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Study of Phase Transition from Cubic to Hexagonal in the CdS Thin Films by using High Resolution XRD with 4 Axis Cradle

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Epitaxially grown CdS thin films on ITO substrates are prepared by using the chemical bath deposition method. As-deposited films are annealed in Ar at 450°C for 6 h and 24 h and the effect of annealing on structural and morphological properties are studied. From the psi rocking curves of high resolution x-ray diffractometer, one can find that after annealing, the metastable nanocrystallite cubic phase transforms into the stable crystalline hexagonal phase, in which its behavior depends on the exposure time to heat. Experimental data revealed that α-CdS thin films were crystallized at an initial stage of annealing and that after crystallization, the phase transition from α to β-CdS took place. STEM microscopy clearly shows the morphological change of as-deposited and annealed CdS thin films.

Keywords High resolution XRD; CdS; phase transition

Introduction

Many fundamental investigations [1–3] have been and are being carried out on CdS with $CuInSe_2$ (CIS) or CdTe heterojunctions by various groups in order to understand the role played by CdS in certain devices. In CIGS thin film solar cells, CdS has been used as a buffer layer which reduces the effective density of holes at the interface and thereby reduces the recombination of electron hole pairs [4]. A reported band gaps E_g for CdS are 2.42 and 2.62 eV for cubic and hexagonal structures, respectively. In addition, the reported lattice parameters are well matched with those of CIS. CdS with a hexagonal structure is highly favorable for use in solar cell applications as a window layer because of its suitable band gap and stability [5]. A variety of techniques such as electrodeposition, thermal evaporation and chemical bath deposition [6–16] have been used for growing of CdS thin films. Among various methods, the chemical bath deposition (CBD) method is found to be a cheap and simple way to deposit large area nanocrystalline as well as

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polycrystalline metal chalcogenide thin films. The properties of materials prepared by the CBD method are critically dependent on various preparative parameters such as the sources and concentration of metal and chalcogenide ions, the pH of the resultant solution, deposition time, temperature etc and subsequent heat treatments, like annealing in air, vacuum or different gaseous environments such as H2, N2, Ar etc. The present studies are focused on the deposition of nanocrystalline cubic CdS film using the CBD method and its modification into a hexagonal phase after air annealing. To study the effect of annealing on the various film properties, films were annealed in Ar at 450°C for 6 h and 24 h. As films go through the as-grown phase to the hexagonal one after thermal annealing, here we shall concentrate on those details which are of relevance to characterize from x-ray diffraction the cubicand hexagonal structure presented.

2. Experimental Setup

In our previous works, the experimental configuration was described in detail [17, 18]. In this study, we will give just a summary for the deposition of the CdS films by chemical bath. First, a beaker containing the reactants in a magnetically stirred solution was immersed in a temperature controlled water bath. The proportions of 3 mM $CdSO_4$, 0.1 M thiourea and 1.5 M ammonia were kept constant in every experiment. All the films were grown on commercially available indium tin oxide (ITO) glasses. The structural properties of the CdS thin films before and after annealing were investigated using X-ray diffractometer (XRD) with a primary wavelength of Cu-Kα1 1.5406 Å. Philips X'Pert PRO MRD equipped with four axes Euler cradle with variable azimuth pi and tilt angle psi was also used for the observation of psi rocking curve analysis. A scanning transmission electron microscope (STEM) was utilized in order to study morphological properties.

3. Results and Discussion

Figure 1 shows the XRD patterns of CdS films annealed at various conditions. As shown in Fig. 1(a), two primary diffraction peaks, H (0 0 2)/C (1 1 1), and H (1 1 0)/C (2 2 0) were observed in the CdS thin films, most of the peaks correspond to the ITO peaks. XRD profiles 2θ ranging from 23.5 to 29.3° was separately exhibited in Fig. 1(b), a Gaussian line shape is fitted with this interval which is associated with H (0 0 2)/C (1 1 1) plane. Table 1 lists the quantitative peak information including full width half maximum (FWHM), area, position and intensity obtained by the Gaussian fitting method. As shown in FWHM of Table 1, the poor crystal quality of the as grown CdS films can be fairly improved by an annealing. As the annealing time increases, the FWHM gets narrower. It implies the crystallinity of CdS thin films are significantly enhanced due to exposure time to heat.

