Structural, morphological and optical properties of CdO nanostructures synthesized by chemical bath deposition method

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Abstract

In the present work, we have successfully synthesized CdO nanostructures with various molar concentrations by a two-step chemical method. The crystal structure of our nanostructured CdO thin films is cubic phase while the microscopic images show the formation of nanoparticles, spindles, and coconut fiber bark shaped CdO nanostructured films. These different structures were achieved merely by controlling the molar concentration of cadmium nitrate tetrahydrate and hexamethylenetetramine. The size of the CdO nanostructure slightly increases monotonically with molar concentration. Our chemical synthesis approach is inexpensive, reproducible and scalable.

Keywords: Semiconductor, CdO nanostructures, Chemical method, Optical absorption,

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1. Introduction

The transparent conducting oxide (TCO) thin films such as titanium oxide (TiO_2), copper oxide (CuO), zinc oxide (ZnO), tin oxide (SnO_2) and cadmium oxide (CdO) have been widely

used in many technological applications [1-5]. Among them, CdO with a typical band gap of 2.2 eV is one of the most important semiconductors for potential applications in solar cells, photodetectors, and gas sensors [6-8]. Millesi et al. [9] have prepared nanostructured CdO thin films using metal organic chemical vapor method and have achieved nanoparticles with cubic crystal structure and 22 nm size, oriented along the (200) plane. Nanostructured CdO films were prepared by Imer [10] using ultrasonic spray coating technique and reported that the band gap of the CdO film could be modified by Al doping. Sahin et al. [11] have reported that the band gap of CdO films reduced with an increase of annealing temperature. Cubic phased CdO films were also been synthesized by Khallaf et al. [12] using chemical bath method. Kaviyarasu et al. [13] have reported the formation of CdO nanofibers with diameters of around 40 nm and lengths of few microns.

Recently, CdO thin films have been synthesized by various techniques such as thermal evaporation, pulsed laser deposition, metal organic chemical vapour deposition, chemical bath deposition, spray pyrolysis, successive ionic layer adsorption and reaction, magnetron sputtering and microwave irradiation technique. In this work, we employed two-step chemical method to deposit nanostructured CdO thin films with different molar concentrations. The structural, morphological and optical properties of nanostructured CdO thin films were analyzed and reported. Our chemical method to make nanostructured CdO films could be useful because of its low cost, reproducibility and ability to produce in large scale.

2. Experimental details

The synthesis process for our nanostructured CdO thin films includes two-steps: synthesis of CdO thin films as the seed layers using sol-gel spin coating techniques, and then CdO nanostructures grown by chemical bath deposition method. For the preparation of seed

layer CdO films, cadmium acetate dihydrate ($Cd(CH_3COO)_2.2H_2O$) (0.5 M) and ethanolamine ($H_2NCH_2CH_2OH$) (0.5 M) were dissolved in 2-methoxyethanol (10 mL) and solution was stirred for 2 hour. The sol was dropped onto a substrate and spin-coated at 3000 rpm. Finally, the films were annealed at 500 °C for 1 hour. In the second step, cadmium nitrate tetrahydrate ($Cd(NO_3)_2.4H_2O$) and hexamethylenetramine ($(CH_2)_6N_4$) (0.01M, 0.03M, 0.05M and 0.07M) were dissolved in deionized water. The molar ratio of cadmium nitrate to hexamine was kept at 1:1. The CdO seed layer substrates were vertically immersed in the solution, which was heated at 90°C for 4 hours for film deposition. After that, nanostructured CdO films were cleaned with deionized water and annealed at 500°C for 1 hour.

The crystal structures of the CdO films were confirmed by x-ray diffraction (XRD) method (New D8 Advance). The elemental analyses of the CdO films were done by x-ray photoelectron spectroscopy (XPS). The morphology of the CdO films was investigated with a Zeiss Supra 55VP field emission scanning electron microscope (FESEM). A spectrophotometer (JASCO V-570) was utilized to measure the optical absorbance spectra of CdO films.

3. Results and discussion

We first characterized the structure, crystallinity of synthesized CdO films. X-ray diffraction patterns of CdO films with various molar concentrations are shown in Fig. 1a. Three peaks appear at (111), (200) and (220) were indexed to the cubic phase of CdO (JCPDS Card No.: 05-0640). The absence of other impurity peaks suggested the formation of highly pure CdO nanostructures. The lattice constant (a) has been calculated and is found to be a = 4.70 Å. The increase of peak intensities with molar concentration implies the crystallinity improvement when we increased the molar concentration. The crystal size of the CdO films can be calculated by Scherrer's formula: $D = K\lambda/\beta \cos\theta$, where D is the grain size, K is a constant taken to be 0.94,

λ is the wavelength of the x-ray radiation, β is the full width at half maximum and θ is the angle of diffraction. The grain size was found to be 31.5±0.3 nm, 32.7±0.2 nm, 34.3±0.4 nm, and 35.4±0.3 nm for 0.01M, 0.03M, 0.05M, and 0.07M CdO films respectively. Our observation that the crystallinity and the grain size of the CdO films were increased with higher molar concentration is in good agreement with reports by Salunkhe et al. [14] and Beevi et al. [15].

