Structural Characteristic of CdS Thin Films and Their Influences on Cu (In, Ga) Se_2 (CIGS) Thin Film Solar Cells

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Abstract: Deposition and structural characteristics of cadmium sulfide (CdS) thin films by chemical bath deposition (CBD) technique from a bath containing thiourea, cadmium acetate, ammonium acetate and ammonia in an aqueous solution are reported. Researches are made on the influence of the fundamental parameters including pH, temperature, and concentrations of the solution involved in the chemical bath deposition of CdS and titration or dumping of the thiourea solution on the structure characteristic of CdS thin films. The pH of the solution plays a vital role on the characteristic of the CdS thin films. The XRD patterns show that the change in the pH of the solution results in the change in crystal phase from predominant hexagonal phase to predominant cubic phase. The CdS thin films with the two different crystal phases have different influences on CIGS thin film solar cells. The crystal mismatch and the interface state density of the c-CdS (cubic phase CdS) and CIGS are about 1.419 % and 8.507 $\times 10^{12}$ cm^{-2} respectively, and those of the h-CdS (hexagonal phase CdS) and CIGS are about 32.297 % and 2.792 $\times 10^{12}$ cm^{-2} respectively. It is necessary for high efficiency CIGS thin film solar cells to deposit the cubic phase CdS thin films.

Key words: CdS; Cu(In, Ga) Se_2; cubic phase; hexagonal phase
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1 Introduction

Extensive research has been made on the deposition and characteristics of cadmium sulfide (CdS) thin films for photovoltaic application because of their intermediate band gap, good optical transmittance, high absorption coefficient and electron affinity, low resistivity, and easy ohmic contact[1]. CdS is considered to be the best-suited window material for CdTe and Cu(In, Ga) Se_2 solar cells[2]. There are many deposition methods for CdS thin films[3]. CdS thin films, the buffer layers of CIGS thin film solar cells by chemical bath deposition (CBD) technicque, are very important for fabricating high-efficiency CIGS thin film solar cells. At present, the maximal conversion efficiency of the kind of solar cells is 19.2 %[4].

CdS thin film is a II-VI group compound semiconductor with a direct band gap of 2.42eV at room temperature. CdS thin films are of two kinds of crystal phases: cubic phase (with zinc blende structure) and hexagonal phase (with wurtzite structure), and it is possible to grow CdS films in both different phases. The two kinds of crystal phases of CdS buffer layers have different influences on CIGS thin film solar cells.

The formation of the two crystal phases depends on many factors, such as pH, temperature, and concentrations of the solution and titration or dumping of the thiourea solution, and the pH of the solution is the most important factor in all.

There leads to the crystal lattice mismatch and produces interface state density when the heterojunction in CdS/CIGS solar cells is formed. The crystal

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mismatch and the interface state density of the c-CdS (cubic phase CdS)/CIGS and those of the h-CdS (hexagonal phase CdS)/CIGS are quite different.

In this paper, we discuss the influence of different deposition conditions on the characterizations of CdS thin films deposited by CBD and the difference of two kinds of crystal mismatch and the interface state density.

2 Experiment

The CdS thin films were deposited on glass substrates of dimension 4.4cm × 4.2cm from a chemical bath containing thiourea, cadmium acetate, ammonium acetate, and ammonia using CBD technique. The solution pH ranged from 11.26 to 11.62, the temperature from 80 to 90 ℃, the cadmium ion concentration from 0.005 to 0.01M, the thiourea concentration from 0.12 to 0.2M, the ammonium acetate concentration from 0.2 to 0.5M, and the ammonia concentration from 0.33 to 0.82M. The additions of the thiouea solution to the bath were done in two different manners: one was the titration of the solution, namely, adding it to the bath drop by drop; the other was its dumping, namely, adding all the solutions to the bath at a draught.

The deposition time was 30min. The bath was covered and continuously stirred during the deposition for a homogeneous distribution of the chemicals. The deposited thin films were washed with deionized water and dried in N_2.

The film thickness was measured with XP-2. The XRD patterns of the thin films were obtained with X-ray diffractometer.

