Phase structure of the CPD prepared CdS films before and after Ar^+ ion irradiation

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Abstract CdS films prepared with chemical pyrolysis deposition (CPD) at different temperature during film growth were characterized by XRD. Hexagon-like structure appeared at the temperature of 350–500°C, while wurtzite phase was observed at temperature of 540°C during film growth. Also CdS films prepared by CPD at 400°C were undergone post annealing at different temperature of 200–600°C or post Ar^+ ion irradiation. It is found that wurtzite phase happened when the annealing temperature rose to 600°C. And hexagon-like structure existed at the annealing temperature from 25°C to near 500°C. Ar^+ ion irradiation could not cause phase transformation, but induce some preferred orientations and an increase in grain size for the CdS films.

Keywords Phase transformation, CdS film, Annealing, Ar^+ ion irradiation

CLC numbers O485, TN305

1 INTRODUCTION

Cadmium sulfide is the most interesting materials in the chalcogenides which have attracting significant features of nonlinear and luminescent properties, quantum size effects and other important physical and chemical characters.[1,2] CdS is used in a variety of optoelectronic devices including thin film solar cells and photo detectors.[3,4] CdS thin films prepared with various methods can be different essentially from each other in their phase structure, grain size, orientation degree, different kinds of structural defects, different impurities and their contents, etc. Consequently, the properties, such as optical and electric, of CdS thin films are greatly dependent on the preparation procedures. It is well known that the structural transformation of the materials can usually lead to the change of their properties. Also a few investigations were reported on CdS attempting to cause phase transformation by ion irradiation. Some of those researchers found that the amorphization of vacuum deposited CdS thin films during argon ion irradiation, while others reported that no changes in the crystal structure or amorphization took place,

Partly supported by the Visiting Scholar Funds of The Key Laboratory in University of China

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Manuscript received date: 2001-09-17

though irradiation gave rise to radiation damage in the films.[5,6] It seems that the effect of ion irradiation on crystal structure of the CdS thin film with different preparation methods is different according to the results reported therein.

Chemical pyrolysis deposition is one of the prospective procedures used to prepare CdS thin films, it is possible to fabricate sufficiently perfect thin films with large area having strong adhesion to the substrates and high mechanical strength in comparison with the other methods. In our work the CdS thin films prepared with chemical pyrolysis deposition (CPD) were undergone Ar^+ ion irradiation. And phase structure were measured with microanalyses before and after ion irradiation to check the stabilization of the crystal structure of CdS thin films prepared by CPD.

2 EXPERIMENTAL

CdS thin films were prepared on glass substrates with chemical pyrolysis deposition (CPD). Chemical cleaned glass substrates were dipped in the aqueous solutions, the reaction was carried on as follows:

$$CdCl_2 + SC(NH_2) + 2H_2O \longrightarrow CdS + 2NH_4Cl \uparrow + CO_2 \uparrow \tag{1}$$

The substrate was kept at 400°C, and the volatile components of the salts and the solvent are released in the vapour form leading to the formation of CdS film during this process. The substrate temperature should be as high as possible to allow the chemical reaction to take place between the components of the desired deposited materials. But the substrate temperature should not be too high, otherwise it deteriorates the quality of the CdS films due to an increase in density of structural defects and enhancement of the diffusion of impurities into the film from environment. Also the substrate temperature should not be too low, otherwise it decreases the chemical reaction activity leading to a decrease in decomposition rates of the salts, and the surface of the deposited CdS films looks rough.

The CPD prepared CdS films of about 2 μm thickness on glass substrates were vertically irradiated with 120 keV argon ion beam at doses of $(1\text{–}6)\times10^{16}$ ions/cm^2. The measurement in phase structure of the CPD prepared CdS films before and after ion irradiation was performed using a D/MAX-RAX-ray diffractometer. A Cu k α radiation (λ=0.154178 nm) from a Cu anode operating at 40 kV was used with a nickel monochromator filter. Data were acquired over an angle range 2θ from 10 to 80°.

