

Structural and optical properties of $(ZnO)_x(CdO)_{1-x}$ thin films obtained by spray pyrolysis

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Thin films of $(ZnO)_x(CdO)_{1-x}$ oxides were deposited on glass substrates by spray pyrolysis and annealed in air at 450º C. The structural and optical properties of the as grown and thermal annealed thin films are presented. The crystalline structure was studied by X-ray diffraction (XRD) having found the presence of the CdO cubic phase pattern for low Zn concentrations and a mixing of cubic-CdO and hexagonal-ZnO phases for low Cd concentrations. The crystallinity of all samples improves with the thermal annealing. The optical band-gap was also studied from the optical transmittance for the as grown and annealed samples. As expected, the band-gap changes between that for pure CdO and that for ZnO.

1. Introduction

Transparent conducting oxide (TCO) thin films have been widely used in solar cells applications. CdO and ZnO have high transparency in the visible region of the electromagnetic spectrum and show n-type conductivity, mainly due to oxygen vacancies. With a ranging band gap of 2.2-2.7 eV [1], CdO present the advantage of a low resistivity with respect to the high values obtained for ZnO, but this exhibits a higher transparency, having a band gap around 3.2 eV. It is known that it is difficult to obtain simultaneously a high transmission coefficient in the visible region and good conductivity qualities [2], however a ternary compound which combines these properties in a controlled way may allow the optimization of the window layer.

On the other hand, it is usual that for solar cell fabrication several deposition and thermal treatment steps are necessary in order to improve the photovoltaic characteristics. Many of these steps are made in the temperature range of 350 - 500^0 C, after the deposition of the window materials [3-5]. From this point of view, it is very important to know the post-thermal annealing effect on the properties of the window thin films, if we want to use them as heterojunction partners on different solar cells. In this paper, we report the effect that a post-annealing at 450º C in air causes on the structural and optical properties of cadmium-zinc oxide with variable composition x, grown by spray pyrolysis.

2. Experimental details

The films were grown onto corning glass substrates, using a typical spray pyrolysis system. The experimental setup used is similar to that described in reference [6]. The spray solution was prepared by mixing the appropriate volumes of cadmium acetate (0.1 M) and zinc acetate (0.1 M) dissolved in a mixture of methanol and deionized water (1:1). The substrate temperature was fixed at 250ºC and was controlled within ± 5 ºC through a thermocouple (chromel-alumel) as a sensor for the temperature controller. The solution flow rate and gas pressure was kept constant at 5 ml/min. and $5x10^4$ Kg/m^2 respectively. N_2 was used as the carrier gas. The distance between the nozzle and the substrate was 0.25 m. Taking into account the growth rate for each composition x [6], the samples were grown for different deposition times in order to obtain similar thickness for all films of about 0.35 μm. The X-ray diffraction spectra were obtained by means of a D-500 Siemens X-ray system using the Cu-K_α line. Optical transmission data were obtained with an UV-Visible Shimadzu 3101 PC double beam spectrophotometer. The band-gap was obtained from the transmission spectra, and the layer thickness was measured with a Sloan Dektal II profilometer. The sample post-deposition thermal treatments were performed in a open quartz tube furnace in an air atmosphere at 450^0 C for two hours. For each sample with different composition (x = 0; 0.25; 0.50; 0.75 and 1), the structural and optical properties were measured, before and after the annealing.

3. Results

Figure 1 shows the X-ray diffraction patterns for samples grown with different compositions at 250 °C. For x=0 (CdO), two different peaks were identified as the (111) and (200) reflections of the cubic structure with a lattice parameter of 4.71 Å. For x=1 (ZnO) three peaks related to the (100), (002) and (101) planes of the hexagonal structure are observed with lattice parameters

