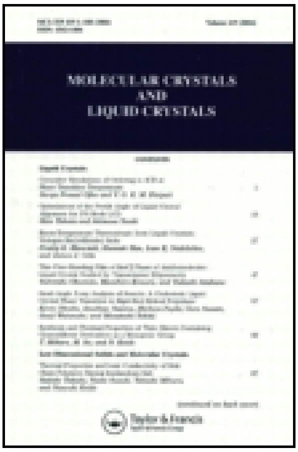

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Dependence of Cu(In,Ga)Se2 Solar Cell Performance on Cd Solution Treatment Conditions

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In the current study, chemical bath deposition (CBD) was used to grow CdS thin films on a Cu(In,Ga)Se2 (CIGS) absorption layer, in order to examine the effects of CdS deposition conditions on the properties of CIGS solar cell devices. The dip time leading up to the start of CdS synthesis is thought to be an important process variable determining the concentration of Cd ions diffused into the CIGS as well as the condition of the CIGS surface. Accordingly, the behavior of the CIGS solar cell efficiency variation was observed while different dip times were applied, at 4, 15 and 30 minutes, respectively. When the dip time was extended, the series resistance (Rs) of the device fell by a substantial margin, leading to improved photoelectric conversion efficiency and enhanced uniformity in device properties. This can be attributed to the effect of CIGS surface cleaning by the NH_4OH *contained in the reaction solution.*

Keywords CIGS Solar Cell; Chemical Bath Deposition; CdS

Introduction

Cadmium sulfide (CdS) is a Group II-VI compound semiconductor that has been widely studied due to its engineering significance and broad-ranging applicability. CdS is a direct transition-type semiconductor with an energy band gap of 2.42eV at room temperature. Because it has an appropriate energy band gap and a low absorption coefficient, as well as costing relatively less to create a sample, it sees particularly frequent use as a buffer layer material in CIGS solar cells. The most generally used method of CdS deposition is chemical bath deposition (CBD).[1,2] This method uses a comparatively low growth temperature ($< 80°C$), which allows for such advantages as reproducibility, control over particle growth, and the growth of thin films with a large area.

When CBD-CdS is used as a CIGS buffer layer, it is known to provide additional benefits resulting from the chemical bath process, besides the material properties unique to CdS.[3] Such benefits include type conversion and surface cleaning of the p-CIGS surface layer by Cd doping. When surface conversion occurs, an n-CIGS/p-CIGS homojunction is

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formed rather than a CdS/CIGS heterojunction. This greatly reduces the recombination loss of minority carriers, which results in improved open circuit voltage. Meanwhile, NH_4OH used as a pH control agent in CBD, is a weak alkali that eliminates surface oxides from CIGS. In this case, the resulting diminution in CdS/CIGS contact resistance can be expected to lessen series resistance in the developed device.[4]

In the current study, different dip times are applied to CdS thin film synthesis using CBD to produce variations in the amount of Cd diffusion into the CIGS or in the degree of surface cleaning, for the purpose of examining the resulting electrical properties of the device.[5,6]

Experimentals

The CdS sample was grown through CBD, using the following solution. As the ion source for cadmium and sulfur, cadmium sulfate ($CdSO_4$) and thiourea ($(NH_2)_2CS$) were used, respectively. As the pH control agent, ammonium hydroxide (NH_4OH) was used. The concentrations of both the cadmium sulfate and thiourea were fixed at 0.014M, with the pH maintained in the 11-12 range. Prior to the deposition, the substrate has been degreased in $NH_4OH + H_2O_2 + H_2O$ (1:1:5) solution at 90°C for 10min and rinsed in distilled water for 20min respectively. Before beginning the deposition of CdS thin film, the necessary solution ($CdSO_4$, $(NH_2)_2CS$, NH_4OH) was prepared. Then, distilled water, $CdSO_4$, and NH_4OH were poured into a double beaker and mixed using a magnetic stirrer. After stirring, reaction is induced using a constant temperature tank until the temperature reaches 70°C, with pH measurements taken in between. When the mixed solution reaches a temperature of 70°C, CIGS/Mo/glass and a test glass for measuring the thickness of the thin film are attached simultaneously to the holder and placed within the solution. From this point to the point prior to the addition of the thiourea solution was defined as the "dip time." In this study, dip time was set to 4, 15, and 30 minutes. During growth, the mixed aqueous solution was continually stirred. Upon completion of the predefined dip time in each case, the thiourea solution was added to the mixed solution and the CdS thin film was grown over the course of 3 minutes. Once the reaction was over, the substrate was quickly removed and placed in distilled water, where it underwent ultrasonic cleaning for 10 minutes. Then, CdS precipitation was detached from the substrate surface, and the sample was dried using nitrogen. Using the CdS on the test glass, the thickness of the prepared thin film (α-step), optical transmittance, and band gap (UV-visible spectrophotometer) were checked for variation. To fabricate the solar cell, Al-doped ZnO (300nm) and un-doped ZnO (100nm) were deposited via magnetron sputtering, and Ag grid electrodes were formed through screen printing. Each sample contained 9 unit cells, and performance evaluation was carried out for 9 devices for statistical data processing.

