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HIGH EFFICIENCY Cu(In,Ga)Se₂ THIN FILM SOLAR CELLS WITHOUT INTERMEDIATE BUFFER LAYERS

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ABSTRACT: The nature of the interface between CuInGaSe₂ (CIGS) and the chemical bath deposited CdS layer has been investigated. We show that heat-treating the absorbers in Cd- or Zn- containing solutions in the presence of ammonium hydroxide sets up an interfacial reaction with the possibility of an ion exchange occurring between Cd and Cu. The characteristics of devices made in this manner suggest that the reaction generates a thin, n-doped region in the absorber. We suggest that this aspect might be more important than the CdS layer in the formation of the junction. It is quite possible that the CdS/CuInSe₂ device is a buried, shallow junction with a CdS window layer, rather than a heterojunction between CdS and CIGS. We use these ideas to develop methods for fabricating diodes without CdS or Cd.

Keywords: Copper Indium Diselenide-1, Buried Junction-2, Cd Doping-3

1. INTRODUCTION

Thin films of ternary chalcopyrite semiconductor CuInSe₂ (CIS) and its solid solutions with CuGaSe₂ (CIGS) and CuInS₂ are one of the two principal options for realizing low-cost photovoltaic devices. Excellent device efficiencies have been demonstrated in small and large areas [1,2]. The devices are also known for their long-term stability in the field. All of these factors bode well for CIS photovoltaic technology becoming commercial in the near future. One of the critical elements of this technology is the junction formation step. The preferred approach is the deposition of a thin CdS layer produced by a chemical reaction in an aqueous bath, called the chemical bath deposition (CBD) process. No other semiconductor layer substituted for the CBD CdS has demonstrated devices comparable in efficiency or stability. Similarly, devices made by using CBD CdS exhibit better characteristics than those with CdS layers deposited by other methods such as vacuum evaporation or sputtering.

A set of explanations have been put forth to account for the fortuitous advantages of the CBD CdS. The commonly held beliefs are that the CBD process produces uniform, thin, covering films. The films are highly resistive, and this leads to the notion that the CdS layer in a device is fully depleted. The CdS/CIS junction has been treated as an abrupt heterojunction, and this assumption has never been put to rigorous experimental test. The existence of ordered vacancy phases (OVC) such as CuIn₃Se₅ and CuIn₅Se₈ at the surface region of the chalcopyrite is thought to yield a buried junction [3,4]. However, when these compounds are synthesized separately, they do not show sufficiently high conductivity or definite conductivity type to persuade us to believe they can create a junction with the (112) chalcopyrite phase [5]. It is not clear whether the OVC phases exist in all films or if they appear as segregated layers of finite thickness at the surface. The surface regions of the absorbers are also sinks for large amounts of alkali impurities such as Na diffusing out of the substrate. For a device engineer, this is a complicated picture to contend with. Given the fact that the OVC and the CdS layers are both low in carrier density, one must

explain where the n-side of the device is, and where the electric field is developed.

Another interesting aspect of the junction formation by CBD CdS process is the inability to fabricate high efficiency devices for CuIn_{1-x}Ga_xSe₂ films when $x > 0.3$. EBIC scans show that for $x \leq 0.3$, the junction is buried, and for higher Ga contents it is found at the metallurgical plane [6]. The difficulty of obtaining higher efficiency devices with higher Ga levels has not been overcome.

Experience prior to the advent of CBD CdS was with evaporated CdS layers. Regardless of whether thin films or single crystals were used, buried junctions were observed. The first CuInSe₂ homojunctions were obtained by converting the surface of p-type single crystals by extrinsic doping to n-type with Cd or Zn [7]. The electrical activity of II_B elements in CuInSe₂ was established, and the experimental data up to this point showed that homojunctions or buried junctions actually resulted. The picture we have at present is different in many ways, and one must put this to experimental tests as much as possible.

