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Structural and optical properties of CdS thin films prepared by RF sputtering

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Abstract: Cadmium sulfide thin films were grown on transparent conductive oxide coated glass substrates by radio frequency magnetron sputtering with a substrate temperature ranging from 30 ℃ to 200 ℃. X-ray diffraction measurements reveal that cadmium sulfide films were polycrystalline with the hexagonal wurtzite structure. The scanning electron microscope images show a good crystalline quality of the films which can also be confirmed by the Raman spectra, ultraviolet-visible absorption spectra and the photoluminescence spectroscopy. The Raman spectra measurements indicate that the compressive stress in the CdS films increases with increasing growth temperature.

Key words: CdS; magnetron sputtering; solar cell
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低温磁控溅射制备 CdS 薄膜的结构和光学特性

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摘要: 用磁控溅射的方法在透明导电氧化物衬底上制备了 CdS 薄膜, 制备时的衬底温度为 30~200 ℃. X 射线衍射测试结果表明在这一条件下制备的 CdS 薄膜是六角纤锌矿的多晶结构. 扫描电子显微镜结果显示薄膜具有较好的晶体质量, 这一结论也和拉曼光谱、紫外-可见吸收光谱、光致发光光谱的结果一致. 拉曼光谱显示 CdS 薄膜内部的压应力随着制备温度的提高而增大.

关 键 词: CdS;磁控溅射;太阳能电池
中图分类号: P578.2; TN305.92; TM914.4　　**文献标识码**: A

1 Introduction

Cadmium sulfide (CdS) is a group Ⅱ-Ⅳ compound semiconductor which has great potential in applications such as solar cells, optical detectors and optoelectronic devices. The electrical and optical properties make it extremely useful as window layer material for many photovoltaic solar cell modules[1-7]. Furthermore, CdS has remained as a focus of the material science community due to its band gap, conversion efficiency, high absorption coefficient, stability and its significantly low cost. CdS has a wide and direct band gap (about 2.42 eV at room temperature), n-type semiconducting material and found in two crystalline

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forms, cubic(zind-blend) phase and hexagonal(wurtzite) phase. CdS thin films have been deposited by many techniques such as the chemical bath deposition (CBD)[1-3], vacuum evaporation[4], thermal vacuum evaporation[5], and r. f. magnetron sputtering[6, 7]. In those techniques, r. f. sputtering is one of the simplest and nontoxic techniques to grow CdS films. Furthermore, it is suitable for depositing on substrates having large areas. However, a systematically and in-depth investigation about CdS thin films by r. f. magnetron sputtering is rarely reported. Moreover, investigations on structural and optical properties of CdS films are still underway to enrich the knowledge in this area, for example, the unambiguous origins of some PL emission peaks are still unclear. From those results of various researchers[1-3], it is well evident that the crystal structure and optical-electric properties of CdS films are sensitive to the specific methods and conditions employed during fabrication. Therefore, the deposition conditions of CdS are undoubtedly major issues, because not only the chemical properties, but also the optical, electrical properties and the solar cell efficiency all depend greatly on the structure of CdS.

In this work, CdS thin films were deposited on different substrates with different conditions. It was found that the Ar partial pressure and the sputtering power influence the growth rate, rather than the crystallites of CdS films. However, the substrate temperature may play an important role not only on the growth rate but also on the crystalline quality of films. The growth rate firstly increases with a substrate temperature and then begins to decrease at the temperature above 150 ℃. The as-grown CdS films have the hexagonal wurtzite structure and show clearly a preferential orientation along the (002) planes. The effects of growth temperature on the structural and optical properties of CdS thin films indicate that the crystalline quality of films increases with the increase of substrate temperature from 30 to 200 ℃.

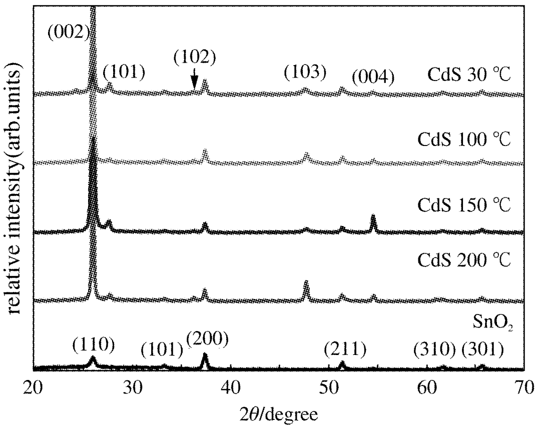

Fig. 1 XRD patterns of the CdS films deposited at substrates with different temperature

