

Influence of annealing temperature on properties of nanocrystalline CdO thin films synthesized via thermal oxidation process

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Abstract: Chemical bath deposited CdS thin films have been annealed in air at different temperatures to obtain CdO films via thermal oxidation route. The obtained nanostructured and highly transparent thin films of CdO have wide range of applications in solar cells, smart windows, optoelectronic devices, gas sensors; etc. The influences of annealing temperature on structural, morphological, optical and solid state properties of prepared CdO films have been investigated. The techniques used for the investigation includes x-ray diffractometry, scanning electron microscopy, UV-VIS spectroscopy. The optical energy band gap and other optical constants were evaluated

Keywords: cadmium oxide, nanostructure, thin films, thermal oxidation, CO gas sensor

1. Introduction

Metal oxide materials in thin film form have attracted major attention due to its wide spread applications in the fields of solar cells, optoelectronic devices, temperature controllers in satellites, flat panel displays, photoresistors, etc. [1, 2] CdO, ZnO, BaO and Cu₂O thin films are the alternative for terrestrial solar cells [3,4]. These are the materials with larger bandgap in comparison to CdS, ZnS; helps to increase the photocurrent of solar cells. Therefore CdO-ZnO are the better replacements for CdS, ZnS. Thin films of cadmium oxide (CdO) have been prepared by variety of routes, such as spray pyrolysis [5], sputtering [6], sol gel [7], chemical bath deposition technique (CBDT) [10]. CBDT is most common, inexpensive, convenient and controllable method for large preparation of thin films at low temperatures [8,9]. At earlier, our group have been reported a new approach to fabricate nanostructured CdO films by post thermal annealing treatment over CdS thin films prepared through controlled chemical reaction bath [10]. In this work, the special emphasis is given for the study of influence of annealing temperature on various properties of thermally oxidized CdO thin films.

2. Experimental

To prepare CdO films, aqueous solutions of cadmium sulphate and thiourea with calculated proportion was added in 130 ml of de-ionized water. Complexing agent ammonia was added slowly to adjust the pH between 9.5 and 10. The solution was stirred and transferred to another container containing substrate. The resulting solution was kept at $70 \pm 2^\circ\text{C}$ for 1 hour. The substrate used is commercial glass slide. Cleaning of substrate is important in fabrication of thin films, cleaning steps and growth procedure is reported elsewhere [11-13]. After 20-30 minutes the bath solution in beaker turned yellowish, thus indicating the onset CdS deposition on the glass slide. After a reaction time of 1 hour the glass slides were taken out and dried in air for 15 minutes. Then for the post annealing treatment in air, the as-deposited CdS films were kept in the oven at various temperatures between 400°C and 750°C for 10 hours. The CdS films get oxidized in the oven to form highly transparent thin films of CdO. Film thicknesses of obtained films have been measured using weight difference method. The technique used for the study of crystal structure was x-ray diffractometry (EXPERT-PRO) by using Cu- K_α lines ($\lambda = 1.542\text{\AA}$). The average grain size was obtained by Debye-Scherrer's formula. Surface morphology was examined by JEOL model JSM-6400 scanning electron microscope (SEM). The optical transmission spectra for a range of samples were obtained in UV-VIS-NIR region using Perkin-Elmer UV-VIS lambda-35 spectrophotometer [13].

3. Results and Discussio

3.1 Structural properties

Fig. 1 shows the X-ray diffraction pattern of CdO thin film obtained from post annealing treatment over CdS films at temperature 600°C . The XRD study confirms that the films annealed in air at higher temperature ($>500^\circ\text{C}$) gets completely oxidized in the oven to form CdO thin films. The film shows a phase transition from cubic to pure hexagonal at higher annealing temperatures. The film shows reflections from (111), (200) and (220) planes at 600°C , indicating the formation of CdO nano particles having pure hexagonal structure (matches with JCPDF data). The average size of grain (g) have been obtained from the XRD patterns using Debye-Scherrer's formula, [12-14]

$$g = K\lambda / \beta \cos\theta \quad (1)$$

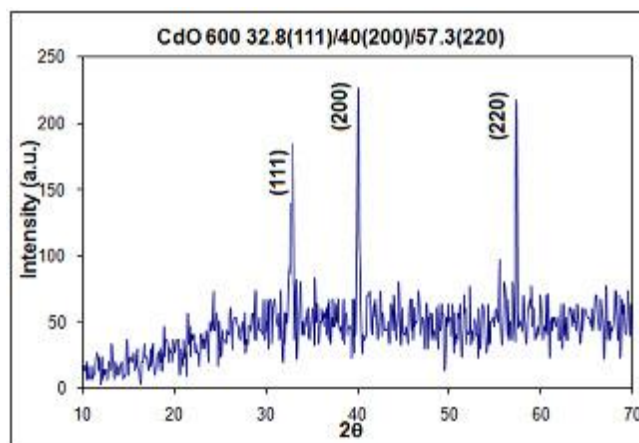


Figure 1: XRD pattern of CdO thin film annealed at 600°C .

Where, K = constant taken to be 0.94, λ = wavelength of X-ray used (1.542\AA), β = FWHM of the peak and θ = Bragg's angle. The grain sizes were found to be within the range from 16 to 29 nm. The sharp peak shows the good crystallinity of the films. The average value for lattice parameter is 0.4684 nm.

