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Characterization of CdS Thin Films Depending on the Processing Conditions

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CdS thin films were grown by a chemical bath deposition method. The physical properties of the CdS thin films were investigated depending on the various processing conditions. A surface morphological study was done by atomic force microscope(AFM) and the structural property was investigated by scanning electron microscope(SEM) and transmission electron microscope(TEM) alternating the processing temperature. Optical transmittance measurement was obtained by UV-Vis-NIR spectrometer. From the experimental results, it was confirmed that the kinetics of CdS film growth was associated with the heterogeneous growth mechanism proposed by Ortega-Borges and Lincot. With an appropriate processing temperature of 55°C and with 0.3 mM $CdSO_4$, 0.1 M thiourea (T.U), and 1.5 M mole concentration of ammonia, transparent and high-resistivity CdS thin films resulted with good conformal coverage.

Key words CdS; CBD; window layer; heterogeneous reaction

1. Introduction

In Cu(In,Ga)Se_2 (CIGS) thin film solar cells, CdS has been used as a buffer layer functioning to reduce the effective density of holes at the interface and thereby the recombination of the electron hole pair [1, 2]. In order to prepare transparent and high-resistivity CdS thin films with good conformal coverage, various deposition techniques can be used [3–5]. Among those methods, the chemical bath deposition (CBD) method has been known to be the most promising method to fabricate the most efficient CIGS solar cells [6–9]. The CdS formation consists of two types of mechanisms [10]. The first one involves growth of the layer from individual atoms in solutions, and it is referred to as the ion-by-ion process. The second one is the cluster-by-cluster growth, where the clusters form in a solution by parallel homogeneous reactions. In other words, CdS precipitation can take place either in the bulk of the solution with the formation of colloids by a homogeneous reaction or at the surface of the substrates leading to the formation of a continuous heterogeneous reaction [11]. The homogeneous reaction for CdS formation from thiourea and cadmium salt in an

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ammoniacal medium which can be written as follows [12]:

$$Cd(NH_3)_n^{2+} \leftrightarrow Cd^{2+} + nNH_3 \quad (1)$$

$$SC(NH_2)_2 + 2OH^- \rightarrow S^{2-} + CN_2H_2 + 2H_2O \quad (2)$$

$$Cd^{2+} + S^{2-} \rightarrow CdS \quad (3)$$

In this sequence, S^{2-} ions are released by alkaline hydrolysis of thiourea, and Cd^{2+} ions are released by the dissociation of the corresponding ammine complexes. The coordination number of the cadmium–ammonia complexes (n) varies from 1 to 6 depending on the ammonia concentration. As soon as the product of the free $S^{2-}$and Cd^{2+} ion concentrations exceeds the solubility product of CdS (about 10^{-25}), precipitation of CdS takes place. The classical mechanism is a homogeneous one that dominates the formation of the CdS precipitate that occurs simultaneously with the formation of the CdS thin films on the surface of a substrate suitably submerged in the reaction solution [13]. The heterogeneous reaction for the CdS formation proposed by Ortega-Borges and Lincot can be written as follows [14]:

1. Reversible adsorption of dihydroxo-cadmium species

$$Cd(NH_3)_2 + 2OH^- + -site \leftrightarrow [Cd(OH)_2]_{ads} + nNH_3 \quad (4)$$

2. Adsorption of thiourea by formation of a metastable complex with the dihydroxo-cadmium adsorbed species

$$[Cd(OH)_2]_{ads} + SC(NH_2)_2 \rightarrow [Cd(OH)_2SC(NH_2)_2]_{ads} \quad (5)$$

3. Formation of CdS and site regeneration by the metastable complex decomposition

$$[Cd(OH)_2SC(NH_2)_2]_{ads} \rightarrow CdS + CN_2H_2 + 2H_2O + site \quad (6)$$

[11] In this study, the appropriate processing temperature and proof of the heterogeneous reaction for CdS formation proposed by Ortega-Borges and Lincot was pursued.