图 1 不同衬底温度下制备的 CdS 薄膜的 X 射线衍射图

1 Experiment

CdS thin films were deposited by radio frequency (r. f.) magnetron sputtering from a sintered ceramic CdS target with a purity of 99.99%. The substrates were transparent conductive oxide(TCO) coated glass on which SnO_2: F was spray-deposited. The distance between target and substrate was around 5.5 cm. The sputtering gas Ar was controlled by a mass flow controller. The base pressure of chamber was below 7×10^{-4} Pa. To clean the target surface, pre-sputtering was carried out for 10 min at an Ar gas pressure of 1.0 Pa. The sputter power was 150W and the gas pressure was 1.2 Pa. The substrate temperature was varied from 30 to 200 ℃. The thicknesses of all the as-deposited films under different substrate temperatures were 200 nm. X-ray diffraction(XRD) (Rigaku D/Max II-IC) measurements were used to study the crystallinity and crystal orientation of the films. The compressive stress in the CdS films was studied by Raman. The surface morphologies of the films were observed by scanning electron microscope (SEM) images from JEOL JSM-6700F. The optical properties of the films were measured by the ultraviolet-visible(UV-Vis) spectrophotometer and the photoluminescence(PL) measurements from HORIBA LabRAM HR evolution.

2 Results and discussion

2.1 Structural analysis

Figure 1 shows the XRD patterns of the CdS films deposited at different substrate temperatures. The pattern for the substrate coated with spray-deposited SnO_2: F was is also shown in Fig. 1 for comparison. It is found that all the CdS films grown at different temperatures possess similar XRD patterns. Diffraction peaks with Bragg angle $2\theta = 26.66°$ are due to the (002) reflections in the hexagonal phase for the CdS films[1-7]. This sharp peak indicates preferential orientation and good crystal quality in these samples. Other peaks at 28.33°, 36.77°, 48.08° and 54.86° are associated with the hexagonal wurtzite (101), (102), (103) and (004) planes. These results clearly show that deposited CdS films are mainly of poly-crystalline nature with hexagonal wurtzite structure and with no or negligible cubic phase, which is consistent with other reports[6,7]. It is noticed that (004) peak is strongest for the CdS film grown at 150 ℃. And the ratio of (004)/(103) peak is largest, which indicates that the films grown at 150 ℃ are least influenced by the interface and almost determined only by the surface energy of itself because the (002) planes have the lowest surface energy for the hexagonal CdS as compared with other planes. Further, the full width at half maximum (FWHM) of (002) planes are 0.30°, 0.30°, 0.28°, 0.24° for CdS thin films prepared at different substrate temperatures of 30 ℃, 100 ℃, 150 ℃ and 200 ℃ respectively, implying that the relatively high growth temperature is beneficial to the film crystalline quality.

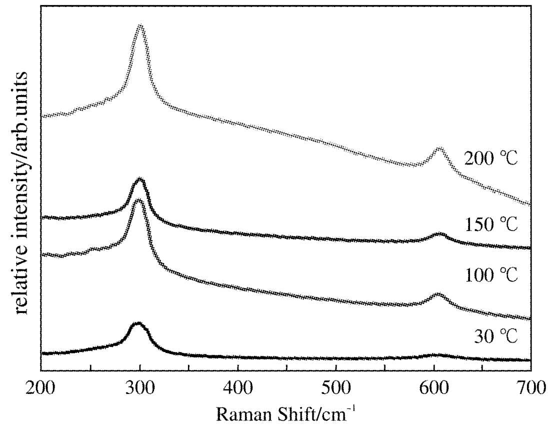

Fig. 2 Raman spectra of CdS films deposited at different temperatures of 30 ℃, 100 ℃, 150 ℃ and 200 ℃
图2 不同衬底温度(30 ℃, 100 ℃, 150 ℃, 200 ℃)下制备的 CdS 薄膜的拉曼光谱图

The room temperature Raman spectra of all the CdS films are shown in Fig. 2 which were obtained by an Ar ion laser with excitation wavelength of 514.5 nm. Two characteristic CdS peaks are observed. One is located at approximately 301 $\mathrm{cm^{-1}}$ which corresponds to longitudinal optical (LO) phonon, the other at around 600 $\mathrm{cm^{-1}}$ origins from the 2LO phonon. The FWHM of the 1LO peaks for the CdS films deposited at 30 ℃, 100 ℃, 150 ℃ and 200 ℃ are 21.4 $\mathrm{cm^{-1}}$, 18.9 $\mathrm{cm^{-1}}$, 17.6 $\mathrm{cm^{-1}}$, 16.1 $\mathrm{cm^{-1}}$ respectively, indicating that the crystalline quality of the films is improved by increasing the growth temperature which is well consistent with the results obtained by XRD. It can be seen from Fig. 2 that the LO phonon peak shifts to higher energy with increasing substrate temperature. This blue-shift can be ascribed to the increase of the compressive stress in the CdS films with the growth temperature. This observation most likely results from different thermal expansion coefficients between the films and substrates.