Results & Discussion

Figure 1 shows the optical transmittance of the CdS films relative to dip time. Regardless of the reaction time, an absorption edge can be observed around 500nm, which corresponds to the energy band gap of the CdS film. It can be seen that, when reaction time is at its shortest, i.e. in 4-minute testing, transmittance falls to 85%. When transmittance was measured in relation to changes in optical energy, the CdS films used in this study displayed an energy band gap of 2.3 to 2.35eV depending on growth time, which is slightly lower than the energy band gap of 2.42eV characteristic to bulk CdS.

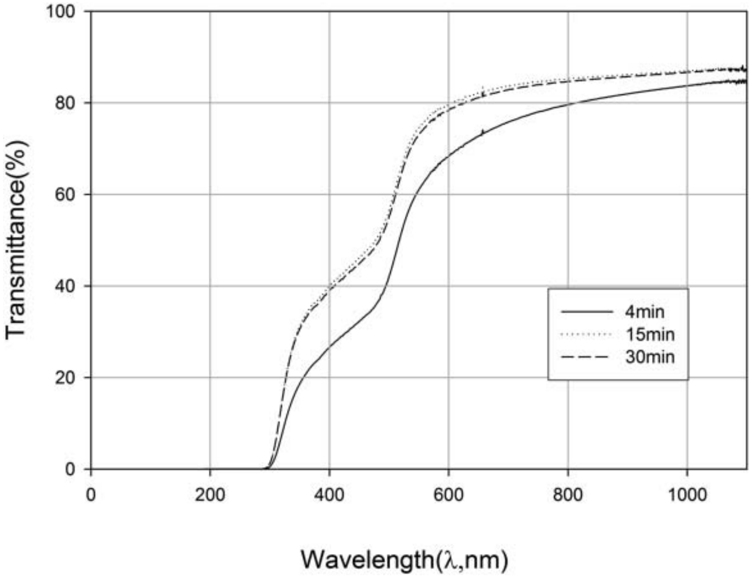

Figure 1. Optical transmittances of CdS films deposited at different dipping time.

Since transmittance reduction due to CdS is reflected in the short circuit current, it will be taken into consideration in the performance comparison below. Figure 2 shows the results of calculating the absorption coefficient α using the transmittance values shown in Figure 1. The definition of the absorption coefficient can be expressed as the equation below.

