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MICROSTRUCTURE OF CdS FILMS PREPARED WITH CHEMICAL PYROLYSIS DEPOSITION

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Abstract: CdS solid thin films were prepared on the substrates of slide glass or ITO coated glass by using chemical pyrolysis deposition technique (CPD) at different deposition temperature from 350 to 540℃ during film growth. Some of the prepared CdS films were undergone thermal annealing treatments at temperature from 200 to 600℃. The microstructures of as-deposited CdS films before and after thermal annealing were investigated with SEM, AFM and XRD measurements.

It is found that hexagonal structure-like phase can be obtained for CdS films prepared with CPD when the deposition temperature is below 540℃. Wurtzite phase appears when CdS films are prepared at deposition temperature higher than 540℃, or the CdS films are prepared with CPD at deposition temperature of 400℃ and post-annealed at the temperature above 500℃. The grain size of CdS films, which is dependent on deposition temperature and on different substrates, is also discussed.

Key words: chemical pyrolysis deposition; CdS films; microstructure

用化学热解沉积法制备硫化镉薄膜的微结构

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摘要:在载玻片或ITO涂覆的玻璃上采用化学热解法沉积CdS固体薄膜,沉积温度在350~540℃之间.部分制备的CdS薄膜进行200~600℃的退火热处理.由SEM,AFM和XRD分析测量退火热处理前后的CdS薄膜的微观结构.结果表明,沉积温度低于540℃以下制备的CdS薄膜具有类六方结构相,当高于540℃沉积的CdS薄膜则显示纤锌矿相.在400℃化学热解沉积的CdS薄膜经高于500℃的后热处理也可获得纤锌矿相.CdS薄膜的晶粒尺寸依赖于沉积温度及不同基体的情况也在本文中进行了讨论.

关 键 词:化学热解沉积;CdS薄膜;微结构
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Introduction

CdS thin film have been extensively studied in the development of solar cells[1~2]. CdS films were initially fabricated mainly by evaporation, sputtering, or spray pyrolysis. Since 1990s, the techniques of chemical, electrodeposit or photochemical preparation have attracted much attention since these techniques of deposition from liquid solutions have great advantages of economy, convenience, and the capability of large-area deposition[3~5].

In our work, CdS thin films are prepared by chemical pyrolysis deposition (CPD). Characterization of the microstructure for the CdS films prepared with CPD at different deposition temperature and post-annealing temperature is investigated with SEM, AFM and XRD.

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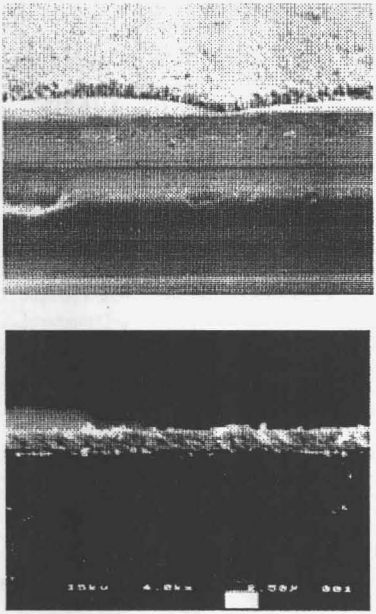


Fig. 1 Cross section morphologies of the CdS films prepared with CPD
图1 化学热解法制备 CdS 薄膜的截面形貌

1 Experiment

CdS thin film was prepared on glass or ITO/glass substrates with a method of chemical pyrolysis deposition(CPD). The procedure was as follows. $CdCl_2$ and Thiorea(H_2NCSNH_2) were mixed with distilled water. The ratio between Cd and S was 1∶ 1. The prepared solution was about 2,000ml in Vycor. Substrate of slide glass or ITO glass was put into the solution for 3 or 5 seconds. Flectric furnace was used to perform pyrolysis of the solution containing Cd and S and to deposit and crystallize CdS on substrates. The substrates deposited with polycrystalline CdS were pulled out from furnace after 30 seconds' dry. Usually deposited CdS substrates were too hot, so they needed to be cooled in air for 2 minute in order to protect the glass substrate from breakage before bathing into solution again. Such steps can go on continuously in order to get the thick CdS films. It will take 4 hours to deposit about 1μm thick CdS film on glass substrate. The chemical reaction is as follows:

$$CdCl_2 + SC(NH_2)_2 + 2H_2O \rightarrow CdS + 2NH_4Cl + CO$$

Substrates of glass or ITO coated glass were preheated at 400℃ for 30 minutes before deposition. After finishing the deposition process, some of samples were annealed for 20 minutes at the temperature from 200 to 600℃ respectively.

Samples were investigated with SEM, AFM and XRD, where morphologes and grain size of the CdS films were checked by SEM and AFM. Phase structure of the samples were characterized by X-Ray diffraction (XRD) with Cu Kα radiation($\lambda = 1.54$Å).