From a practical viewpoint, it would be most desirable to replace the wet chemistry step with a vacuum process step. A second objective is the replacement of Cd to make the devices environmentally friendly. The ultimate goal is to make this the final step of the absorber preparation such that the entire processing can proceed in a seamless manner. To accomplish this, it would be helpful to know how the CBD process creates the junction, and use that knowledge to find alternative processes. At present, the alternatives consist of In_xSe_y and ZnIn₂Se₄ layers evaporated at the end of the absorber fabrication [8]; Zn (OSOH) complex grown by CBD [9]; and ZnO buffer layers by CVD [10]. A general comment that can be made of the first two approaches is that the devices made by these processes are sensitive to light and temperature, and they become fully efficient only after long heat treatments or light soaking. This is obviously a handicap.

2. EXPERIMENTAL

The CIGS thin films used in this study were grown by the three-stage process described elsewhere [11]. Soda

lime silicate glass was used as the substrate. A 1 μm thick molybdenum (Mo) layer was deposited by sputtering, and this serves as the back electrode. The CuInGaSe_2 films were grown by coevaporation of the elements in Se atmosphere. First, an $(\text{InGa})_2\text{Se}_3$ layer was deposited at 300°C, and this is followed by evaporation of Cu and Se at 550°C to make the film composition slightly Cu rich. The composition was restored to a slightly Cu deficient one by the addition of $(\text{InGa})_2\text{Se}_3$ again. Film composition was determined by electron probe microanalysis. P-type single crystals of CuInSe_2 were used for some studies, and these were grown by gradient freeze method. They were mechanically polished to a mirrorlike finish. To fabricate devices, a 50-nm thick CdS layer was deposited by CBD in about 4-5 minutes as the bath temperature was ramped from 40°C to 70°C. The bath composition was as follows: 0.0015 M CdSO_4 , 1.5 M NH_4OH , and 0.15 M thiourea. A ZnO top electrode was deposited by r.f sputtering in two layers. First, a 50 nm ZnO film was deposited in Ar/O_2 ambient to yield a high resistivity layer. A 350-nm Al-doped ZnO was then deposited to serve as the conductive top electrode. Ni/Al metal grids were deposited on the ZnO for current collection. Current-voltage characteristics of the devices were measured under AM 1.5 Global spectrum adjusted for 1000 W/m^2 illumination. Secondary ion mass spectrometry (SIMS) was used to determine the distribution of the elements in the films and crystals. A low beam energy of 5 kV was chosen to minimize the effect of sputter mixing, and the sampling rate was high to ensure high depth resolution. The analyzed area was about 60 μm diameter. $(\text{M}+\text{Cs})^+$ were used to minimize matrix and surface ion yield variations. This also maximized the Cd signal.

We used partial electrolyte (PE) solutions to study the effect of the CBD reactants separately. For example, a Cd PE solution contains the cadmium salt and ammonium hydroxide in the same molar proportions as the CBD bath, described above, and is designated Cd PE. This allowed us to subject the absorbers to Cd and ammonium hydroxide only without the influence of thiourea. Absorbers were

subjected to the Cd PE treatments for different times and temperatures. Similar baths were also constituted for the case of Zn. Following the solution treatments, a standard bilayer ZnO was sputter deposited to complete the devices.

We have also attempted to react Zn compounds in vapor or solid state. The idea is to diffuse Zn into the surface region and dope it n-type. ZnCl_2 dispersed in methanol was applied to the surface of the CIGS films, and they were baked at 200°C for 1-2 h in air. Following this step, the reaction products were etched in 10%-50% HCl. This ensured removal of residual chloride and hydroxide phases, and rendered the surfaces free of contaminants. Bilayer ZnO was again sputter deposited for device completion.

3. RESULTS

First, we describe the results from Cd or Zn PE treatments of CuInSe_2 films at 85°C for 10 min. The window layer is standard bilayer ZnO described above, and it has not been specially designed to optimize the performance of devices without CdS. Fig. 1 shows the current-voltage (I-V) curves for three devices made from the same CuInSe_2 film. The corresponding photovoltaic parameters are shown in Table 1.

The CdS device efficiency is 12.8%, which compares very favorably with the best devices reported to date. A comparison of its parameters with those of the Cd- and Zn-

Table 1: Light I-V parameters of CuInSe_2 devices with CdS, Cd PE and Zn PE treatments. Total area, 0.43 cm^2 . After MgF_2 antireflection coating.