$$I = I_0 \exp(-\alpha t) \tag{1}$$

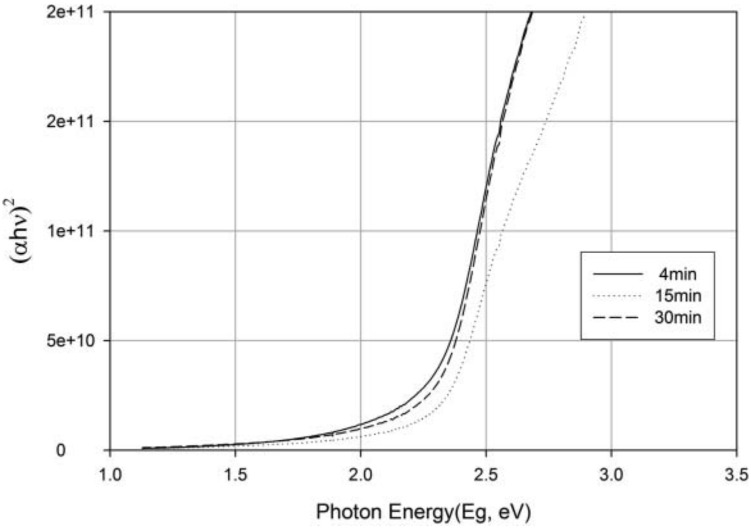

Figure 2. Square of the absorption coefficients of CdS films deposited at different dipping time.

where, I and I_0 stand for transmitted intensity and incident intensity, respectively, α for the absorption coefficient, and t for the thickness[11] of the film. In this case, I/ I_0 is the optical transmittance shown in Figure 1, so it is a known value. Film thickness t is also given. Hence, it is possible to calculate the absorption coefficient α according to the optical energy hν. As can be seen in Figure 2, α^2 changes almost linearly in relation to hν. To this type of interband transition, we may apply the following equation,[7]

$$\alpha^2 = \mathrm{A}(\mathrm{h}\nu - \mathrm{Eg}) \tag{2}$$

where, A is a constant. The energy band gap of the CdS sample with 4, 15 and 30 minutes dip times can be obtained using this equation by setting the value of α^2 to 0. In this case, hν would be equal to Eg. The results of thus calculating the Eg of each CdS sample were Eg = 2.3, 2.32, 2.3eV for 4, 15, 30 minutes, respectively. While these results do not show significant variation, they can be considered slightly low considering that the energy band gap of a single bulk CdS crystal is 2.42eV.[8]

Figure 3 is images analyzed of scanning electron microscope (SEM). Reaction time is 3 minutes regardless of dip time of 4, 15 and 30 minutes. Therefore, thin film of CdS was almost deposited similarly at surface and cross of SEM. Figure 4 was also indicated I-V curve of variation dip time. The stabilization of efficiency was observed by increasing dip time in widen sight of I-V curve.

Figure 5 compares the characteristics of ZnO/CdS/CIGS/Mo/glass solar cells relative to dip time. Measurements from a total of 9 unit devices are expressed in box plat form. Variations in the mean value (thick solid line inside the box) will be discussed with due consideration for fabrication error and the non-uniformity of each film layer. When dip time was increased from 4 to 30 minutes, photoelectric conversion efficiency improved from 9% to 11%. The main contributors to this change were judged to be the short circuit current and the fill factor. As mentioned above, in the case of the 4-minute device, there is a drop in the short-circuit current stemming from a CdS transmittance that is some 10% lower. This drop is 1mA/cm^2 or less (assuming a conversion efficiency of 10%, short-circuit current loss = transmittance loss x conversion efficiency = 10% × 10% = 1%), indicating that the results provided in the figure 1 are unrelated to CdS transmittance. Meanwhile, open circuit voltage was seen to decrease slightly from 0.55V to 0.52V. It has been reported that ordered defect clusters (OVC) with a composition of Cu(In,Ga)$_3$Se$_5$ are present on the surface of deposited CIGS.[9] OVC shows n-type conductivity and has a band gap of 1.3eV, which exceeds that of CIGS and thus plays a role in raising the open circuit voltage. This means that the reduction in open circuit voltage resulting from extending the dip time bespeaks

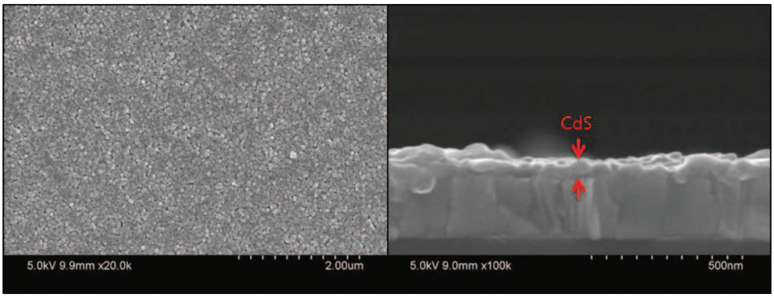

Figure 3. Scanning electron microscope of CBD CdS film.