Table 1. The quantitative peak information associated with Fig. 1(b) XRD data by Gaussian fitting method

Samples	Area	Position	FWHM	Height
As-deposited	1027	26.85	0.399	2054
450°C 6 hr	2016	26.64	0.364	4419
450°C 24 hr	1748	26.60	0.316	4413

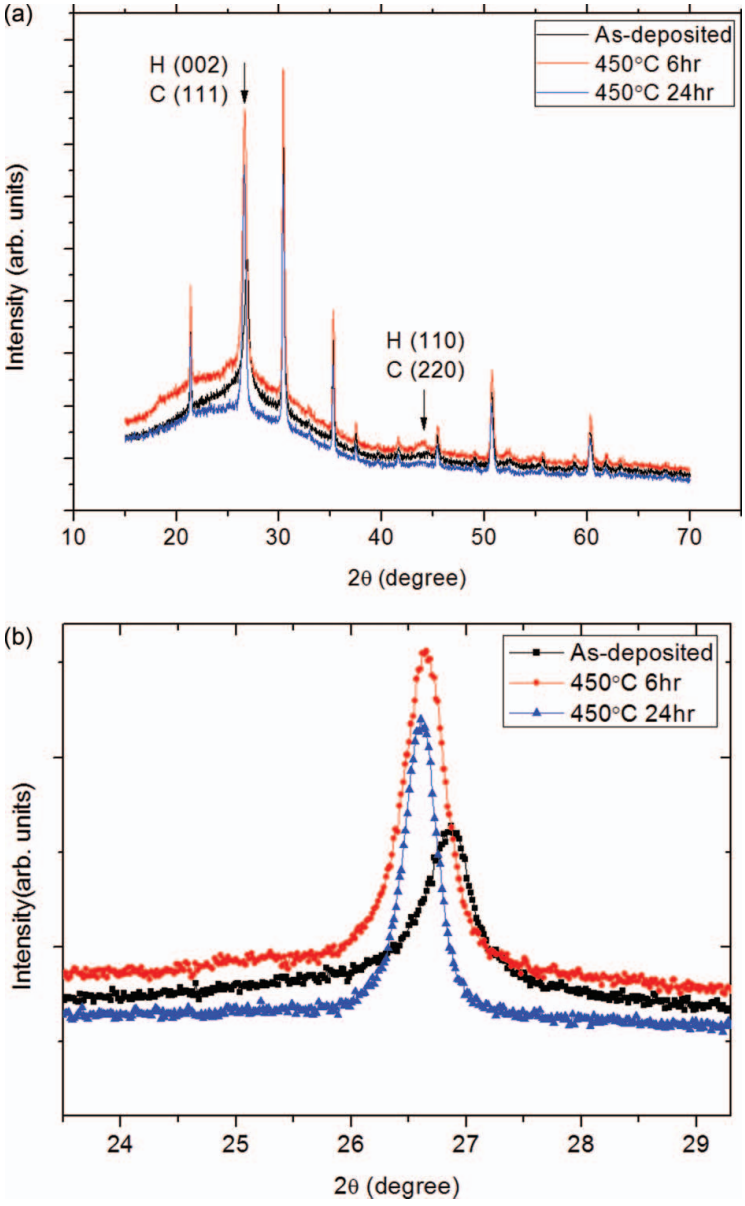

Figure 1. XRD profiles of CdS films annealed at various conditions (a) 2 θ ranging from 15 to 70° and (b) 23.5 to 29.3°.