3 Results and discussion

In CBD technique, the CdS thin films are deposited by decomposition of thiourea in an alkaline solution of cadmium salts according to the following reactions[4]:

$$(NH_2)_2SC + 2OH^- \longleftrightarrow S^{2-} + CH_2N_2 + 2H_2O \quad (1)$$

$$Cd^{2+} + 4NH_3 \longleftrightarrow Cd(NH_3)_4^{2+} \quad (2)$$

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^- \quad (3)$$

The overall reaction is

$$Cd(NH_3)_4^{2+} + (NH_2)_2SC + 2OH^- \longleftrightarrow CdS\downarrow + CH_2N_2 + 4NH_3\uparrow + 2H_2O \quad (4)$$

3.1 Influence of ammonia concentration

Figure 1 shows the XRD patterns of the CdS thin films at various ammonia concentrations from 0.33 to 0.82M, and other conditions are constant. The pH of the solution increases from 11.26 to 11.59 with the increase of ammonia concentration. The crystal phase of the film deposited with 0.33M is predominant hexagonal phase. As ammonia concentration increases, the crystal phase gradually transforms from predominant hexagonal phase into predominant cubic phase. The crystal phase of the film is predominant cubic phase when the ammonia concentration is up to and above 0.82M. However, when the concentration exceeds 0.66M, the CdS films is powdery and nonadherent.

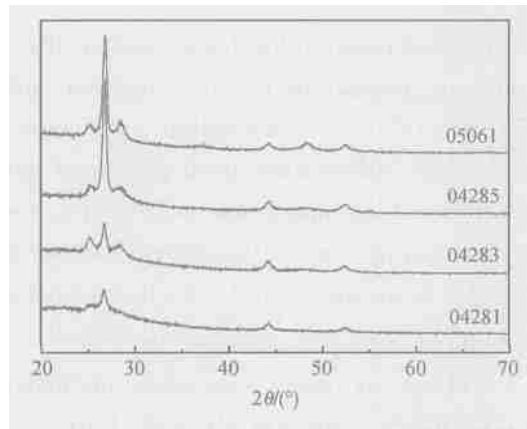

Fig. 1 XRD patterns of CdS thin films with various ammonia concentrations (from top to down: 0.33, 0.49, 0.66, and 0.82M, and the pH is 11.26, 11.37, 11.48, and 11.59, respectively)

The thickness of the films first increases from 47, 54 to 78nm with the decrease of the ammonia concentration (0.82, 0.66, and 0.49M), and then it decreases when the concentration continues decreasing (the thickness of the film deposited with 0.33M is 55nm). Excesss ammonia increases the pH of the so-

lution which in turn promotes the formation of S^{2-} and decreases Cd^{2+} concentration. Therefore, the pH of the solution (that is, the ammonia concentration) can be used to control the growth rate and the thickness of the CdS films.

3.2 Influence of ammonium acetate concentration

The XRD patterns of CdS films at different ammonium acetate concentrations from 0.2 to 0.5M are shown in Fig. 2. The pH of the solution decreases from 11.61 to 11.53 with the increase of the ammonium acetate. Therefore, the influence of the ammonium acetate can be attributed to the pH of the solution. The crystal phase of the film deposited with 0.5M is predominant hexagonal phase, gradually transforms into predominant cubic phase with the decrease of the ammonium acetate, and is predominant cubic phase when the ammonium acetate concentration is 0.2M.

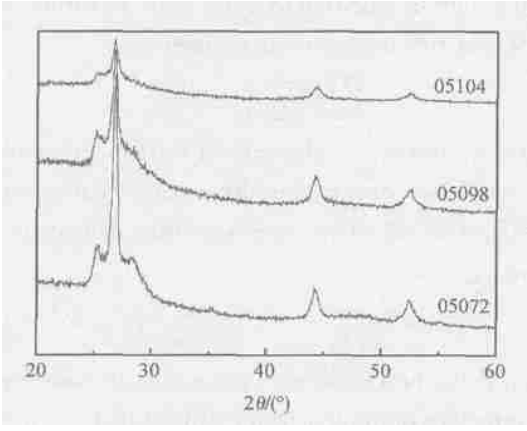

Fig. 2 XRD patterns of CdS films with various ammonium acetate concentrations (from top to down: 0.2, 0.3, 0.5M, and the pH is 11.61, 11.57, 11.53 respectively)

Similarly, the thickness of the films increases from 60, 71, to 105nm with the increase of the pH of the solution (that is, the decrease of the ammonium acetate).

3.3 Influence of cadmium acetate concentration

Figure 3 shows the XRD patterns of the thin films deposited with various cadmium acetate concentrations from 0.005 to 0.01M.. The pH of all of the solution is almost 11.52, so all films are of the same crystal phase. However, the thickness of the four films increases (it is 40, 41, 47, 77nm respectively) with the increase of the concentration.