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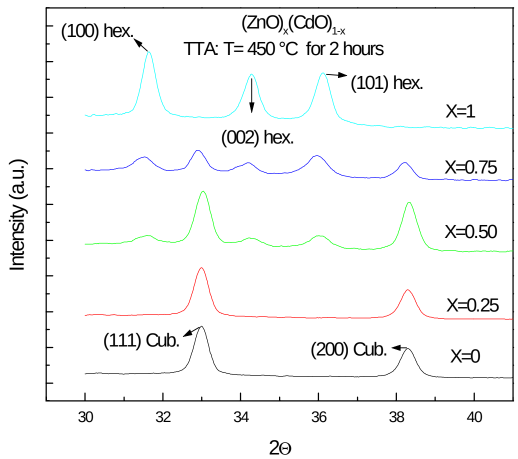

Fig. 1. X-ray diffraction patterns for different compositions (x) of as-grown $(ZnO)_x(CdO)_{1-x}$ thin films.

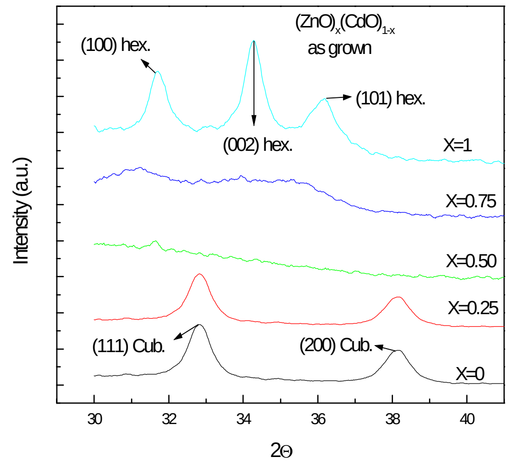

Fig. 2. X-ray diffraction patterns for different compositions (x) of $(ZnO)_x(CdO)_{1-x}$ films annealed for two hours in air.

a=3.24 Å and c=5.20 Å. Notice that the XRD patterns for x=0.25 resemble the pattern for pure CdO. This fact could be associated to the poor crystallinity of ZnO resulting from the low temperature used. When the samples were annealed in an air atmosphere during two hours (Fig. 2), the peaks corresponding to the CdO and ZnO structures were present for samples with intermediate compositions (x = 0.50 and x = 0.75), telling us about the re-crystallization and the formation of a mixed oxide. For these compositions a defined mixing of CdO and ZnO phases is observed. A relative lower intensity of the peaks is obtained when the concentration of Zn is increased. This fact could be associated to a poor crystallinity of ZnO respect to CdO. For the ZnO sample, the film as deposited exhibits a (002) preferential orientation, but it changes to a (100) orientation after the thermal annealing. This result is in agreement with those obtained for $Zn_xCd_{1-x}O$ compounds grown by sol-gel [5].

Optical transmission spectra for as-grown films are shown in the Fig. 3. When the samples are annealed, a shift to lower energy in the transmission threshold and a reduction of the average transmission are observed, as can be seen in the Fig. 4. This behavior varies with the value of the composition x. Band-gap (calculated by using α^2 Vs photon energy plot), for the as-grown and annealed samples as a function of the composition x is shown in Fig.5. Note that the band-gap decrease with the thermal annealing, except for x = 0.75, for which the band-gap energy is above that for the as grown sample.

This behavior may be attributed to a transition form a poor crystalline phase to the cubic-hexagonal mixing phase. A similar behavior has been found for CdS thin films grown by chemical bath and annealed at different temperatures and atmospheres, where a transition from cubic to hexagonal phase has been

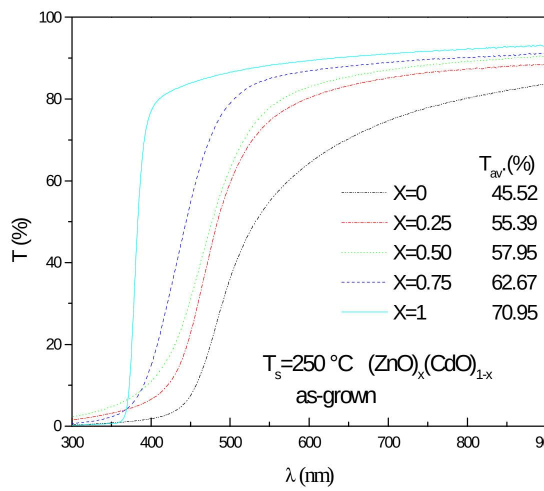

Fig. 3. Optical transmission spectra of as grown $(ZnO)_x(CdO)_{1-x}$ films.

