

Research on structural characteristics of large-scale CdS thin films deposited by CBD under low ammonia condition*

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Cadmium sulfide (CdS) buffer layers with the scale of 10 cm×10 cm are deposited by chemical bath deposition (CBD) with different temperatures and thiourea concentrations under low ammonia condition. There are obvious hexagonal phases and cubic phases in CdS thin films under the conditions of low temperature and high thiourea concentration. The main reason is that the heterogeneous reaction is dominant for homogeneous reaction. At low temperature, CdS thin films with good uniformity and high transmittance are deposited by adjusting the thiourea concentration, and there is almost no precipitation in reaction solution. In addition, the low temperature is desired in assembly line. The transmittance and the band gap of CdS thin films are above 80% and about 2.4 eV, respectively. These films are suitable for the buffer layers of large-scale Cu(In,Ga)Se₂ (CIGS) solar cells.

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The cadmium sulfide (CdS) thin film as a key layer is widely used in Cu(In,Ga)Se₂ (CIGS) and Cu₂ZnSnS₄ (CZTS) solar cells. The chemical bath deposition (CBD) is deemed to be a potential method in deposition of CdS thin films without pins or holes. CBD method can be used to prepare CdS thin films with less lattice mismatch^[1]. In this method, it can be classified by the use of ammonia as low ammonia method^[2], high ammonia method^[3], or even without ammonia^[4]. Because of the harm to the health of operator and the volatility of the ammonia, the low ammonia method is considered as the best one. However, the deposition of large-scale CdS thin films under low ammonia condition has few reports. In this paper, large-scale CdS buffer layer is deposited by CBD under low ammonia condition, which can avoid the gradient of the temperature and the precipitation of the heterogeneous reaction to prepare CdS thin films with high transmittance, large-area uniformity, good adherence and proper band gap. The deposition of CdS thin films by CBD can be labeled as two mechanisms of ion by ion growth (called as heterogeneous reaction) and cluster by cluster growth (called as homogeneous reaction). Powdery and non-adherent films are attributed to heterogeneous reaction^[5,6]. So controlling the tempera-

ture and the releasing rate of S²⁻ is the key factor, and the concentration of the Cd²⁺ ions should be controlled properly^[7].

There are many advantages in preparing large-area CdS thin films by CBD under low ammonia condition. First, it is hard to control the pH of the solution, but it can be operated easily and has wide tolerance to the amplification of the solution. Second, it could make use of the solution sufficiently and reduce the cost^[8]. Third, it has a better tolerance to the temperature than that in the deposition of small-area CBD-CdS films.

In this paper, there are three different conditions for preparing CdS thin films with the scale of 10 cm×10 cm. In the premise of non-precipitation and with good adherence, we compare these conditions. We change the temperature and the releasing rate of S²⁻ to obtain high quality CdS films. Under the low temperature condition, the activation energy of the ions is lower, which is hard for the reaction of Cd²⁺ and S²⁻ and the absorption to the bulk. Then we increase the concentration of the thiourea solution to accelerate the releasing rate of S²⁻. High quality and good adherence of CdS thin films are attributed to the heterogeneous reaction^[9]. The four different conditions are shown in Tab.1. The weight ratio of the ammo-

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nia is 25%–28% by putting about 5 drops to the 2 L solution which consists of cadmium salt, thiourea and buffering agent (CH₃COONH₄). The concentration of the ammonia is about 0.000 23 mol/L. There is good accommodation with the co-operation of the ammonia and the buffering agent^[10]. In these experiments, the stirring speed is 140 r/s.

Tab.1 Four different conditions for preparing CdS thin films

No.	The proportion of the solution ((CH ₃ COO) ₂ Cd:CH ₃ COONH ₄ :SC(NH ₂) ₂)	Temperature
a	0.001 mol/L:0.004 5 mol/L:0.01 mol/L	80 °C
b	0.001 mol/L:0.004 5 mol/L:0.02 mol/L	75 °C
c	0.001 mol/L:0.004 5 mol/L:0.04 mol/L	70 °C
d	0.001 mol/L:0.004 5 mol/L:0.06 mol/L	65 °C