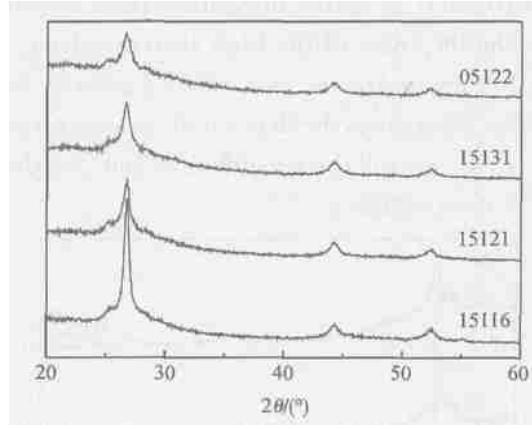

Fig. 3 XRD patterns of CdS films with various cadmium acetate concentrations (from top to down: 0.005, 0.00625, 0.0075, 0.01M, and the pH is almost 11.52)

3.4 Influence of thiourea concentration

Figure 4 shows the XRD patterns of CdS films deposited with different thiourea from 0.12 to 0.2M. The pH of the solution increases from 11.37 to 11.62 with the increase of the thiourea concentration. Therefore, the crystal phase of the film deposited with

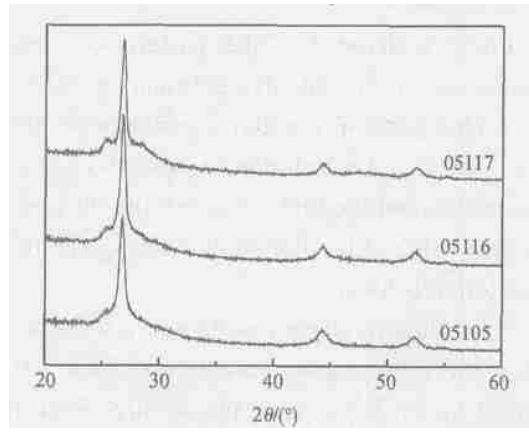

Fig. 4 XRD patterns of CdS films with various thiourea concentration (from top to down: 0.12, 0.16, 0.2M, and the pH is 11.37, 11.48, and 11.62 respectively)

0.2M is more predominant cubic phase. However, these films are almost of the same thickness.

3.5 Influence of deposition temperature

Figure 5 shows the XRD patterns of CdS films deposited with different temperatures from 80 to 90 ℃. The three films are almost of the same crystal phase, but the crystallization of the films deposited with 90 ℃ is better than other films. Furthermore, the thickness of the films increases from 49, 59 to 70nm with the increase of the deposition temperature. Therefore, the deposition temperature can be used to control the growth rate and the thickness of the CdS films.

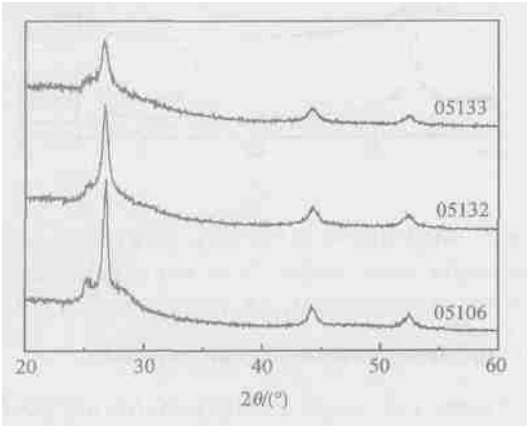

Fig. 5 XRD patterns of various deposition temperatures (from top to down: 80, 85, 90 ℃)

3.6 Influence of titration or dumping of the thiourea solution

Figure 6 shows that XRD patterns of titration or dumping of the thiourea solution is different. The crystal phase of the film deposited with dumping of the thiourea solution is more predominant cubic phase, and the film is thicker (the thickness is 70nm, and that of the film of dumping of the thiourea solution is 69nm).

According to above results and discussion, we obtain the following optimized conditions for the films of predominant cubic phase (deposition time is 30min):

ammonia concentration: 0.66M
cadmium concentration: 0.01M
ammonium acetate concentration: 0.2M
thiourea concentration: 0.2M
deposition temperature: 90 ℃

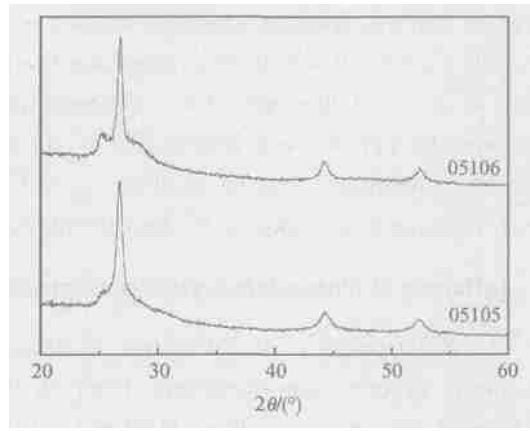

Fig. 6 XRD patterns of titration or dumping of the thiourea solution (from top to down: titration and dumping)