Further description associated with a kind of crystal structure of CdS films cannot be made because only with Bragg Brentano geometry measurement, namely θ–2θ analysis, it is very difficult to differentiate the cubic from the hexagonal structure. The reason is that the cubic (111) and the hexagonal (002) lines coincide within 1% [19]. In order to confirm the phase transition during annealing, psi rocking curve were obtained at two specific 2 θ positions. Figure 2 denotes the psi rocking curves depending on annealing conditions. It is acquired at 52.099° (2 θ) attributed with cubic (311) plane. If it has a cubic crystal structure, due

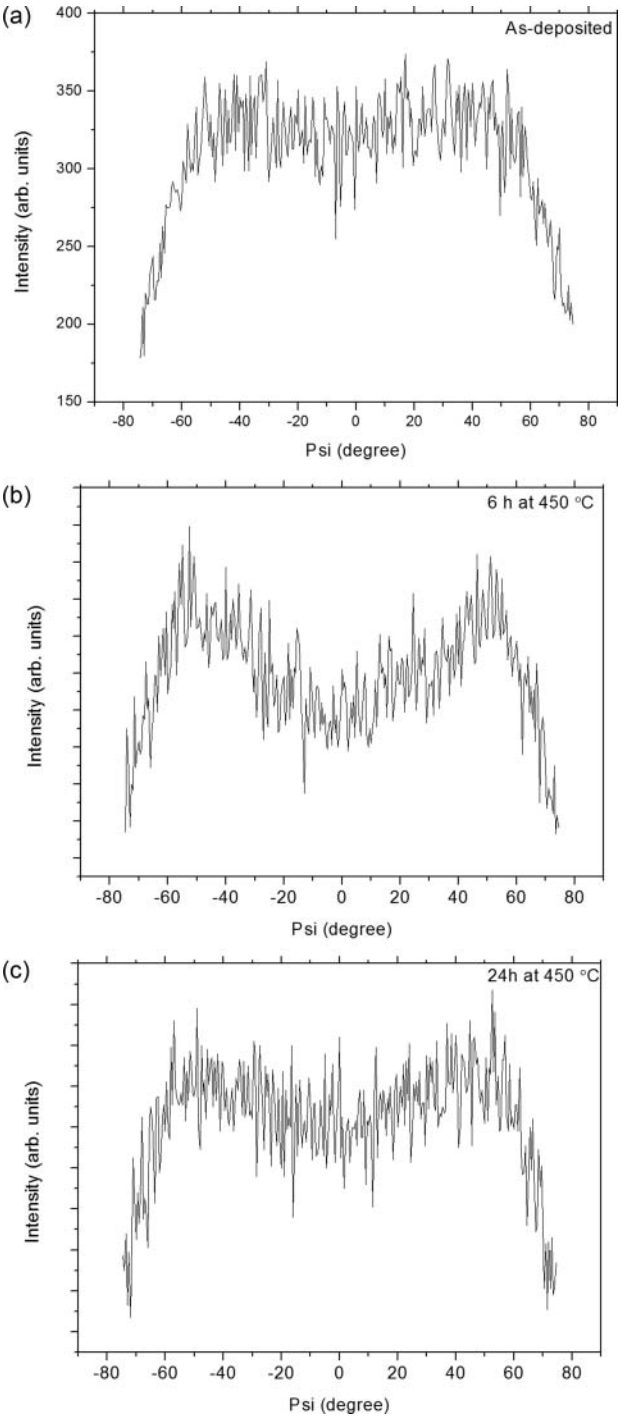

Figure 2. Psi rocking curves acquired at cubic (311) plane: (a) as deposited (b) 6 h at 450°C and (c) 24 h at 450°C.