Fig.1 shows the variation of pH of the reaction solution with time. Because of the low ammonia CBD for CdS, the pH values are all about or below 9.8 for different methods, which is must be done for operator's healthy consideration. As time goes by, the pH values will decrease. For No.a condition with higher reaction temperature, the decrease speed of the pH value is higher than those of others, and its pH value is 6.5 in low acidity after 30 min. When the stirring speed is accelerated, the rate of the reaction will be quicker. However, there will be much precipitation in reaction solution if the stirring speed is too fast, while there will be obvious temperature gradient in CdS thin films to lead to the film nonuniformity if the stirring speed is too slow. To solve this problem, we dilute the solution to reduce the speed of reaction and set the stirring speed as about 140 r/s to reduce the temperature gradient. The reaction process can be described as three stages of preparing stage, reaction stage and saturation stage. In preparing stage, the reaction energy is not enough, and the ions are not reacted to generate CdS powder. The heterogeneous reaction is the dominant process in the reaction stage. In saturation stage, there is no CdS growth.

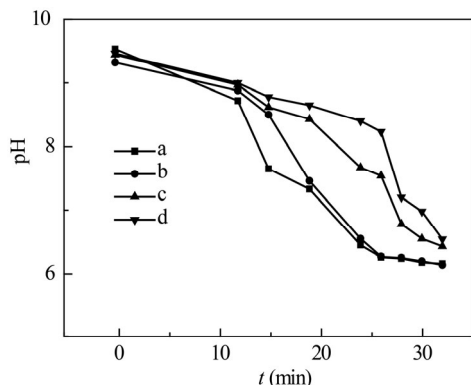


Fig.1 The changes of pH values for CdS thin films deposited under four different conditions

The thicknesses of CdS thin films were measured by KLA Tencor mechanic profiler. A Rigaku TTRIII X-ray diffraction (XRD) was used to measure the crystal phases of the films. The surface morphology of the films was measured by Hitachi S-4800 SEM. The transmittance and band gap of the CdS thin films were measured by the ellipsometry.

Fig.2 shows XRD patterns of the CdS thin films under four different conditions. The temperature and the releasing rate of S²⁻ are the key factors for depositing CdS thin films with good crystallization. It can be seen from Fig.2 that there is almost no diffraction peak for the films in the conditions of Nos.a and d, and there are two diffraction peaks corresponding to (112) (hexagonal) and (220) (cubic) planes for No.b. The (112) peak is obviously higher than the (220) peak. The situation for No.c is similar to that of No.b, but its peak has higher intensity. It was reported that there should be both two crystallized orientations in CdS thin films for the conductivity and adherence of the films^[11]. The hexagonal CdS films have good conductivity, and the cubic CdS films have less lattice mismatch or interface state intensity. The interface state intensity between hexagonal CdS and CuIn_{0.7}Ga_{0.3}Se₂ is about 10¹⁴ cm⁻², but that between cubic CdS and CuIn_{0.7}Ga_{0.3}Se₂ is about 10¹² cm⁻², even if the interface state intensity lattice is about 10¹² cm⁻² for perfect heterojunction^[12].

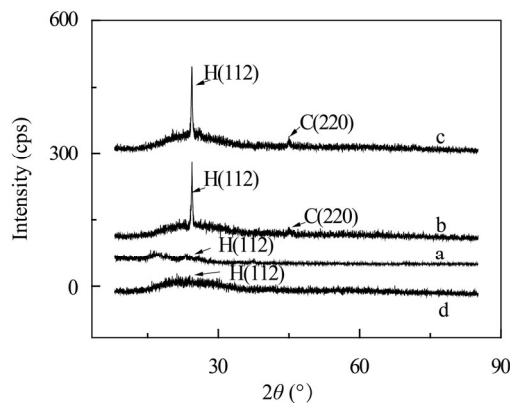


Fig.2 XRD patterns of CdS thin films deposited under different conditions

The samples of CdS thin films are divided into 9 zones for their uniformity measurement as shown in Fig.3(a), whose thicknesses were measured by step apparatus. To characterize the uniformity of the CdS buffer layers, we use the probability of the thickness as shown in Fig.3(b). The thickness uniformity of the CdS thin films deposited under the condition of No.c is better than those of other films, which can be maintained with the variation of about 3 nm. Although there will be less time to grow 50 nm-thick CdS thin films in condition of No.a, the uniformity is worse, and the precipitation is more. We calculate the thickness variance of each zone in the CdS sample by

$$\delta = \sum_{i=1}^n \frac{(d_i - d_0)^2}{d_0^2}, \quad (1)$$

$$d_0 = \frac{\sum_{i=1}^n d_i}{n}, \quad (2)$$

where d_i is the thickness of the zone marked as i , and n is equal to 9. The variances are $\delta_1=18.49$, $\delta_2=48.64$, $\delta_3=7.56$ and $\delta_4=97.86$, respectively. δ_3 is the minimum, which means that the sample No.c has the best uniformity, and it agrees with the result shown in Fig.3.

