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Low temperature synthesis and characterization of nanocrystalline CdO film by using a solvothermal method without any additives

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Abstract: Cadmium oxide film is synthesized via solvothermal method which benefits from simple low temperature technique. A uniform and crack free film of CdO is coated on a glass substrate. The synthesized film is annealed at 350°C for 1 hour in order to produce pure phase of CdO with good adherence. Films are characterized by X-ray diffraction, scanning electron microscopy (SEM), thermogravimetric (TGA)- differential thermal (DTA) analysis, Fourier Transform Infrared (FT-IR) and Photoluminesence (PL) spectroscopy. Grain size of the annealed film is proved to be about 30-100 nm. Band gap was also calculated using UV-Visible spectroscopy.

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Introduction

Cadmium oxide (Eg ~2.3eV) is an n-type semiconductor and one of the promising transparent conducting oxides (TCO) with high electrical conductivity which has found extensive applications in electronic, optical devices and other applications like transparent conducting oxide (TCO), solar cells, smart windows, optical communications, flat panel display, photo-transistors, photodiodes, transparent electrodes and gas sensors [1-5].

Band gap values higher than 3eV have also been reported for CdO films deposited by CVD method [6]. Various techniques, such as spray pyrolysis, sputtering, activated reactive evaporation, sol-gel and chemical bath deposition (CBD), have been employed for CdO thin film preparation [7-11]. Here, we report a low temperature solvothermal method to obtain cadmium oxide film from cadmium acetate dihydrate in methanol as starting solution. X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric (TGA) and differential thermal (DTA) analyses, Fourier Transform Infrared

(FT-IR), UV-Vis and (PL) spectroscopy are applied for characterization of the sample.

Experimental

Precursor solution of cadmium acetate dihydrate in methanol (0.15M) was prepared in a 100 ml pyrex bottle, without using any additives, and vigorously stirred for 20 min at room temperature. A glass slide (75mm×25mm×1mm) was cleaned with mild soap solution, thoroughly washed with deionized water, cleaned ultrasonically in acetone, and finally dried over nitrogen gas stream. The glass substrate was entered into the reaction mixture and leaned against the bottle wall. The system was then sealed and heated to 60°C for 55 hours. As prepared films were cooled to room temperature, rinsed with ethanol, and dried. Annealation was performed at 350ºC for 1 hour in air. Thickness of the synthesized film was measured by cross sectional SEM (Holland Philips XL30 microscope). Structural properties of the film were also studied using XRD (Holland Philips X-pert) ($\lambda CuK\alpha$ = 1.5406 Å, rate = 2°/min, 2θ = 10°-80°). FT-IR (Bruker, Equinox 55), TGA, and DTA (PL-STA 1500) analyses were applied for further characterization. The optical studies were carried out on UV-Vis. spectrophotometer (Shimadzu 2100). The PL spectra were recorded on a Varian Cary-Eclipse spectrometer at room temperature.

Results and discussion

XRD patterns of as-prepared and annealed films are depicted in Figure 1a and b, respectively. (111), (200), (220), (311) and (222) reflections in Figure 1b indicate that the annealed film is polycrystalline in nature and has cubic structure (JCPDS 05-0640). Mean crystallite size corresponding to the annealed film is calculated to be 32.5 nm for (111) reflection using Scherrer's formula, D = (0.9 λ)/(βcosθ) [12]. A porous morphology having fine nanostructure is detected by scanning electron microscopy (Figure 2). Cross sectional SEM analysis showed a thickness of ~7.1 μm for the film.

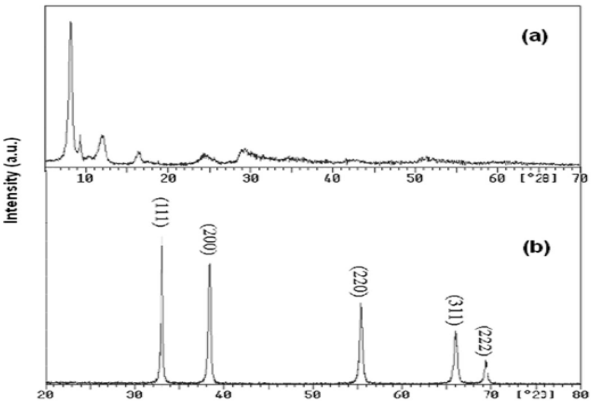

Figure 1 XRD patterns of as-prepared (a) and annealed films (b).

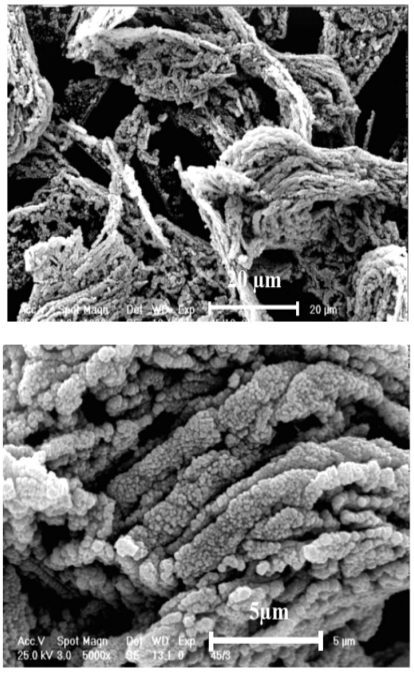

Figure 2 SEM images of annealed CdO film.