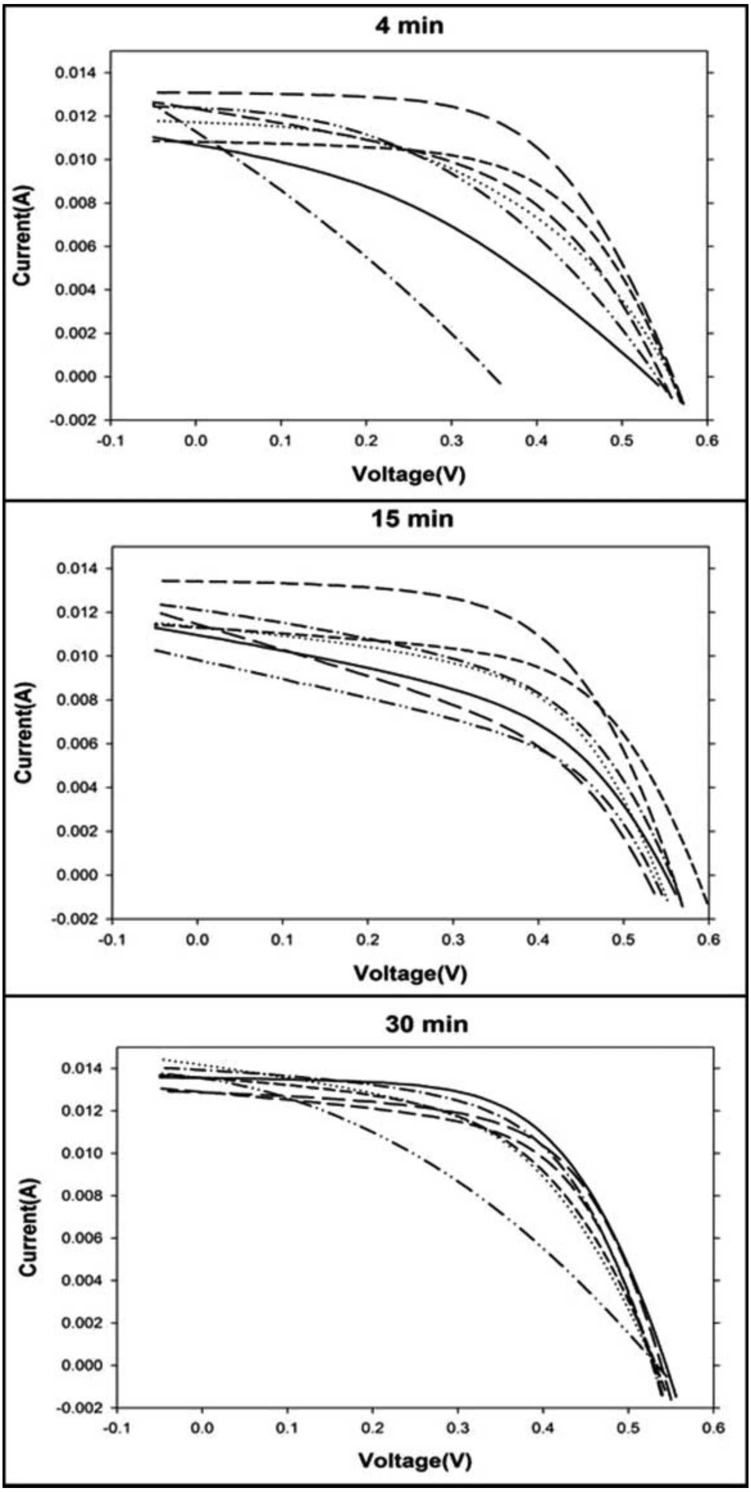

Figure 4. I-V characteristics of CdS films deposited at different dipping time.