2. Experimental Setup

The CdS thin films were prepared on commercial ITO glass as a window layer for the CdTe thin film solar cell by using a conventional CBD method. A commercialized heating mantle was used to control the temperature of the reaction solution using a programmable PID control via a temperature sensor embedded in the heat jacket. Additionally, in order to confirm the actual temperature of the solutions, a thermocouple sensor directly immersed in the reaction solution was used. Deionized (DI) water, 0.3 mM $CdSO_4$, and 0.1 M thiourea (T.U). were mixed in the deposition bath. As the temperature approached a set point, ammonia water (25 wt%) was added to the solution to maintain the solution at pH 10–11. The PID-controlled reaction bath maintained the temperature deviation within $\pm 1^\circ$C. After the addition of ammonia water, the solution turned from an opaque liquid to a yellow-green color. At this point, the ITO substrate was attached to a Teflon zig which was immersed in the bulk solution [11]. After 20 minutes, the samples were removed and placed in distilled water, where it underwent ultrasonic cleaning for 1 minute to get rid of the CdS clusters from the film surface, and the sample was dried using nitrogen. Structural properties of

CdS thin films were investigated by XRD (Philips X pert pro X-ray diffractometer) with a primary wavelength of Cu-Kα1 1.5406 Å. Optical transmittance measurement was obtained by UV-Vis-NIR spectrometer (Perkin Elmer Lambda 950 model). The surface morphology and surface roughness were measured by AFM (Digital instruments NanoScope III) in the tapping mode. SEM (Hitachi S-4200 model) was used to investigate the surface morphology.

3. Results and Discussion

In order to study the structural properties of CdS thin films, XRD measurements have been done on CdS thin films grown at various processing temperatures. Figure 1 represents the X-ray diffraction (XRD) patterns of the CdS films grown at various processing temperatures with exactly the same experimental parameters, mole concentration, stirring speed etc. There are two crystalline phases, hexagonal and cubic, in cadmium sulfide fabricated by the CBD method [15]. As shown in Fig. 1, the two main diffraction peaks, H(1 0 0) and H (0 0 2) or C (1 1 1) were observed in the CdS thin films. Most of the peak was related to ITO peaks. As shown in Fig. 2, a Gaussian line shape was fitted to the X-ray diffraction data. A peak of $2\theta = 25.3$ associated with a hexagonal (1 0 0) plane was observed. A peak of $2\theta = 26.7^\circ$ is related to a mixture of hexagonal (0 0 2) and cubic (1 1 1) planes [16, 17]. Table 1 shows the peak information of the FWHM(Full Width Half Maximum), area, center position, and intensity obtained by the Gaussian fitting method. As shown in Table 1, a similar XRD peak pattern appeared at the CdS film grown at different processing temperatures. The primary peak for all specimens was a peak at $2\theta = 26.7^\circ$. With only these XRD measurements, it cannot be decided whether the structures are hexagonal and cubic crystalline structures because the peak at $2\theta = 26.7^\circ$ is associated with a mixture of hexagonal and cubic structures. Figure 3 represents the TEM Micrograph of the CdS thin film grown on ITO glass. Fast Fourier Transform (FFT) image (Fig. 3 inset) was also