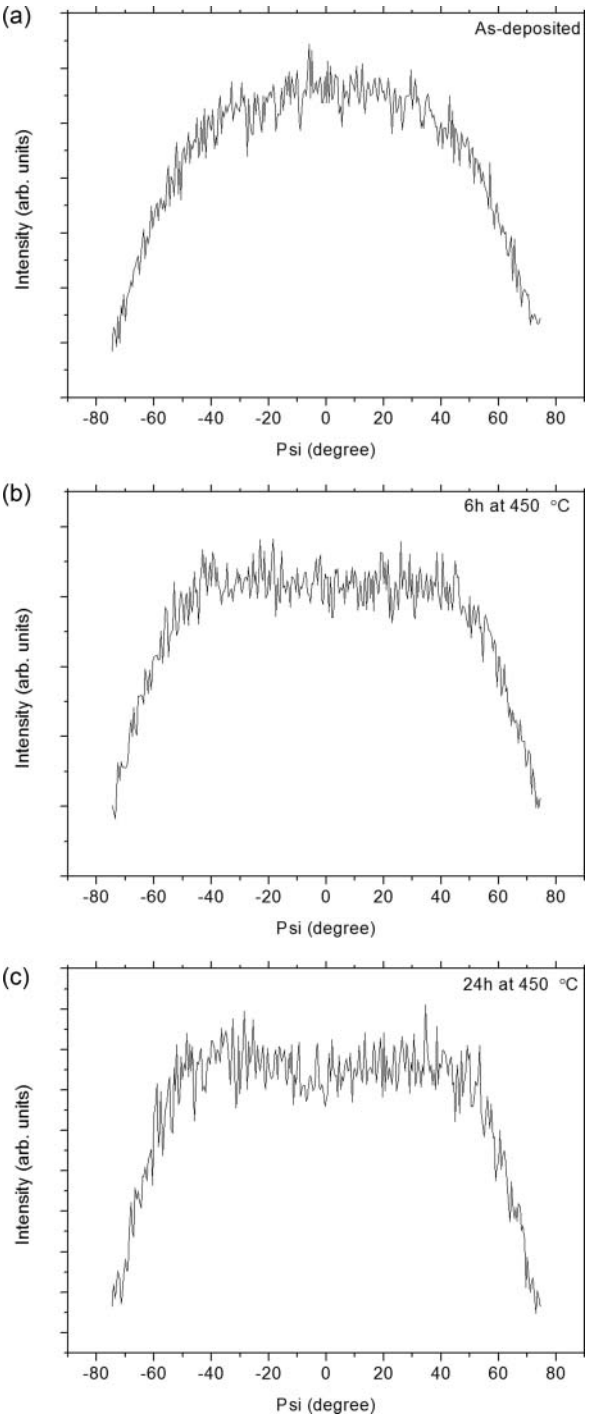

Figure 3. Psi rocking curves acquired at hexagonal (101) plane: (a) as deposited (b) 6 h at 450°C and (c) 24 h at 450°C.

to the intrinsic symmetry of cubic crystal structure, apparent diffraction peaks should be detected at specific psi angle (excluding 0°). As-deposited CdS thin films reveal no sharp peaks throughout the whole psi angles as exhibited in Fig. 2(a), while the large amount of the diffraction peaks are detected on the annealed samples indicating the significant increase in crystallite size with the cubic modification. The peak sharpness between 6 h and 24 h shows not monotonic but narrowing and widening behavior proportional to annealing time. It implies that as time passes during annealing, the crystal structure transform from the disordered cubic to the ordered cubic structure. It seems that further heating on ordered cubic structure forces it to transform into hexagonal structure. Figure 3 denotes psi rocking curves acquired at 28.21° (2θ) associated with hexagonal (101) plane. If it has a hexagonal structure, diffraction peak should be observed at the specific psi angle. As-deposited CdS thin films shows a parabolic distribution of hexagonal (101) plane centered at 0 psi position without any apparent sharp peaks as exhibited in Fig. 3(a). As the annealing time increases, though absolute intensity is weak, the observed diffraction peaks gets sharper. It suggests that the hexagonal phase portion within CdS thin films are prevailing after sufficient annealing time. It implies that as time passes by during annealing the hexagonal structure transform from the disordered cubic to the ordered cubic structure.