Residual powder formed in the reaction vessel was collected, washed with ethanol, and dried in air. Thermal decomposition behavior of the collected powder was investigated in static air atmosphere from ambient to 700°C and studied by thermal gravimetric (TG) and differential thermal analysis (DTA) (Figure 3). Decomposition of compound begins at 60°C. The

initial weight loss ~13.0% observed in TGA curve between 160-200ºC corresponding to elimination of adsorbed and intercalated water with a small endothermic effect. A loss of weight of ~25.0% at about 295ºC is assigned to decomposing of acetate groups with three exothermic effects. The solid residue formed at around 350°C is suggested to be CdO. These losses of weights are matching with the computed values.

The powder was also characterized by FT-IR analysis (Figure 4(a)). The three fundamental bands in 1300-1600 cm^{-1} region correspond to the acetate group and the broad band at 3500 cm^{-1} is assigned to the stretching vibration of OH. In the annealed CdO film, no absorption bands are detected for acetate groups (Figure 4(b)). The CdO is a material with a direct band gap in the range: 2.2-2.7 eV [13]. According to Figure 5, band gap energy of annealed CdO powder, collected from the reaction vessel, can be obtained through UV-Vis [14]. Eg is calculated to be about 2 eV which is in good agreement with those reported in the literature [10, 15].

The photoluminesence (PL) spectrum of the CdO nanocrystaline were shown in figure 6. According to the figure, a blue – green emission are observed in the PL spectrum of the sample, which is considered due to transition between valence and the conduction bands [16].

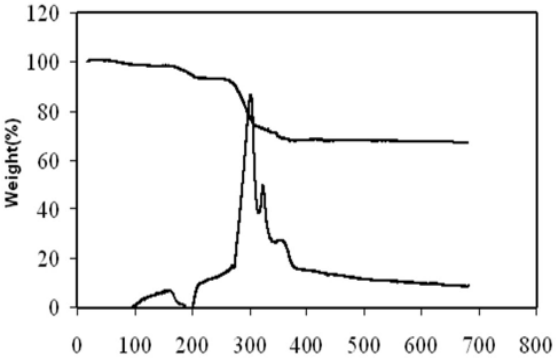

Figure 3 TGA-DTA curves corresponding to residual powder formed in the reaction vessel.

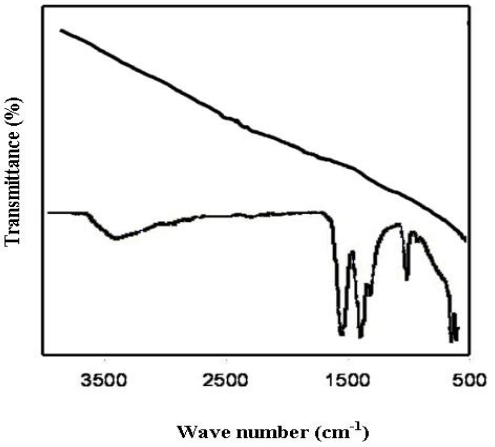

Figure 4 FT-IR spectra before (a) and after annealation (b).

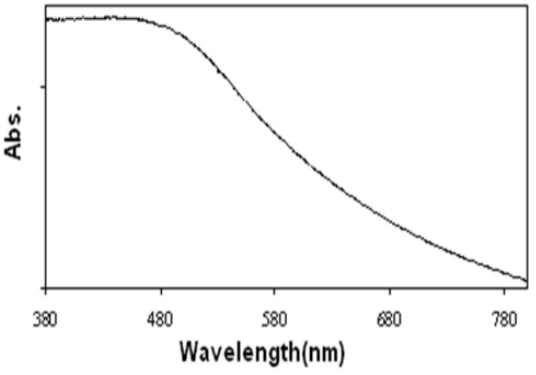

Figure 5 UV-Vis. spectrum of annealed CdO powder.

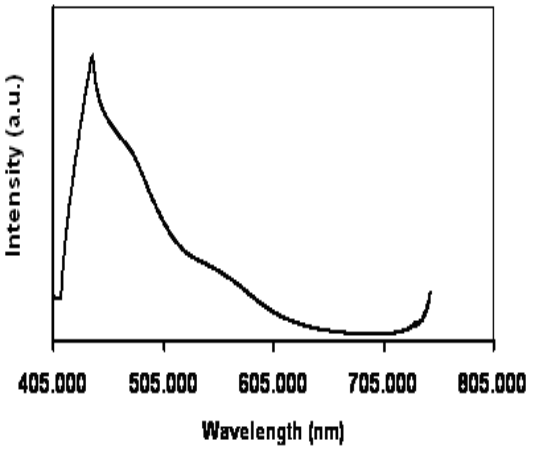

Figure 6 PL. spectrum of annealed CdO film.

Conclusion

We have successfully prepared cadmium oxide film on glass substrate via solvothermal method by using cadmium acetate dihydrate as starting material. The film was annealed at 350ºC in order to remove organics. Average crystallite size of 32.5 nm was calculated for the annealed film. SEM micrograph revealed a porous morphology having fine nanostructure and cross-sectional SEM measurement indicated a thickness of ~ 7.1µm for the film. FT-IR and TG-DT analyses also confirmed formation of CdO film. UV-Vis. studies revealed a band gap of about 2 eV for the CdO powder. Photoluminesence (PL) spectrum show that the transition between valence and the conduction bonds has a blue–green emission.

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