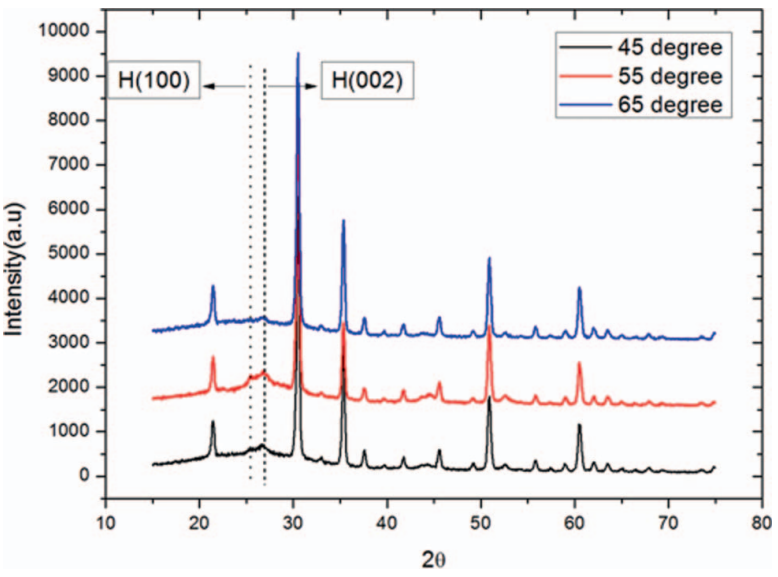

Figure 1. The X-ray diffraction (XRD) patterns of the CdS films grown by the various temperatures.

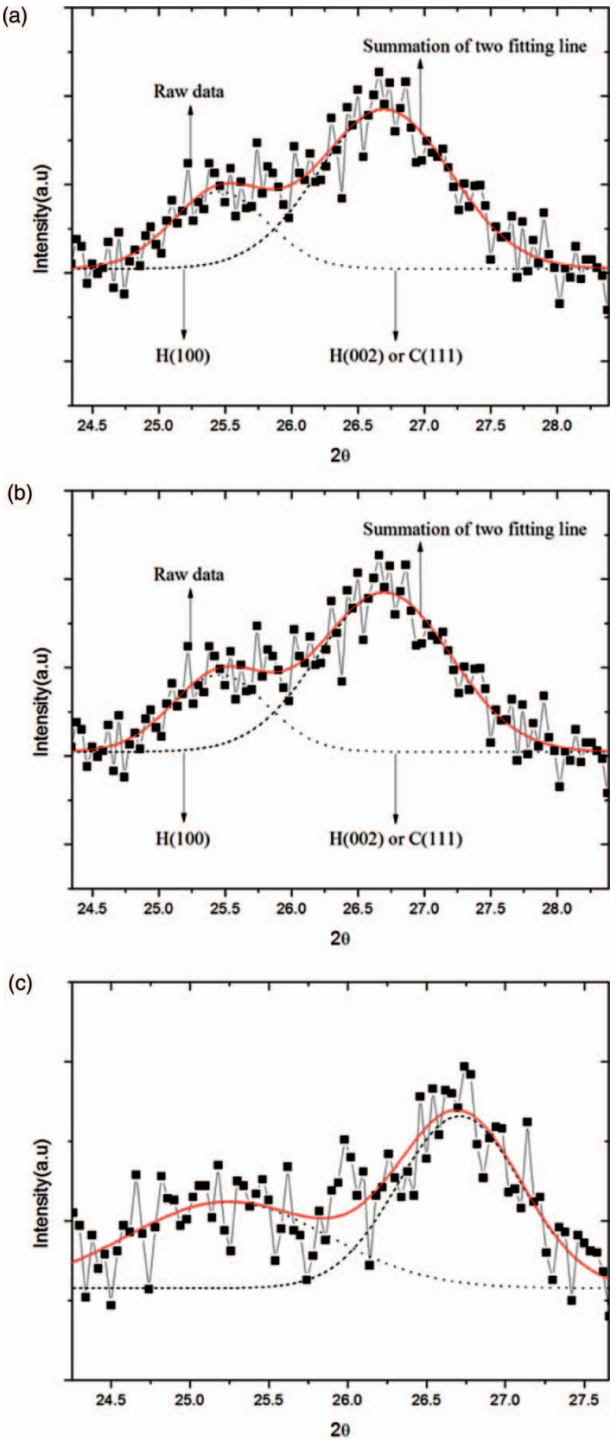

Figure 2. A Gaussian line shape fitted to the X-ray diffraction data, (a) 45°C (b) 55°C, and (c) 65°C, associated with a hexagonal (1 0 0) plane and a hexagonal (0 0 2) and cubic, (1 1 1) planes.