The combined analysis with psi rocking curve obtained at cubic (311) and hexagonal (101) plane proposes that at initial stage during annealing cubic phase and hexagonal phase crystallize into itself, after that the phase transition from the ordered cubic phase to hexagonal phase. This hypothesis is well fitted with other experiments related with energy gap shift depending on the CdS crystal structure. Zelaya-Angel et al. [19] reported that the energy gap of CdS films decreases with increasing thermal annealing temperature, reaching a minimum of 2.28 eV at critical temperature, and then increases rapidly in a roughly symmetrical way with increasing temperatures. This phenomenon can be explained by a narrowing-widening-like behavior. According to their analysis, such phenomenon shows that at critical temperature a transition occurs from cubic to hexagonal structure. However, the analysis related with band gap decreasing region was not provided evidently in the paper. Based on the our results, it can be suspected that the interatomic spacing of amorphous structure would be relatively long and more disordered than crystalline structure due to the

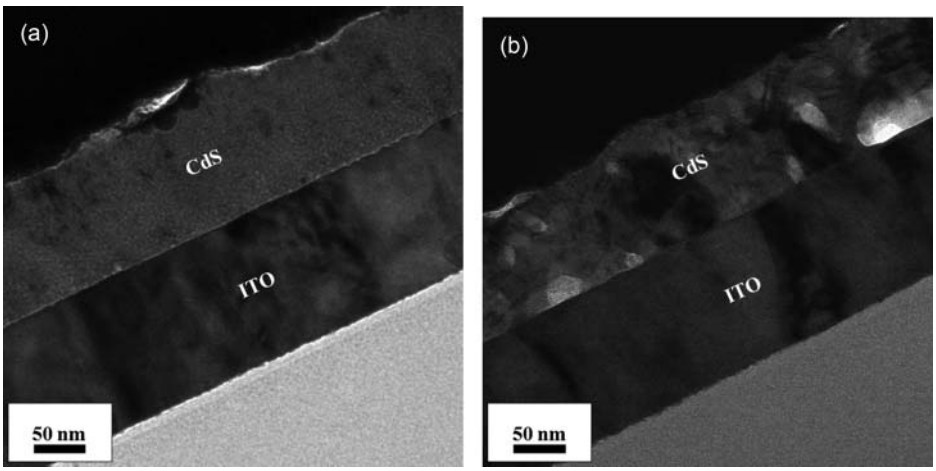

Figure 4. Cross sectional STEM images as deposited CdS thin films (a) and after annealing during 24 h at 450°C (b).

absence of long-range translational periodicity. As the fraction of amorphous CdS phase increases in the films grown at low temperature, the extended localization in the conduction and valence bands increases [20]. As a result, the absorption of photon is mainly contributed by amorphous CdS and hence the absorption edge appears the blue-shift. On the other hand, for samples annealed at higher temperature around 400°C, the crystallinity of CdS thin films becomes better. Therefore, the optical band gap reduces to that of the crystalline CdS.

Figure 4 represents cross sectional images of CdS thin films before and after annealing. As shown in Fig. 4(a), it is hardly to observe the grain of CdS films because of nanocrystalline grain size. On the contrary, for the films after annealing, about 60 nm size grain is clearly detected. It implies that the poor crystal quality of the films grown at low a temperature can be greatly improved by annealing. This result coincides with the results argued in the XRD analysis.

4. Conclusion

In summary, experimental results indicate the phase transformation from the as-deposited metastable nanocrystalline cubic phase of the CdS film to the stable polycrystalline hexagonal after annealing. Thus, after annealing the film at a higher temperatures, recrystallization takes place and the hexagonal polycrystalline phase prevails over the amorphous and/or nanocrystalline one. The phase transformation is probably occurred due to the increase in crystallite size, the change of an interatomic spacing and the crystal structure of the CdS thin films.

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