	ZnO/ CdS	ZnO/Zn PE	ZnO/Cd PE
V_{oc} (V)	0.485	0.444	0.443
J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	36.6	38.97	38.09
Fill factor	0.72	0.67	0.68
Efficiency (%)	12.78	11.56	11.46

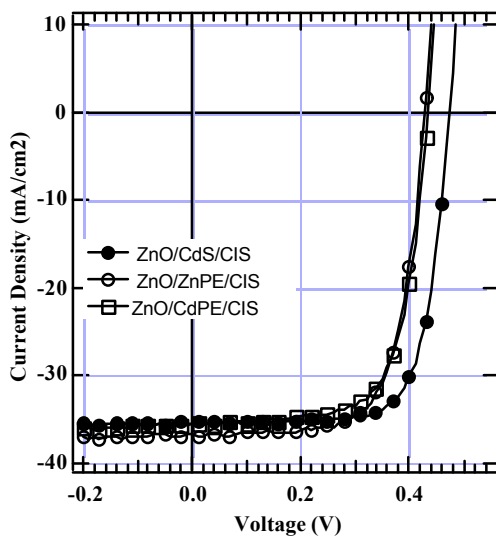


Fig. 1: Light I-V parameters of CuInSe_2 devices with CdS, Cd PE and Zn PE treatments. All have two layer ZnO window. Total area, 0.43 cm^2 . Before AR coating.

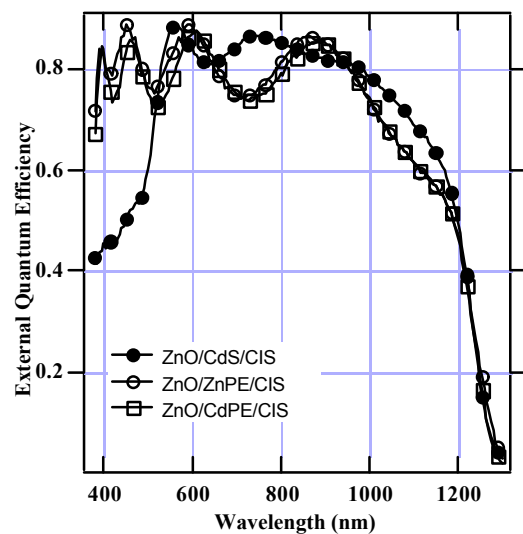


Fig. 2: Spectral response of the CuInSe_2 devices shown in Fig. 1. Measured before AR coating.

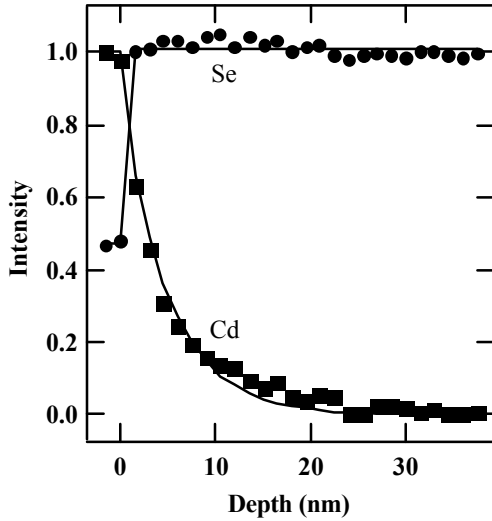


Fig. 3: XPS profile of Cd after Cd PE treatment. The absorber is CuInGaSe₂ thin film.

treated devices shows that there is an increase in the current density (J_{sc}) and this is the expected gain when CdS-related absorption losses are eliminated. Reflectance losses of devices without CdS are considerably higher, and an antireflective coating increases the J_{sc} even further. The other interesting features are that the open circuit voltages (V_{oc}) of the Cd and Zn treated devices are within 50 mV of the CdS device, and the fill factors are close to 0.7. These losses are a consequence of a higher diode quality factor and a higher reverse saturation current density, and these are likely to arise from ZnO/CIS interface recombination. We must point out that devices made by directly sputtering ZnO on the CIS films result in poor diode characteristics. Typically, much lower voltages and fill factors are observed in comparison to the Cd-or Zn-treated devices. The spectral response of the above devices is depicted in Fig. 2, and the gain in the blue region is obvious.