reported [7,8]. The band gap energy corresponding to x=0 decreases to 2.29 eV with the annealing for two hours. The values of the band-gap energy and the lattice parameter corresponding to x = 0 for this annealing time are in agreement with the reported values reported for bulk CdO [9].

This observation shows that the changes in the band-gap values in the annealed samples are associated to a size growth of the crystallites. This mechanism is related to the post-deposition thermal treatment and will be studied in detail in future works.

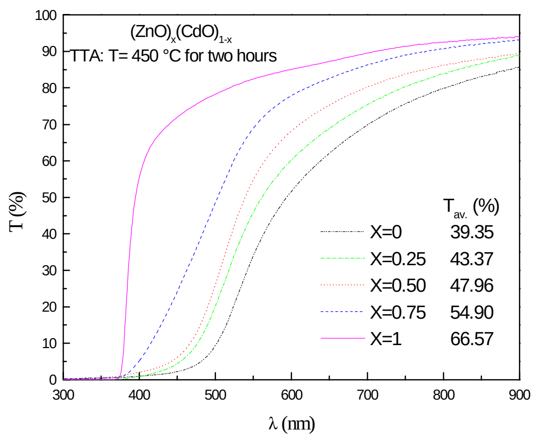

Fig. 4. Optical transmission spectra of $(ZnO)_x(CdO)_{1-x}$ films annealed for two hours in air.

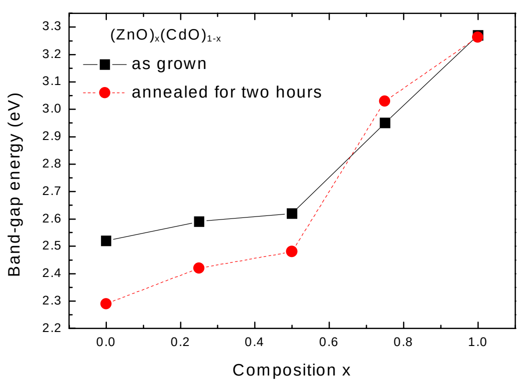

Fig 5. Band-gap variation for the as grown and annealed samples as a function of the composition x.

4. Conclusions

Structural and optical analysis show that spray pyrolysis technique is a useful method for the deposition of $(CdO)_{1-x}(ZnO)_x$ thin films. For $x \geq 0.5$ a mixing phase corresponding to cubic-CdO and hexagonal-ZnO is formed. The hexagonal-ZnO phase has a poorer crystallinity than the cubic-CdO phase, and the prevalent presence of a cubic phase throughout the range $0 \leq x < 0.5$ agrees with the trend observed for $(ZnO)_x.(CuO)_{1-x}$ thin films grown by sol-gel. The lattice parameters variation around x = 0 can be understood due to the lower size of the Zn atom as compared to the Cd atom resulting in a lattice reduction and a band-gap energy increase. Changes in the transmission spectra and on the corresponding values of the band-gap energy are correlated with the intermixing of transparent ZnO crystallites in-between CdO crystallites.

Post-thermal annealing improves the crystallinity of all samples (the FWHM decreases as consequence of the post- thermal annealing processes). The band-gap energy and lattice parameter of pure CdO and pure ZnO reach the reported bulk values at room temperature. Usually a wide variety of band-gap values are reported in the literature for these semiconductor compounds. The band-gap change from 2.29 to 3.28 eV when the nominal composition x is changed from x = 0 to x = 1, respectively, for the annealed samples. The band-gap for each composition is also changed by the post-thermal annealing.

Acknowledgments

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