Table 1. The quantitative peak information associated with Fig. 1 XRD data by Gaussian fitting method

	Area (a.u)	Center (2θ)	FWHM (2θ)	Height (a.u)
45°C	78.23	25.45	0.72	86.90
	224.34	26.70	0.99	180.02
55°C	98.06	25.46	0.55	142.01
	459.22	26.74	1.36	269.10
65°C	86.21	25.24	1.27	54.25
	106.07	26.71	0.78	108.14

acquired in order to verify which crystal structures mainly make up the CdS thin films. It shows that a hexagonal crystalline structure was the dominant crystal plane.

Figure 4 represents the SEM data of specimens grown at several different process temperatures. Depending on the process temperature, it shows different stack coverage and thickness. These morphological properties using the SEM measurement denote that the deposition rates strongly depend on the process temperatures as shown in Figure 4(d), (e) and (f) cross sectional SEM images. The thickness of CdS thin films are about 55nm at 45°C, 98 nm at 55°C and 35nm at 65°C respectively. Figure 5 represents the AFM data of the specimens grown at different temperatures. Table 2 summarizes the quantitative morphology information related to Fig. 4 and 5. The specimen grown at 45°C exhibited the smallest surface roughness and a high conformal coverage as shown in Figure 5 and listed in Table 2. Especially Fig. 5(c) of 65°C process condition shows that islands-type

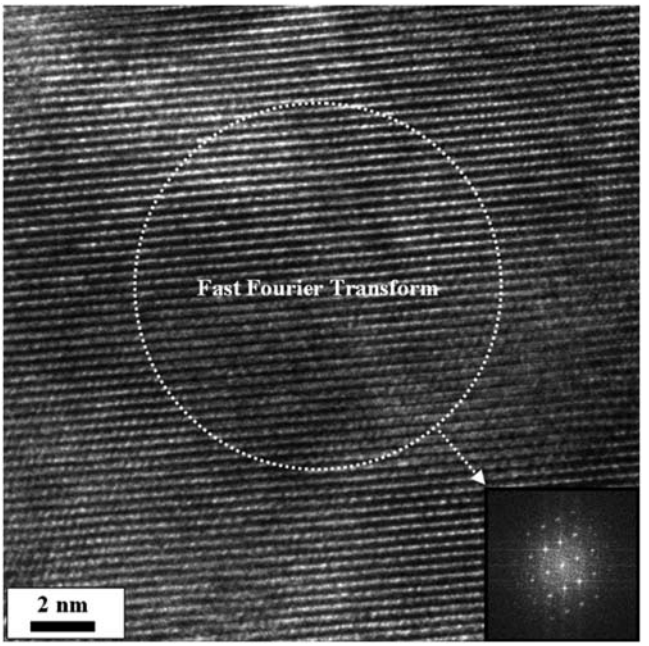

Figure 3. TEM microscopy of a CdS thin film grown on ITO glass.