Similar results have also been obtained for Ga containing absorbers where V_{oc} 's of 0.55 V have been observed as a result of Cd or Zn treatments. Trends in current densities and fill factors are the same as those described for CuInSe₂ devices. A comparison of the parameters for the direct ZnO, Cd PE treatment and the control devices is shown Table 2.

At this point, we must identify the possible mechanisms by which the PE treatments improve the diode properties. It is possible that Cd (Zn) species present in the alkaline solution interact with the absorber and induce some compositional and/or electronic changes. Group II elements are well known n-type dopants in CuInSe₂. To understand these potential effects, we have conducted X-ray Photoelectron Spectroscopy (XPS) and SIMS

Table 2: Light I-V parameters of CuInGaSe₂ devices with for direct ZnO, Cd PE/ZnO and CdS/ZnO. Total area, 0.43 cm². No AR coating.

	ZnO/CdS	ZnO/Cd PE	Direct ZnO
V_{oc} (V)	0.617	0.505	0.405
J_{sc} (mA.cm ⁻²)	30.18	33.54	25.5
Fill factor	0.73	0.67	0.51
Efficiency (%)	13.6	11.4	5.3

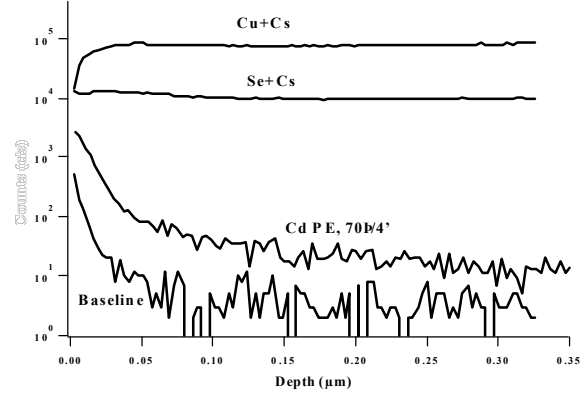


Fig. 4: SIMS profile of Cd, Cu and Se in CuInSe₂ thin films. Baseline refers to the as-grown film. The Cd PE treatment was done at 70°C for 4 min.

measurements of Cd PE treated thin films and single crystals, the results of which are described below.

3.1 XPS and SIMS Results

Fig. 3 shows the XPS profile of a Cd PE treated CuInGaSe₂ thin film. The Cd and Se signals are plotted as a function of depth. We find that appreciable levels of Cd are found in the surface region and possibly deeper. SIMS data show a similar effect, and an increase in the Cd concentration is observed in the Cd PE treated sample as compared to an as-grown CuInSe₂ film. This is shown in Fig. 4. The interpretation of SIMS data must take into account several factors specific to thin films such as surface roughness, and preferential sputtering. Because of these influences, it is difficult to make quantitative determinations of the concentrations. However, one can make the following observations about the trends. There appears to be an increase in the Cd concentration in the front region, possibly to a depth of 0.05-0.1 μm. The Cd level for longer depths is higher than the baseline, and it tends to approach the baseline in an asymptotic manner. This tail might be indicative of a faster diffusion through grain boundaries. The detection limit for Cd in the system is on the order of 10¹⁶ cm⁻³, and this suggests that the measured Cd concentrations might be an order or two higher. Diffusion in polycrystalline thin films can be quite aggressive through the grain boundaries, and it is important