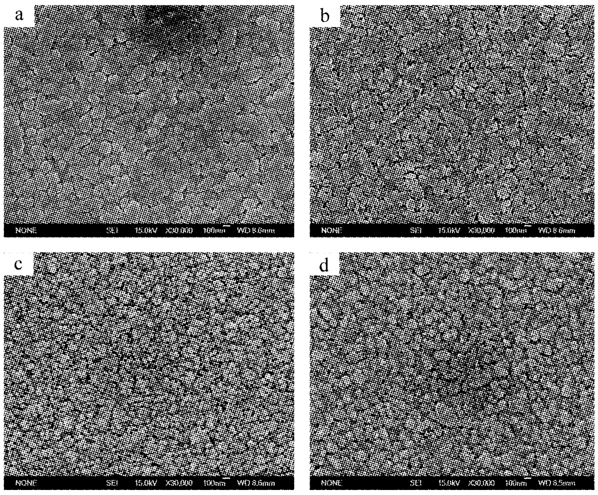

Fig. 3 SEM images of CdS films deposited on substrates at different temperatures (a) 30 ℃ (b) 100 ℃ (c) 150 ℃ (d) 200 ℃
图3 不同衬底温度(30 ℃, 100 ℃, 150 ℃, 200 ℃)下制备的 CdS 薄膜的 SEM 照片

2.2 Morphology

Figure 3 shows the surface morphology of the CdS films measured by the SEM. There are no obvious voids or holes for all the films. The CdS films grown at 30 ℃ are composed of circle-like grain, while for the films grown at a temperature higher than 100 ℃, some bean-like or rectangular-like grains appear, which indicate that the films grown at higher temperatures is denser and the crystalline quality was improved compared with those grown at low temperatures.

2.3 Optical properties

The wavelength dependence of optical transmittance in the wavelength range from 350 nm to 800 nm for films grown at different temperatures are shown in Fig. 4. The transmittance is increased with the increase of the substrate temperature, implying that the films grown at higher temperatures may possess much less defects and thus the crystalline quality of films is improved.

The optical band gap values for these films are evaluated using the Tauc plots (Fig. 5). The values of optical band gap for the CdS films are determined using the empirical relation:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad , \quad (1)$$

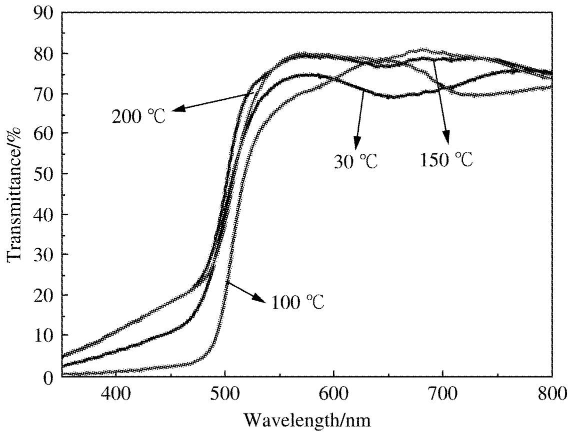

Fig. 4　Transmittance spectrum versus wavelength for CdS films deposited at different substrate temperatures of 30 ℃, 100 ℃, 150 ℃ and 200 ℃
图4　不同衬底温度(30 ℃, 100 ℃, 150 ℃, 200 ℃)下制备的 CdS 薄膜的透射光谱

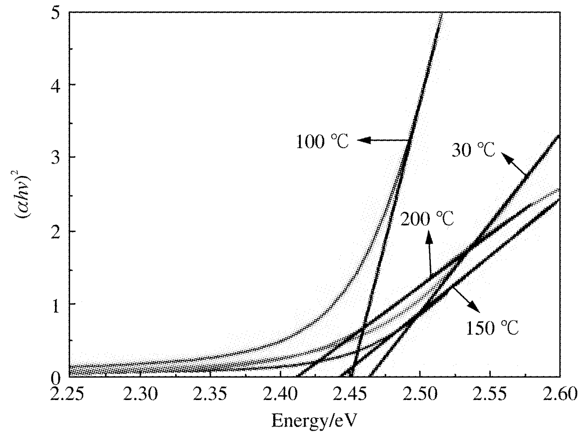

Fig. 5　$(\alpha h\nu)^2$ versus $h\nu$ for CdS films deposited at different temperatures of 30 ℃, 100 ℃, 150 ℃ and 200 ℃
图5　不同衬底温度(30 ℃, 100 ℃, 150 ℃, 200 ℃)下制备的 CdS 薄膜的$(\alpha h\nu)^2$与 $h\nu$ 的关系曲线