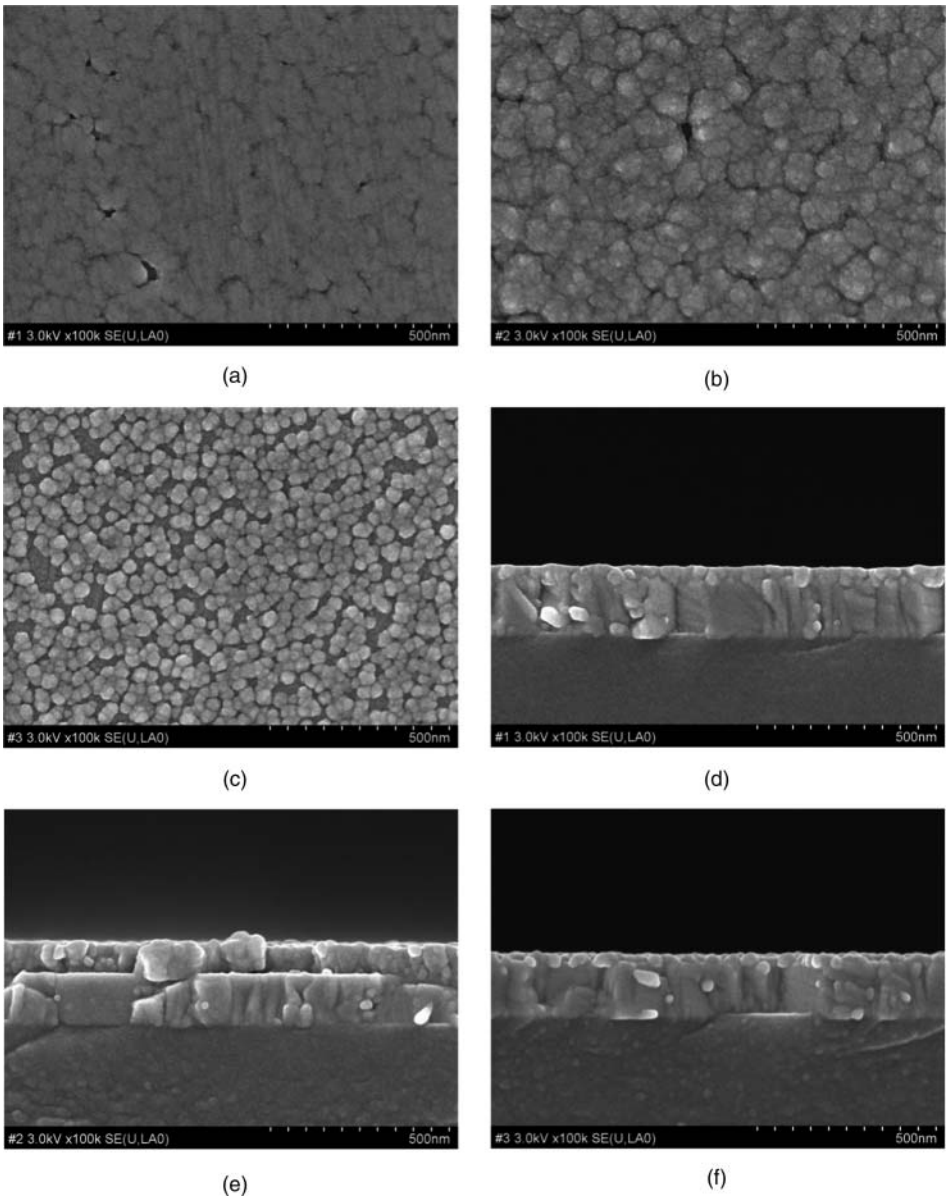

Figure 4. SEM microscopy of specimens grown at different processing temperatures (a), (d) 45°C (b), (e) 55°C, and (c), (f) 65°C respectively.

Table 2. The quantitative information about the morphology of the CdS thin films grown at various process temperatures.

Process Temperature (°C)	45	55	65
RMS (nm)	3.99	4.72	6.58
Ra (nm)	3.15	3.70	4.65
Thickness (nm)	55	98	35