In order to check the chemical states of the compositional elements of the CdS films, x-ray photoelectron spectroscopy(XPS) analysis was carried out using a KRATOS-XSAM 800 system with a monochromatic Mg K α radiation (1253.6 eV) at a pass energy of 20 eV. During measurement a vacuum of better than 1×10^{-6} Pa was maintained in the chamber. XPS data were referred to the C1s line at 284.6 eV. A 2 keV Ar^+ beam was used to etch the top layer of the CdS films formed during ion irradiation due to contamination from the residue such as CO, CO_2 in the chamber.

3 RESULTS AND DISCUSSION

Fig.1 shows the XRD patterns of the CdS films prepared by chemical pyrolysis deposition (CPD) at different temperature during film growth. It should be pointed out that the intensities of the peaks in the same figures are the same scale. It is found that, basically, the CdS films prepared with CPD at growth temperature of a range of 350°C –450°C, the polycrystalline CdS films were dominatedly hexagon-like structure with the lattice constants a=0.4135 nm and C=0.6713 nm, almost the same as the reported data for CdS with wurtzite structure (JCPDS No.41–1049). Detailed scrutiny reveals that the (002) reflection is the most intense in Fig.1(a) and Fig.1(b), whereas the (101) reflection should be the strongest peak in the pure wurtzite phase. Fig.1(c) seems to show that the CdS film is wurtzite structure due to the strongest peak of (101) in it when the CdS film prepared by CPD at growth temperature of 540°. It is found that at temperature up to 500°C during film growth the CdS was still hexagon-like structure.

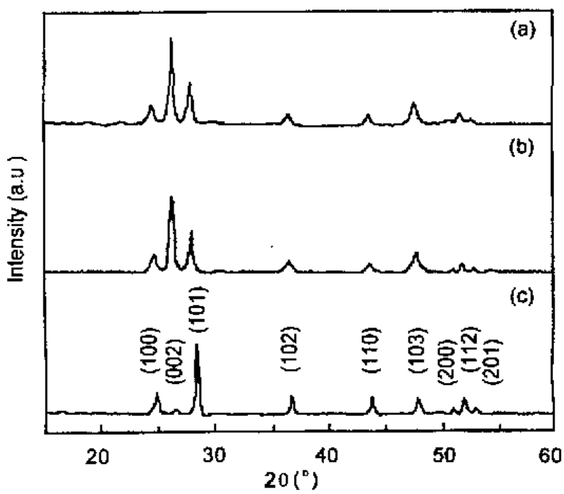

Fig.1 XRD patterns of CdS films prepared at different growth temperature
(a) 350°C, (b) 450°C, (c) 540°C

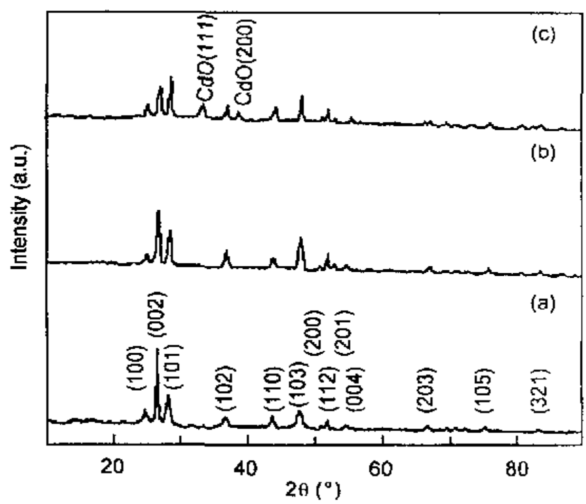

Fig.2 XRD patterns of CdS films at different annealing temperature
(a) 200°C, (b) 400°C, (c) 600°C

The CdS films prepared by CPD at 400°C during film growth were undergone annealing treatment at different temperature of 200–600°C. The XRD patterns of these samples are shown in Fig.2. It can be seen that with increasing annealing temperature from 200°C to 600°C, the intensity of the (002) reflection gradually decreased while that of the (101) one increased. This trend is similar to that shown in Fig.1, the (101) reflection becomes the strongest peak when the annealing temperature was up to 600°C. This means that whenever the temperature is increased to some level higher than 500°C, during CdS film growth or post annealing treatment, phase transformation happens from hexagon-like to wurtzite structure. Apart from this phenomenon, it should be noticed that CdO appeared at annealing temperature of 600°C shown in Fig.2(c). A systematic investigation in annealing temperature shows that CdO were already formed at 500°C for the CdS films prepared by CPD at 400°C.