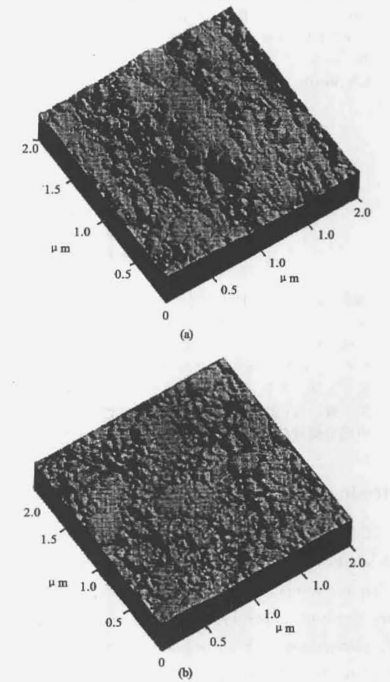


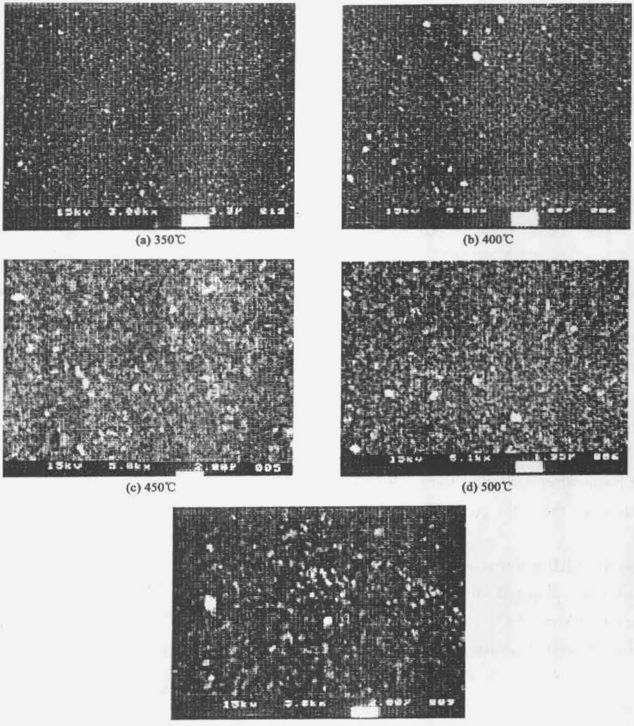
Fig. 2 AFM images of the polycrystalline CdS thin films on different substrates (a) CdS/glass (b) CdS/ITO/glass
图2 多晶 CdS 薄膜在不同基材上的 AFM 图象 (a) CdS/玻璃 (b) CdS/ITO/玻璃

2 Results and discussion

Fig. 1 shows cross section morphologies of as-deposited CdS thin films with scanning electron microscopy(SEM). It can be seen that the films are dense and uniform. The morphologies in Fig. 1 are column structures with an angle to the surface of substrate. This is not like the ones with evaporation, sputtering or other methods[6,7], where the columns are usually vertical to the surface of substrate.

Fig. 2 shows the AFM images of the polycrystalline CdS thin films of about 2μm in thickness on glass substrate and ITO/glass substrate. The deposition temperature was 400℃. The top morphologies of CdS films on different substrate are not similar, and it seems that the uniformity is better on ITO/glass substrate than that on glass substrate. Besides, such a feature of top morphology is also not dependent on deposition temperature within our temperature range. In a word, all CdS films deposited with CPD method have similar top morphologies. It can be confirmed that all CdS films are transparent yellow or bright orange color only depending on the thickness of CdS films. The average grain sizes for CdS films on glass and ITO/glass substrates are 0. 133μm and 0. 093μm, respectively, by AFM photography measurement. It means that the average grain size is smaller on ITO/glass substrate than that on glass substrate. This may be affected by ITO film.

Fig. 3 shows SEM photographs of the CdS films



(a) 350℃ (b) 400℃

(c) 450℃ (d) 500℃

(e) 540℃

Fig. 3 SEM photographs of the CdS films prepared at different deposition temperature

图 3 不同沉积温度下制备 CdS 薄膜的 SEM 照片

prepared at different deposition temperature and with the same deposition time of 30 minutes. With the increase of deposition temperature, the grain size of CdS film is not simply increased. It can be seen that the grain size of the CdS film is decreased a little at the temperature from 350℃ to 400℃. So the morphology in Fig. 3(b) is denser than that in Fig. 3(a). And the grain size is then increased at the temperature from 400℃ to 540℃.

To make it clear, the grain size of CdS polycrystalline versus the deposition temperature is shown in Table 1. The deposition temperature ranges from 350 to 400℃, and it seems to be in benefit of nucleation of CdS films and leads to the decrease in grain size. While deposition temperature increased from 400℃ to 540℃, grain growth is promoted. The grain growth becomes more quickly at deposition temperature from 500℃ to 540℃ due to the change in phase structure as discussed below.

Table 1 The average grain size of CdS polycrystalline thin films

表1 CdS 多晶薄膜在不同沉积温度下的平均晶粒尺寸

Deposition temperature(℃)	350	400	450	500	540
Grain size (μm)	0.033	0.030	0.050	0.075	0.170

The change tendency in grain size of CdS films, prepared by CPD at different deposition temperature and the same deposition time, is summarized in Fig. 4.