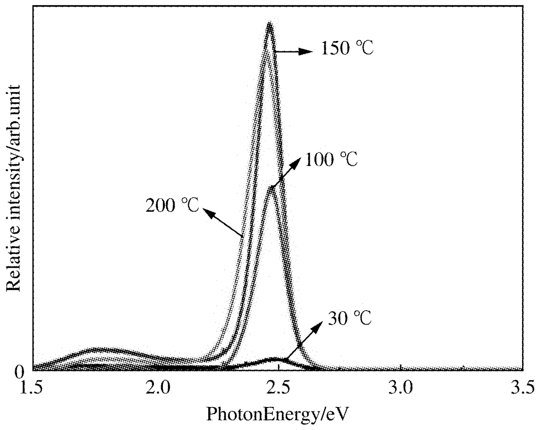

Fig. 6　Photoluminescence spectra of CdS films deposited at different substrate temperatures of 30 ℃, 100 ℃, 150 ℃ and 200 ℃
图6　不同衬底温度(30 ℃, 100 ℃, 150 ℃, 200 ℃)下制备的 CdS 薄膜的光致发光光谱

where E_g is the optical band gap and $n = 2$, $1/2$, $2/3$, respectively, for direct, indirect and forbidden direct transitions, α is the absorption coefficient at frequency ν and A is a constant. We have chosen $n = 2$ which gives a good linear fit as shown in Fig. 5. From the intercept of the straight line portion of the $(\alpha h\nu)^2$ at the axis, the values of the energy band gap can be obtained. The band gap values estimated are 2.47 eV, 2.45 eV, 2.44 eV, 2.41 eV for the films deposited at substrate temperatures of 30 ℃, 100 ℃, 150 ℃ and 200 ℃, respectively. These values were found to be close to the energy gap data reported for CdS films by other methods[8,9]. It is also concluded that the band gap decrease with the increase of substrate temperature which is consistent with the results obtained from the PL spectra. The CdS has very narrow band gap (2.41 ~ 2.47 eV) at visible region, so it acts as a window layer.

Figure 6 shows the PL spectra deposited at different substrate temperatures. The graph shows two main emission peaks. One is located at higher energies at about 2.4 eV and the other at 1.7 eV. The peak around 1.7 eV origins from the sulfur deficient of CdS films[10]. It should be noticed that the peak around 2.4 eV related to the bound exciton becomes narrower with the increase of substrate temperature, indicating that the lattice of films is rearranged more orderly and then the quality of films is improved. This result agrees well with that of transmittance spectra.

As shown in Fig. 6, it should be noted that the growth rate first increases substantially when the temperature increases to 150 ℃. Even worse, when the substrate temperature is higher than 200 ℃, e. g. 250 ℃, the growth rate of CdS films is negligible. The reason for this change can be described as follows. When the substrate temperature firstly increase from the room temperature, the sputtered particles have high kinetic energy and move fast at the growth surface, and then they may have much more chance to move to the local position with the energy minimum. Therefore, these particles are strongly bound in the energy minimum and thus it is more difficult for them to desorb than those particles located in other positions at lower temperatures. So, the growth rate increases with the temperature. With further increasing the temperature, all the particles have enough kinetic energy to climb over the energy barrier to move to the positions of the local energy minimum. However, now, the temperature seems so high that the particles are easy to desorb even if they are in the position of energy minimum, and therefore the growth rate decreases substantially. In conclusion, if we take both the growth rate and the crystalline quality of CdS films into consideration, the best growth temperature of CdS films is from 150 ℃ to 200 ℃.

3 Conclusions

In this paper, CdS thin films have been deposited on TCO-coated glass substrates at different temperatures of 30 ℃, 100 ℃, 150 ℃ and 200 ℃. All CdS films show clearly preferential (002) orientation in XRD. From the measurement of SEM, Raman, transmittance and PL spectrum, it can be concluded that the crystalline quality of films becomes much better with increase of growth temperature. The best growth temperature ranges from 150 ℃ to 200 ℃ with the compromise of the growth rate and crystalline quality of films.

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