Fig.3 shows the XRD patterns of CdS films prepared by CPD at 400°C before and after Ar^+ ion irradiation. No change in phase structure for the CdS films can be found, the CdS films were still hexagon-like structure. But the intensity of the (110) reflection was increased after Ar^+ ion irradiation with a dose of 6×10^{16} ions/cm^2. Carefully detailed observations show that with increasing Ar^+ doses from 1×10^{16} ions/cm^2 to 6×10^{16} ions/cm^2, the intensity of the (200) peak was also increased shown in Fig.4. It comes to the conclusion that Ar^+ ion irradiation could not affect the crystal structure of the CdS films, in other words, Ar^+ ion irradiation could not induce a phase transformation of the CdS films prepared by CPD at 400°C although there happens some preferred orientation in the CdS films due to Ar^+ ion irradiation within the doses of (1–6)$\times10^{16}$ ions/cm^2.

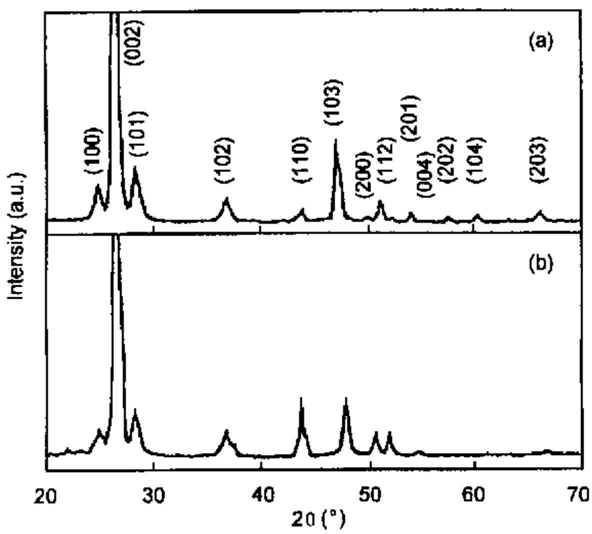

Fig.3 XRD patterns of CdS films before and after Ar^+ ion irradiation
(a) before Ar^+ ion irradiation,
(b) after Ar^+ ion irradiation

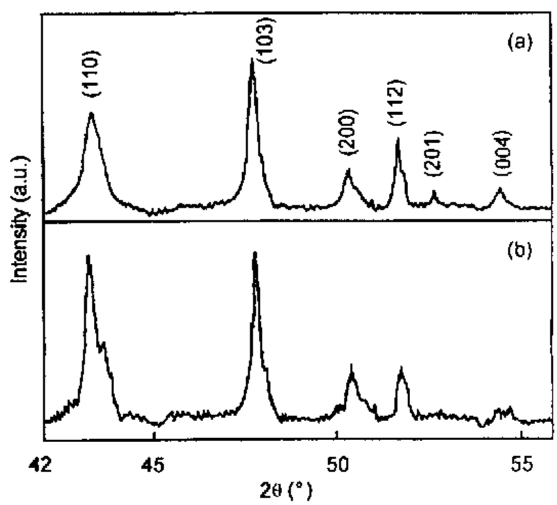

Fig.4 XRD patterns of CdS films with 120 keV Ar^+ ion irradiation
(a) with a dose of 1×10^{16} ions/cm^2,
(b) with a dose of 6×10^{16}ions/cm^2

We also estimate the grain size of these CdS films according to the half-width of diffraction peaks using the Scherrer formula:

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{2}$$

where D denotes the average grain size, λ equals about 0.154 nm, θ is the Bragg angle for the measured diffraction reflection, β is the half-peak width, in radian, of the measured diffraction reflection. For simplicity, here, k=1.

The calculated grain size is about 15 nm for the CdS film prepared by CPD at 400°C, this coincides with that measured with AFM, where about 13 nm of grain size was for the CdS film prepared by CPD at 400°C. The grain size is about 18 nm for the CdS films prepared by CPD at 400°C after Ar^+ ion irradiation with a dose of 1×10^{16} ions/cm^2, and about 25 nm with a dose of 6×10^{16} ions/cm^2. Atomic force microscope (AFM) analysis shows that with increasing temperature during CdS film growth or post-annealing treatment for the CPD prepared CdS films, their grain size were also increased. This means that the influence of Ar^+ ion irradiation upon the CPD prepared CdS films seems partly as a thermal source.