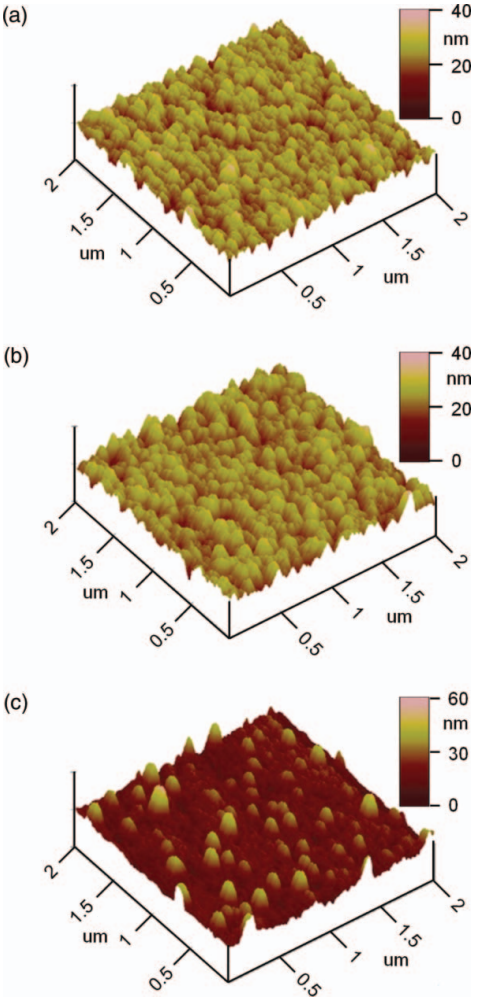

Figure 5. AFM data of the specimens deposited at different processing temperatures (a) 45°C (b) 55°C, and (c) 65°C respectively.

CdS grains were detected which is accordance with SEM data of Figure 4(c). It means that uniform CdS growth hardly occurred even not to cover ITO film. During the observation of the CdS precipitation process, there was an apparent difference between the 65°C processing condition and the others. In the case of 65°C, as soon as ammonia water was added into the mixture solution consisting of CdSO4 and thiourea, the solution became yellow green immediately, in other words, the precipitation process of the CdS within the bulk solution occurred without hesitation. However, at 45°C and 55°C, the solution turned into yellow gradually. This phenomenon strongly suggests that a homogeneous reaction has been stimulated at higher temperature conditions, namely CdS formation in bulk solution is increased, and a heterogeneous reaction is dominant at relatively lower temperatures. Thus, one can conclude that the homogeneous reaction in a solution bath and the heterogeneous reaction on substrates took place independently. The results favor the

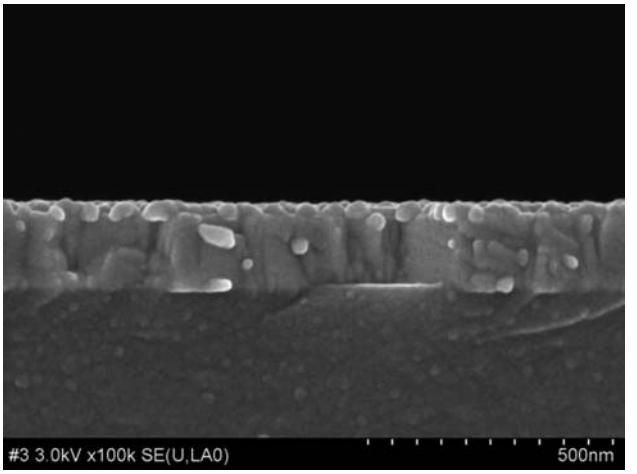

Figure 6. The spectral transmittance data of the CdS thin films by varying the processing temperature.

kinetics of the CdS film growth being associated with the heterogeneous growth mechanism proposed by Ortega-Borges and Lincot [8].

In order to investigate the optical property of the specimens under different thiourea concentrations, a UV-Vis-Nir transmittance measurement was done. Figure 6 shows the spectral transmittance data of the CdS thin films for various processing temperatures.

At a wavelength of 350nm, a significant transmittance drop appeared due to the ITO band gap, about 3.7eV. And at around 500nm, which concerns the CdS band gap of 2.4eV, quite commonly, a 20% transmittance drop throughout all the specimens was observed. According to Table 2, the specimen prepared with a 55°C processing temperature had the maximum thickness of 98nm which was two times thicker than at a 45°C processing temperature. However, the transmittance at a 45°C processing temperature was inferior to that of the 55°C processing temperature. It implies that the relationship between the CdS thickness and transmittance is not so strongly dependent. Therefore, in order to prepare transparent CdS thin films with good conformal coverage, the direction of the research should not be forced to fabricate thinner CdS films.

4. Conclusion

In summary, the effect of the temperature on the growth kinetics of CdS thin films deposited by the chemical bath deposition method was investigated. The study reveals that the processing temperature was a crucial factor for the growth of the CdS thin films by the CBD method. However, the processing temperature does not have any vivid effect on the crystal structure according to the XRD data and TEM microscopy. It was verified that the CdS films were grown by the heterogeneous growth mechanism proposed by Ortega-Borges from observing the precipitation process.

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