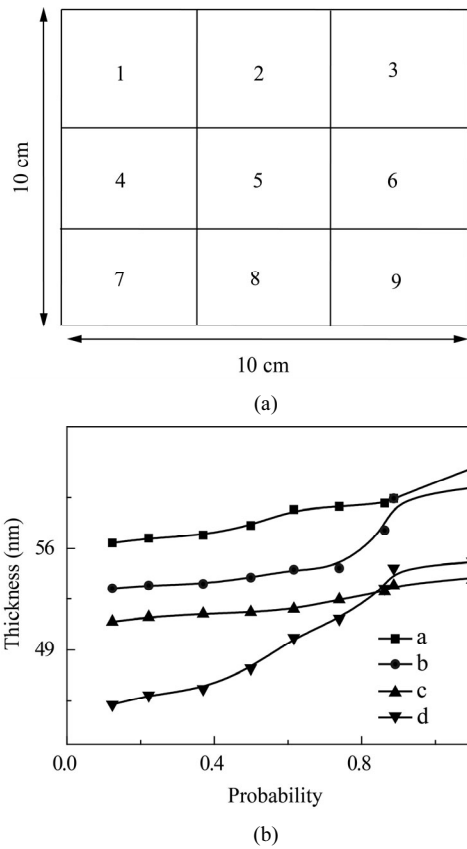


Fig.3 (a) The division of the CdS thin films; (b) The probability of the thickness for CdS thin films deposited under different conditions

Fig.4 shows the scanning electron microscope (SEM) pictures of the CdS thin films. As shown in Fig.4(a), there is no pin or hole in the four films deposited by changing temperature and concentration of the thiourea simultaneously according to the conditions of Nos.a–d. As shown in Fig.4(b), if only changing the temperature, there are many pins and holes which form micro-junction to reduce the photo-current in the films^[12]. It is not desired and should be avoided. It was reported that the purity of the CdS thin film can increase the efficiency of the solar cell^[13]. So it is the most important to control the temperature and the pH value of the reaction solution to get CdS thin films with high purity.