3.2 Surface Morphology

Fig.2 shows the SEM images at different magnifications of nanocrystalline CdO thin films obtained at 750°C . It shows a uniform film, without any cracks and the substrate is well covered. The high magnification SEM image of CdO shows numerous nano walls, interconnected to each other which forms the surface area with more textured. This morphology is advantages for effective light harvesting in photovoltaics and/or solar cells. This makes the prepared CdO films applicable for transparent conducting oxide (TCO) layer used in solar cells. The average grain size obtained from SEM is same as that of obtained from XRD.

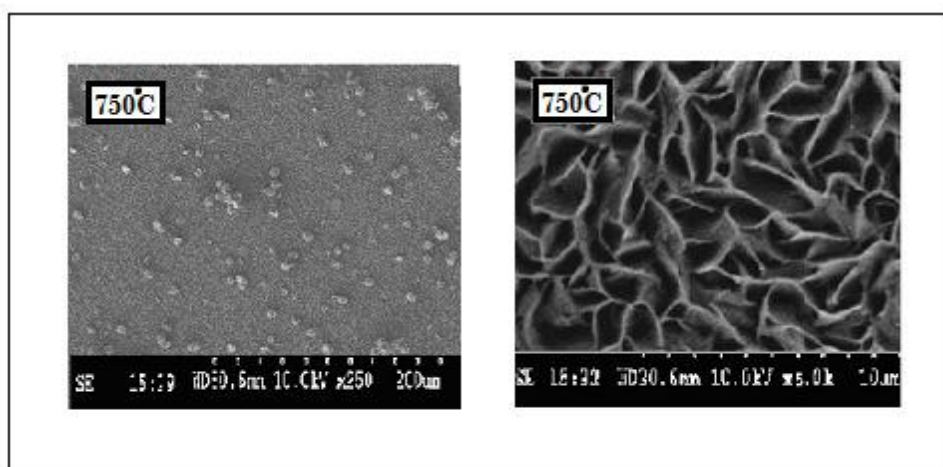


Figure 2: SEM images at different magnifications of CdO thin films obtained at 750°C .

3.3 Optical and solid state properties

Fig.3 shows the optical transmission spectra of CdO thin films in the wavelength range from 200 to 1000 nm for various annealing temperatures.

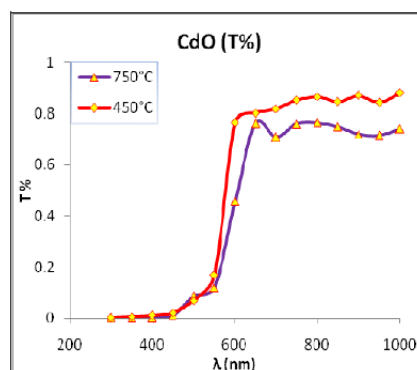


Figure 3: Optical transmission spectra of CdO thin films fabricated at 450°C & 750°C .

All the films are highly transparent in the visible region with an average transmittance of 81%. The sharp rise in transmission is an identification of good crystallinity of films. It is observed that the films obtained at higher annealing temperature shows slightly less transmittance in visible region as compared to the films obtained at lower annealing temperature. These results slightly increase in optical band-gap of the film and it may be due to the small grain size of the polycrystalline films.

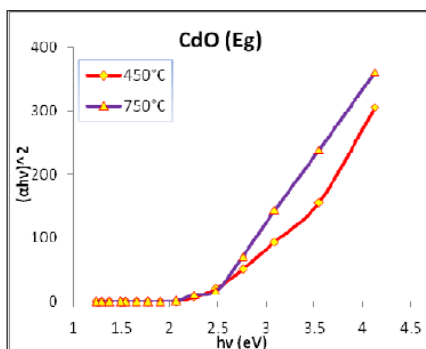


Figure 4: Plot of $(\alpha hv)^2$ vs. $h\nu$ of CdO thin films fabricated at 450°C & 750°C.

The optical energy band gap (E_g) was determined by plotting $(\alpha hv)^2$ versus $h\nu$ and then extrapolating the straight line portion to the energy axis at $\alpha = 0$ (Fig. 4). The band gap energy obtained for each film is different. It was observed that the band gap of CdO films obtained at higher annealing temperature is 2.45eV whereas it is 2.32eV for the films obtained at lower annealing temperature. This difference of 0.13eV in optical band-gap of CdO films may be due to the difference in grain size.

Table 1: Optical & solid state constants of CdO thin films prepared at various annealing temperatures.

Annealing temp. (°C)	Energy bandgap (eV)	Average n	Maximum k	Maximum ϵ_r	Maximum ϵ_i	Maximum $\sigma \times 10^{13} S^{-1}$
450°C	2.32	2.097	0.160	5.18	0.656	19.1
750°C	2.45	2.102	0.197	5.37	0.877	23.2

The optical and solid state constants of CdO films prepared at various annealing temperatures were evaluated. The observed optical and solid state constants were illustrated by table 1. It clearly indicates an increase in refractive index (n), extinction coefficient (k), dielectric constants (ϵ_r, ϵ_i) as well as optical conductivity (S) of the films with increase in annealing temperature. It suggests an improvement in the quality of the film at higher annealing temperature, makes the films more suitable for optoelectronic applications.

4. Conclusions

Nano-structured CdO thin films were successfully prepared by post annealing treatment over CdS films at high temperatures for more than 8 hours. The obtained films were thermally oxidized showing comprehensive results. XRD study reveals the phase transition from cubic to pure hexagonal which is due to the annealing treatment. All the films show pure hexagonal structure. The sharp peaks show good crystallinity, resulting in high quality films. The grain size estimated is in the range of 16 to 29nm. The nanostructured grains densely packed in the form of nano walls improves the quality of the film. As a result the film shows high transmission and increased band gap which makes the films suitable for various optoelectronic and sensor applications.

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