asher, S.E., Niles, D., Bhattacharya, R.N., Keane, J., Contreras, M.A., and Noufi, R., "High Efficiency Cu(In,Ga)Se$_2$ Thin Film Solar Cells without Intermediate Buffer Layers," Proceedings of the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, Austria, July 1998, in press.
2. Wada, T., Hayashi, S., Hashimoto, Y., Nishiwaki, S., Sato, T., Negami, T., and Nishitani, M., "High Efficiency Cu(In,Ga)Se$_2$ (CIGS) Solar Cells with Improved CIGS Surface," Proceedings of the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, Austria, July 1998, in press.
3. Kessler, J., Ruckh, M, Hariskos, D., Rühle, R., Menner, R., and Schock, H.W., "Interface Engineering Between CuInSe$_2$ and ZnO," Proceedings of the 23rd IEEE PVSC, Louisville, KY, (1993) pp. 447-452.
4. R.G. Wilson, F.A. Stevie, and C.W. Magee, *Secondary Ion Mass Spectrometry*, John Wiley and Sons, New York, NY, 1989, p.2.1-1.