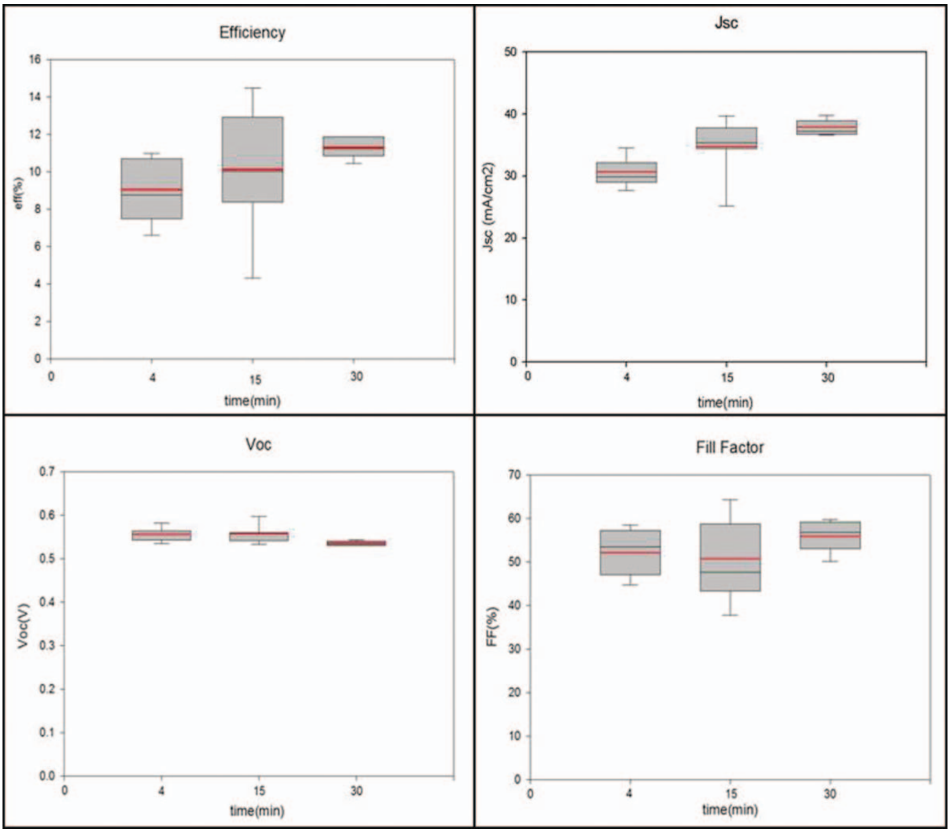

Figure 5. Characteristics of solar cells of CdS films deposited at different dipping time.

damage to the OVC. In fact, R. Hunger et al. demonstrated that the surface composition of CIGS etched with NH_4OH (2.5M) over 10 minutes changed from Cu/(Ga+In) = 0.35 to 0.9.[4] If a longer dip time resulted in increased Cd diffusion into the CIGS, this also serves the same role as OVC, meaning that the open circuit voltage should have increased.[10]

Therefore, it may be concluded that the main effect of extending the dipping time was surface cleaning rather than Cd doping. Also, because NH_4OH easily etches away residual oxides or hydroxides from the surface, it can be expected to have contributed somewhat to the reduction of CdS/CIGS contact resistance. What is notable in Figure 3 is that at 30 minutes, the error quantified to box size is extremely small. In short, it can be seen that around 30 minutes are required for surface cleaning using 1.5M NH_4OH to take place sufficiently over the entire area of the sample.

Conclusion

In the current study, changes in the performance of CIGS thin film solar cells were examined in relation to varied dip time during CdS film deposition using CBD. The analysis results supported the following conclusions.

As dip time was increased, the open circuit voltage of the CIGS thin film solar cells decreased slightly while their short circuit current increased significantly, resulting in improved conversion efficiency and greatly enhanced area uniformity for device performance. This can be understood as the effects of diminished CdS/CIGS contact resistance, due to the elimination of the surface oxidation layer of the CIGS by the NH_4OH in the CBD solution, and of band gap decrease on the surface of the absorption layer, resulting from the removal of the OVC layer. It can thus be concluded that the enhancement in solar cell performance induced by longer dip times stems from CIGS surface cleaning by NH_4OH.

Acknowledgment

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