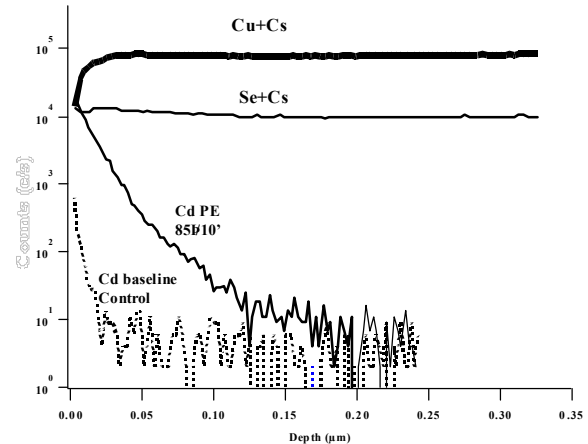


Fig. 5: SIMS profiles of Cd, Cu and Se in as-grown and Cd PE treated CuInSe₂ single crystals.

to sort out the contributions of intergrain and intragrain effects. Single crystals were chosen for this purpose.

The SIMS profile of a Cd PE treated single crystal sample is shown in Fig. 5. Here, the difference in Cd concentrations between the baseline (as grown crystal), and the Cd treated crystal is very clear, and the Cd signal reaches the baseline value. The in-diffusion of Cd coincides with a slight depletion of Cu level in the front region (not shown). We conclude from the above data that Cd is indeed incorporated in the absorber films. The mechanism of the reaction through which this occurs must be clarified. To explore this further, we soaked several large pieces of single crystals in a solution of 1.0 M CdSO₄ in 30% ammonium hydroxide at room temperature. The concentrations in this mixture are much greater than one would use in a CBD reaction, and the purpose here is to exaggerate the effects in a reasonable time. After 4 days, the solution was decanted and analyzed by inductively coupled plasma spectroscopy. The results were compared with a blank solution. The atomic concentrations, in ppm, were as follows, where the blank values are given in parentheses: Cu: 0.90 (0.02); In: 0.08 (0.01); and Se: 0.47 (0.09). We find that Cu is preferentially leached out, and some Se is also carried with it. The crystals were cleaned thoroughly in ultrasonic bath and then examined by XPS. The depth profile of Cd treated crystal shows the presence of Cd (see Fig. 6).

Further analysis of the shapes of the Cd 3d and Se 3d Auger lines demonstrates that the Cd is bound to Se, and the peak positions can be assigned to CdSe. The line shapes of the Cd and Se d levels are both altered by the Cd diffusion. These details will be published separately.

To summarize, our results suggest that the interaction of the absorber with the CBD solution results in an interfacial reaction. This might be the most important aspect of the CBD CdS process. The evidence for this is the fact that excellent devices are obtained simply by treating the absorbers in a combination of a Cd salt and ammonium hydroxide. The implication here is that the introduction of Cd can dope the absorber n-type and create a buried junction. This is consistent with the early observations on single crystals where Cd and Zn were found to dope the crystals n-type [7]. In studying the time

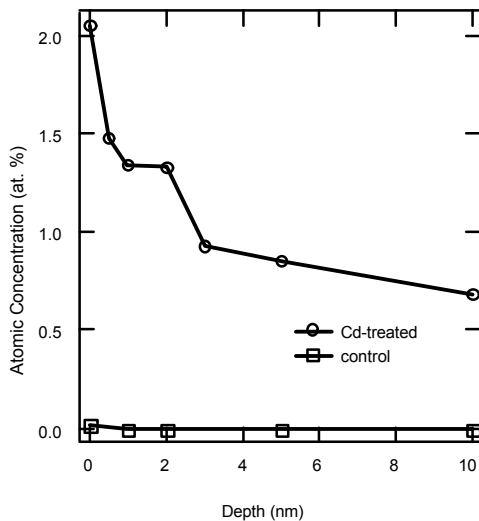


Fig. 6: XPS profile of Cd in CuInSe₂ single crystal after soaking for 4 days in 1.0 M CdSO₄, 30% NH₄OH.

dependence of this reaction, we found that the Cd profiles are established at low temperatures (40°C) and short times (1 min). One might envisage an ion-exchange reaction where the out-diffusion of Cu is driven by the in-diffusion of Cd; both facilitated by the ability of ammonia to complex the ions. The creation of a thin, heavily doped n-region can explain much of the observed phenomena. In a CdS device, the electric field will be supported entirely, or mostly, by this n-region, depending on the doping level. It is also quite possible that the Cu-deficient nature of the surfaces present natural sites for the occupation by Cd. In any case, we find that an enhanced n-doped region is more likely the heart of the device, rather than the CdS layer itself. The latter undoubtedly offers the benefits of a lattice-matched window layer, and it shields the absorber from ZnO and sputter damage. The foregoing discussion applies equally well to Zn as we have demonstrated with the Zn PE treatments.