4 Influences of two crystal phases on Cu(In, Ga)Se$_2$(CIGS) thin film solar cells

There leads to the crystal lattice mismatch and produces the interface state density when the heterojunction in CdS/CIGS solar cells is formed. the crystal lattice mismatch is defined as[6]

$$\frac{2(a_2 - a_1)}{a_2 + a_1} = \frac{\Delta a}{a} \tag{5}$$

where a_1 and a_2 are the crystal lattice constants of the two kinds of semiconductor materials ($a_2 > a_1$), $a = (a_1 + a_2)/2$. The interface state density is defined as

$$N_{ss} = \frac{a_2^2 - a_1^2}{a_1^2 a_2^2} = \frac{(a_2 - a_1)(a_2 + a_1)}{a_1^2 a_2^2} \tag{6}$$

Even if the heterojunction is perfect, the number of its interface state density is still up to 10^{12}cm^{-2}.

Table 1 gives the crystal mismatch and the interface state density of the c-CdS/CIGS and those of the h-CdS/CIGS. The crystal mismatch and the interface state density of the c-CdS/CIGS are about 1.419% and 8.507 $\times 10^{12}$cm^{-2} respectively, and those of the h-CdS/CIGS are about 32.297% and 2.792 $\times 10^{12}$ cm^{-2} respectively. The crystal mismatch of the former is almost neglectable, and the interface state density is perfect (the interface state density of the best heterojunction is about 10^{12}cm^{-2}). Therefore, it is necessary for high efficiency CIGS thin film solar cells to de-

posit the cubic phase CdS thin films.

Table 1　Crystal mismatch and interface state density of c-CdS/ CIGS and those of h-CdS/ CIGS

Heterogeneous pair	Crystal mismatch / %	Interface state density/ cm^{-2}
c-CdS/ CIGS	1.419	8.507×10^{12}
h-CdS/ CIGS	32.297	2.792×10^{14}

5　Conclusion

Two kinds of CdS films with different crystal phases have been successfully deposited by CBD technique. We obtain the following optimized conditions (including pH, temperature and concentrations of the solution involved in the chemical bath deposition of CdS and titration or dumping of the thiourea solution) for the films of predominant cubic phase. The crystal phase of the film is predominant cubic phase when the ammonia concentration is higher, the ammonium acetate and thiourea concentration are lower, and the addition of the thourea solution is dumping. The cadmium concentration does not almost influence on the crystal phase of the films. A higher deposition temperature enhances the crystallization degree of the films. The crystal mismatch and the interface state density of c-CdS/ CIGS are about 1.419 % and 8.507 $\times 10^{12}$ cm^{-2} respectively, and those of h-CdS/ CIGS are about 32.297 % and 2.792 $\times 10^{12}$ cm^{-2} respectively. It is necessary for high efficiency CIGS thin film solar cells to deposit cubic phase CdS thin films.

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CdS 薄膜的结构特性及其对 Cu(In, Ga)Se_2(CIGS) 薄膜太阳电池的影响

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摘要: 报道了 CdS 薄膜的 CBD 法沉积及其结构特性, 其中的水浴溶液包括硫脲、乙酸镉、乙酸铵和氨水溶液. 研究了水浴溶液的 pH 值、温度、各反应物溶液的浓度和滴定硫脲与倾倒硫脲等基本工艺参数对 CdS 薄膜结构特性的影响. 其中, 溶液的 pH 值对 CdS 薄膜的特性起着关键的作用. XRD 图显示了随着溶液 pH 值的变化, 薄膜的晶相由六方相向立方相转变. CdS 薄膜的这两种晶相对 CIGS 薄膜太阳电池性能的影响不相同. c-CdS (立方相的 CdS) 与 CIGS 之间的晶格失配和界面态密度分别为 1.419 %和 8.507 $\times 10^{12}$ cm^{-2}, 而 h-CdS (六方相的 CdS) 与 CIGS 之间的晶格失配和界面态密度则分别为 32.297 %和 2.792 $\times 10^{12}$ cm^{-2}. 高效 CIGS 薄膜太阳电池需要的是立方相 CdS 薄膜.

关键词: CdS; Cu (In, Ga) Se_2; 立方相; 六方相

PACC: 6800; 7280E; 7340L

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