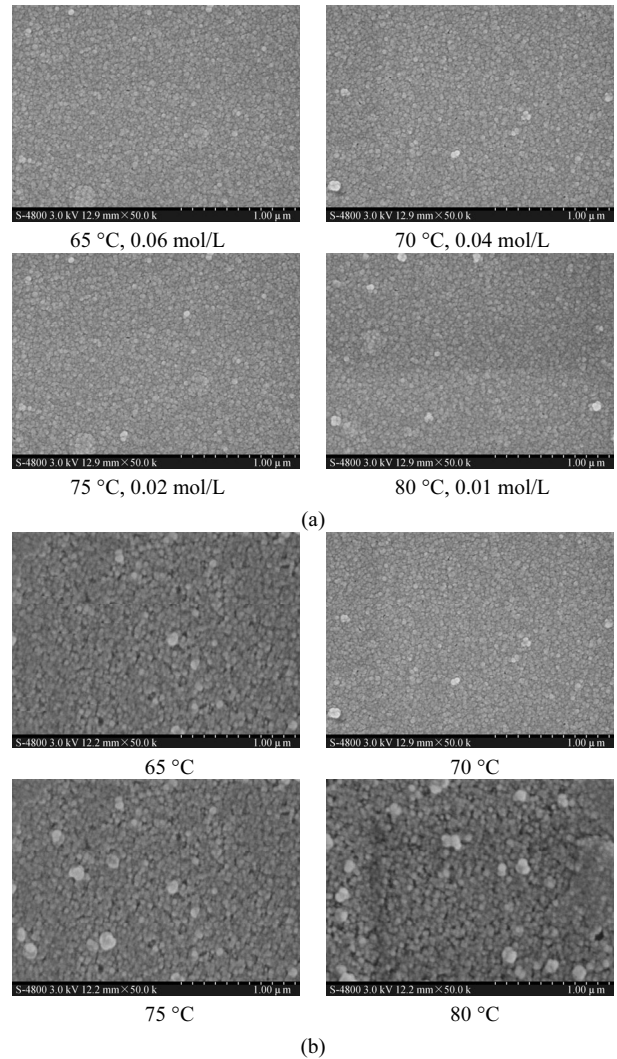


Fig.4 SEM pictures of CdS thin films deposited by (a) changing temperature and concentration of the thiourea simultaneously, and (b) only changing the temperature with the same thiourea concentration of 0.04 mol/L

Fig.5 shows the transmittance of the CdS thin films measured by the ellipsometry. The transmittance of the CdS thin films deposited under the condition of No.c is about 80%, which is higher than those of others in wavelength range of 400–600 nm. As we know, the band gap of the CdS buffer layer is about 2.4 eV. The light with the wavelength below 600 nm is absorbed by the CdS layer, which produces photogenerated charge carriers, whereas the other wavelengths contribute to the solar cell current less, and they can only transmit from the CdS to the CIGS layer which absorbs this kind of wavelength light to produce photogenerated charge carriers and change solar cell current. Because the CdS thin film is a direct band gap semiconductor, we can calculate the band gap of the CdS thin films using the Urbach relation as^[14,15]

$$\alpha = \frac{k(h\nu - E_g)^{1/2}}{h\nu}, \quad (3)$$

$$hv = \frac{hc}{\lambda}, \quad (4)$$

$$\alpha = \frac{\ln(1/T)}{d}, \quad (5)$$

where d is the thickness of the film, T is the transmittance, E_g is the band gap, and λ is the wavelength. Fig.5(b) shows the curves of $(\alpha hv)^2$ versus hv . According to the slopes of these curves, we can deduce the band gaps of the CdS thin films deposited under the conditions of Nos.a–d, which are 2.52 eV, 2.42 eV, 2.40 eV and 2.58 eV, respectively. The band gaps of CdS thin films in condition of No.c are lower than those of others, which can be beneficial to solar cell's current and avoid the angulation of current-voltage curves^[16].

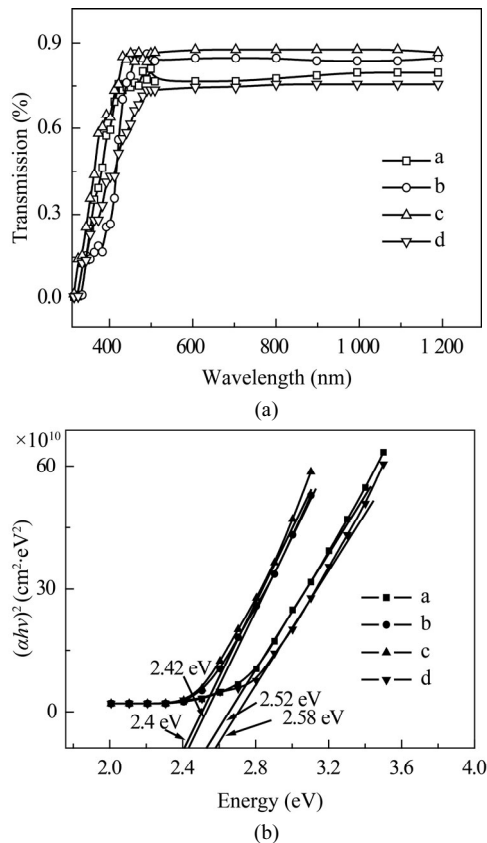


Fig.5 (a) Transmittance spectra and (b) $(\alpha hv)^2$ versus hv for CdS thin films deposited under different conditions

CdS thin films with large scale of 10 cm×10 cm are deposited by CBD under low ammonia condition. The temperature gradient caused by natural convection is overcome to prepare CdS thin films with good uniformity under low temperature condition. The CdS thin films with higher transmittance and good crystallization are deposited under the conditions of higher concentration of thiourea and lower temperature. The CBD method under low ammonia condition can be used to prepare CdS thin films without pins or holes, and the films have proper

band gaps and can be used as buffer layers for large-scale CIGS solar cells.

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