3.2. Alternative Junction Strategies

The solutions to finding an alternative method for forming the junction follow from the previous section. Our approach is to develop methods for forming an n- type, emitter region by extrinsic doping. The most obvious candidates appear to be the II_B elements substituting for Cu; IV elements for the In or Ga; and the halogens for the Se atoms. The efficiency of the Cd “doping” suggests that Zn is the logical choice. Similarly, Cl or F could be effective on the Se sites. We have experimented with a variety of Zn sources, including elemental Zn. ZnCl₂ was chosen as the best candidate because of its low melting point and high vapor pressure at 200°C. The method of delivering the ZnCl₂ to the absorber surface has been varied. In one approach, the ZnCl₂ is dispersed in methanol and applied to the CIGS film. Following an annealing step at 200°C for 1 h, the reaction products are chemically removed by etching in HCl. The standard bilayer ZnO is sputtered to complete the device. The best result obtained by this method is a 13.5% efficiency device, and it did not require a light soak or heat treatment to realize the efficiency. The parameters of this device are: V_{oc} = 0.527 V, J_{sc} = 36.01 mA.cm⁻², and FF = 0.71. On

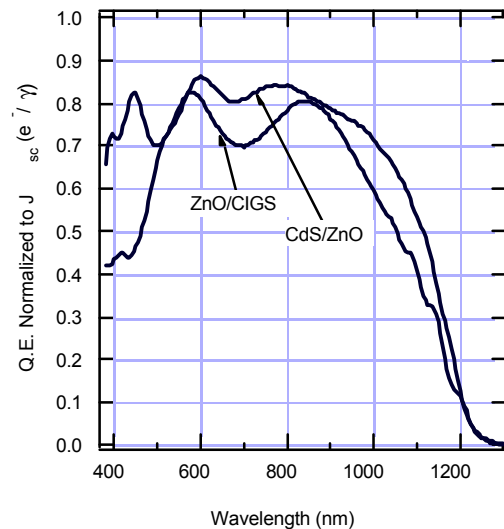


Fig. 7: Spectral response curves for CIGS devices with and without CdS.

another part of the absorber, a standard device (CdS/ZnO) was fabricated. A comparison of the spectral response curves is shown in Fig. 7. The gain in current density of the ZnCl₂ treated device is attributed to the elimination of the CdS related losses. Another interpretation is that the spectral response is indicative of a shallow n⁺p junction with a thin, heavily doped emitter, and the ZnO serves as a conductive electrode.

At present, we are investigating completely “dry” methods such as close-spaced annealing to make the processing more suitable for manufacturing.

4. CONCLUSIONS

We have shown that the interfacial reaction that occurs in the chemical bath is instrumental in creating a buried junction in CIS-based absorbers. Ample evidence has been presented to show that Cd is introduced to such levels that it could form a thin, n-type emitter region. Devices made by wet chemical treatments in Cd or Zn solutions function like n⁺p junctions with a ZnO window layer, and these offer the most compelling proof for this model. During the CBD CdS process, these changes could occur long before the CdS growth commences. The CdS layer provides a good lattice match to the absorber, a possible compositional grading at the interface region, and shielding from the sputter effects. It is unlikely that the junction is created solely by the OVC or the CdS, because neither component has demonstrated the carrier density to provide the electric field. The conductivity of the OVC layer is most likely enhanced by Cd doping, and this enables the formation of a more efficient junction. The inability to make efficient device from CuGaSe₂ or CuIn_{0.5}Ga_{0.5}Se₂ might stem from the fact that the former has not been made usefully n-type by extrinsic doping [12]. Finally, we show how the concept of extrinsic doping can be used to create a homojunction in the CIS based thin films.

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