In order to check the composition of the CdS film prepared by CPD at 400°C before and after Ar^+ ion irradiation, Fig.5 shows the results of the XPS measurement. The $Cd3d_{5/2}$ peak at 405.4 eV and $Cd3d_{3/2}$ peak at 412.1 eV are shown in Fig.5(a) with the spin-orbit splitting of 6.7 eV and the intensity ratio of about 1.48. And the S2p spectrum is shown in Fig.5(b) at 161.8 eV. Both of these XPS spectra show that the measured film prepared by CPD at 400°C consist of pure CdS compound. In the S2p and Cd3d spectra, there seems no obvious change after Ar^+ ion irradiation within the dose of (1–6)$\times10^{16}$ ions/cm^2. This results further confirmed that Ar^+ ion irradiation could not induce any phase transformation of the CdS films prepared by CPD at 400°C within the used range of Ar^+ doses.

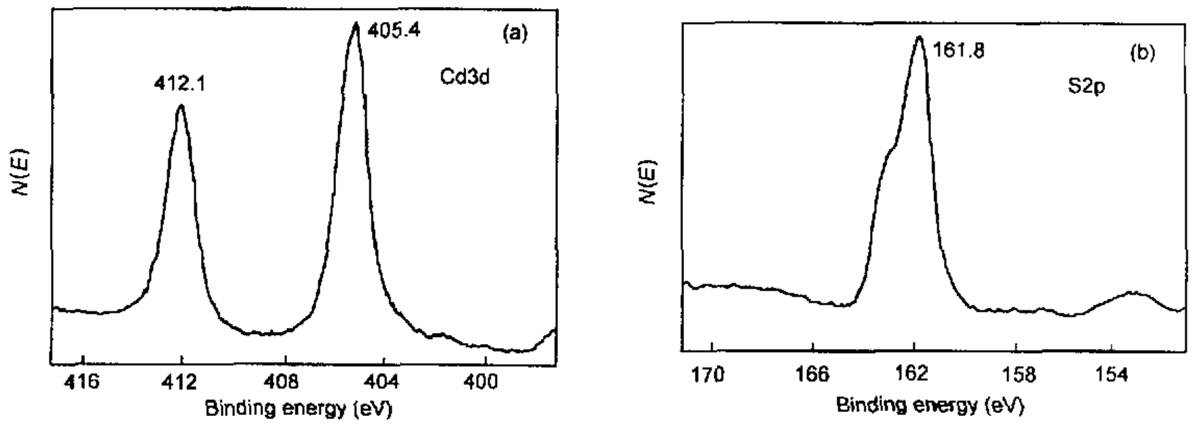

Fig.5 XPS spectra of CdS films prepared with CPD at 400°C
(a) Cd3d, (b) S2p

4 CONCLUSIONS

Phase structure of the CdS films prepared with chemical pyrolysis deposition was determined with XRD. And the effect of Ar^+ ion irradiation on the CdS films prepared by CPD at 400°C were also studied with XRD and XPS analyses. The following conclusions may be drawn from the results presented in this paper.

(1) The CdS films prepared with chemical pyrolysis deposition may be hexagon-like structure or wurtzite phase depending on the temperature during film growth or post

annealing after film formation. The CdS films are hexagon-like structure at temperature of 350–500°C during film growth and also with post annealing at temperature from 200°C to near 500°C for the CdS films prepared by CPD at 400°C. While wurtzite phase of CdS films prepared by CPD could be obtained at temperature as high as 540°C during film growth or with post annealing at temperature over 600°C for the CdS films prepared by CPD at 400°C.

(2) XRD and XPS measurements show that Ar^+ ion irradiation with a doses $(1–6)\times 10^{16}$ ions/cm^2 could not induce the phase transformation of the CdS films prepared by CPD at 400°C, however, some preferred orientation phenomenon and an increase in grain size of the CdS films happened due to Ar^+ ion irradiation.

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