Another phenomenon can be seen from Fig. 2 and Fig. 3. With the increasing of film thickness at the same deposition temperature, in other words, with the increasing of deposition time, the grain size is also increased.

Fig. 5 shows the XRD patterns of the CdS films on the ITO/glass substrates prepared with CPD at different deposition temperature from 350℃ to 540℃. Basically, the CdS films deposited at temperature range of 350℃—500℃ are dominantly hexagonal structure. The values of lattice constant a and c for hexagonal phase based on the equation of Nelson-Riley[8] and obtained by extrapolation are 0.4136 nm, and 0.6713 nm, respectively. Detailed scrutiny reveals that the

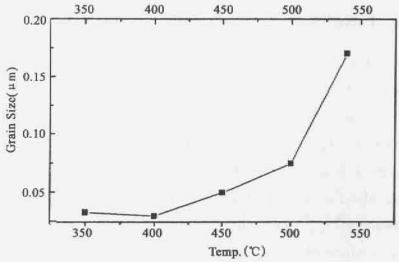


Fig. 4 Grain size of the CdS films as a function of deposition temperature during film growth

图4 CdS 薄膜的晶粒尺寸与薄膜制备温度的关系曲线

(002) reflection is the most intensive in hexagonal phase while the (101) one is the strongest peak in wurtzite phase. This means that the CdS films prepared with CPD at temperature from 350℃ to 500℃ are hexagonal structure-like, but wurtzite phase at temperature over 540℃. It shows that different phases are formed when deposition temperature is from 500℃ to 540℃.

The CdS fims prepared by CPD at 400℃ are undergone post annealing treatment in air at different temperature of 200 ~ 600℃. These samples are analyzed with XRD, as shown in Fig. 6. It can be found that with the increasing of annealing temperature, the intensity of the (002) reflection is gradually decreased while that of the (101) one is gradually increased. This phenomenon tells us that with the increase of post-annealing temperature over 500℃, phase of hexagonal-like is transformed to wurtzite structure. Besides, some oxide- like CdO appears in CdS films at annealing temperature around 500 ~ 600℃.

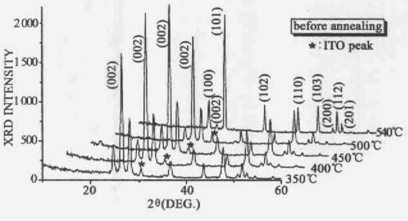


Fig. 5 XRD patterns of the CdS films on the ITO substrates at different deposition temperature

图5 不同温度沉积在 ITO 基体上 CdS 薄膜的 XRD 谱

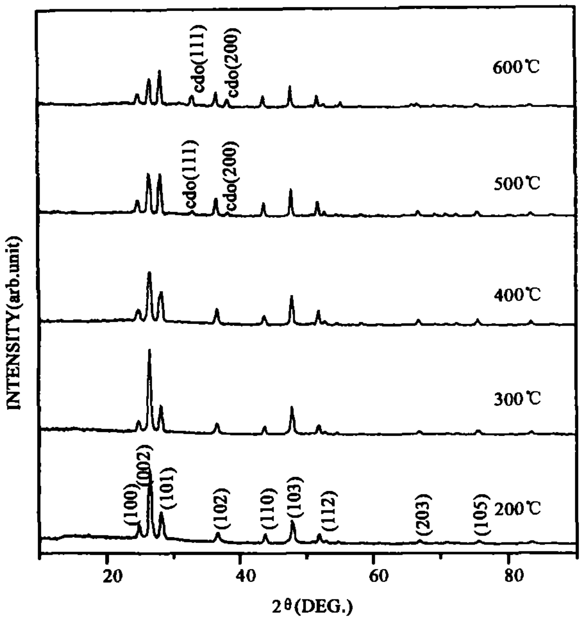


Fig. 6 XRD patterns of the CdS films deposited at 400℃ with post annealing at different temperature
图6 400℃沉积的 CdS 薄膜经不同温度退火后的 XRD 谱

3 Conclusions

Microstructure of CdS films prepared by chemical pyrolysis deposition method and their annealed ones have been studied. The following results are obtained.

1) The CdS films prepared with chemical pyrolysis deposition are dense and uniform. The morphologies of the CdS films show column structure with a tilted angle corresponding to the surface of the substrates.

2) The magnitude of grain size for the deposited CdS films is increased with the increasing of deposition temperature from 400℃ to 540℃ during film growth, while decreased with the increasing of temperature from 350℃ to 400℃. And the grain size is also increased rapidly when the deposition temperature is increased from 500℃ to 540℃ due to the change of phase structure. Another factor is deposition time. With the increasing of deposition time, the grain size of CdS films is also increased.

3) The CdS films prepared with CPD at deposition temperature of 350℃ ~500℃ are hexagonal structure-like, and it becomes wurtzite phase when the deposition temperature is higher than 540℃.

4) Post annealing treatment can lead to the change from hexagonal structure-like to wurtzite phase when the annealing temperature is higher than 500℃ for the CdS films prepared with CPD at deposition temperature 400℃.

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