We investigated the composition of CdO thin films using x-ray photoelectron spectroscopy (XPS). The results for CdO films with concentration of 0.03M and 0.07M are shown in Fig.1 (b-c). The XPS peaks of $Cd3d_{3/2}$ and O1s at 412.75 eV and 538.96 eV were observed to confirm the present of Cd and O in the films.

The different morphologies of CdO films including nanoparticles, nanospindles and coconut fiber bark shaped nanostructures were observed as shown in Fig. 2. The FESEM images of CdO films (Fig. 2a, b) grown by chemical bath deposition with 0.01 M concentration clearly show that grains are agglomerated. Fig. 2(c, d) reveals the morphology of CdO films prepared with 0.03M concentration. We can see that the grains start to form spindle-shaped nanostructures due to Ostwald ripening [16] and furthermore the formation of nanospindle-like CdO structures is confirmed in the FESEM images of CdO synthesized using 0.05M concentration (Fig. 2(e, f)). With increase in molar concentration, the spindle-shaped nanostructures start to self-assemble in to coconut fiber bark shaped nanostructures as observed for the CdO films grown with 0.07M concentration (Fig. 2(g, h)).

The growth process of the nanostructured CdO films can be understood by looking at the chemical reactions involved in the synthesis. The aqueous solution of cadmium nitrate tetrahydrate ($Cd(NO_3)_2.4H_2O$) and hexamethylenetetramine ($(CH_2)_6N_4$) are represented by the following chemical reaction [17].

$$C_6H_{12}N_4 + 6H_2O \rightarrow 4NH_3 + 6HCHO \quad (1)$$

$$NH_3 + H_2O \rightarrow OH^- + NH_4^+ \quad (2)$$

$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2 \quad (3)$$

The hexamethylenetetramine is hydrolyzed with heat, it produces ammonia (NH_3) and formaldehyde (HCHO). The ammonia reacts with water, producing hydroxyl (OH^-) ions. The cadmium nitrate tetrahydrate reacts with water, forming cadmium (Cd^{2+}) ions. The hydroxyl (OH^-) ions combine with cadmium ions to form cadmium hydroxide ($Cd(OH)_2$). To remove hydroxide phase, cadmium hydroxide films were annealed at 500°C for 1 hour [18].

$$Cd(OH)_2 \rightarrow CdO + H_2O \quad (4)$$

Finally, the formed CdO nuclei tends to grow as spindle-shaped nanostructures with an increase in molar concentration, but further increasing concentration results in the formation of coconut fiber bark like CdO nanostructures. We speculate the possible growth process of the CdO structures as presented in Fig. 3.

The UV-visible absorption properties of all the nanostructure CdO films in the wavelength range from 200 nm to 800 nm were characterized by UV-VIS/NIR spectrophotometry. Their absorption spectra shown in Fig. S1 presented finite scattering effects especially for concentration of 0.03M where the nanospindle-like structures look porous. At the shorter wavelength, the behavior is dominant by semiconductor absorption. From these absorption spectra (Fig. S1), the band gap of CdO films can be analyzed by Tauc relation.

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^{\frac{1}{2}} \quad (5)$$

where α is the absorption coefficient, h is the Planck's constant, υ is the frequency of light, A is a constant and E_g is the band gap of the material. The plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for CdO films with various concentrations (0.01M, 0.03M, 0.05M and 0.07M) is shown in Fig. S2. The band gaps of the nanostructure CdO films were estimated by extrapolation the straight linear part to energy axis. The band gaps are found to be 2.74, 2.57, 2.43, and 2.32 eV for the nanostructure CdO films grown at concentrations of 0.01M, 0.03M, 0.05M and 0.07M respectively. These band gaps were slightly higher than that of the CdO bulk material (2.2 eV). The band gaps of the nanostructure CdO films decreased with increasing molar concentration, which is associated with increase of CdO nanostructure size. Similar observation about the band gaps and molar concentration was also reported Duman et al. [19]. We suspect that quantum confinement [20] and Burstein–Moss [21] effects increase the band gap of our nanostructure CdO thin films.

4. Conclusion

CdO films were grown by a two-step chemical method and the effect of molar concentrations on structural, morphology and optical properties of nanostructured CdO films was systematically investigated. The x-ray diffraction patterns showed the cubic phase for our CdO films. The x-ray photoelectron spectroscopy analysis confirmed the presence of cadmium and oxygen in the films while other elements are negligible. The formation of nanoparticles, spindles and coconut fiber bark shape nanostructures were observed under field emission scanning electron microscope. The band gap of the CdO thin films decreased with increasing molar concentration. These nanostructured CdO films can be grown easily while their surface morphology, grain size and band gap are tailored by tuning molar concentrations.

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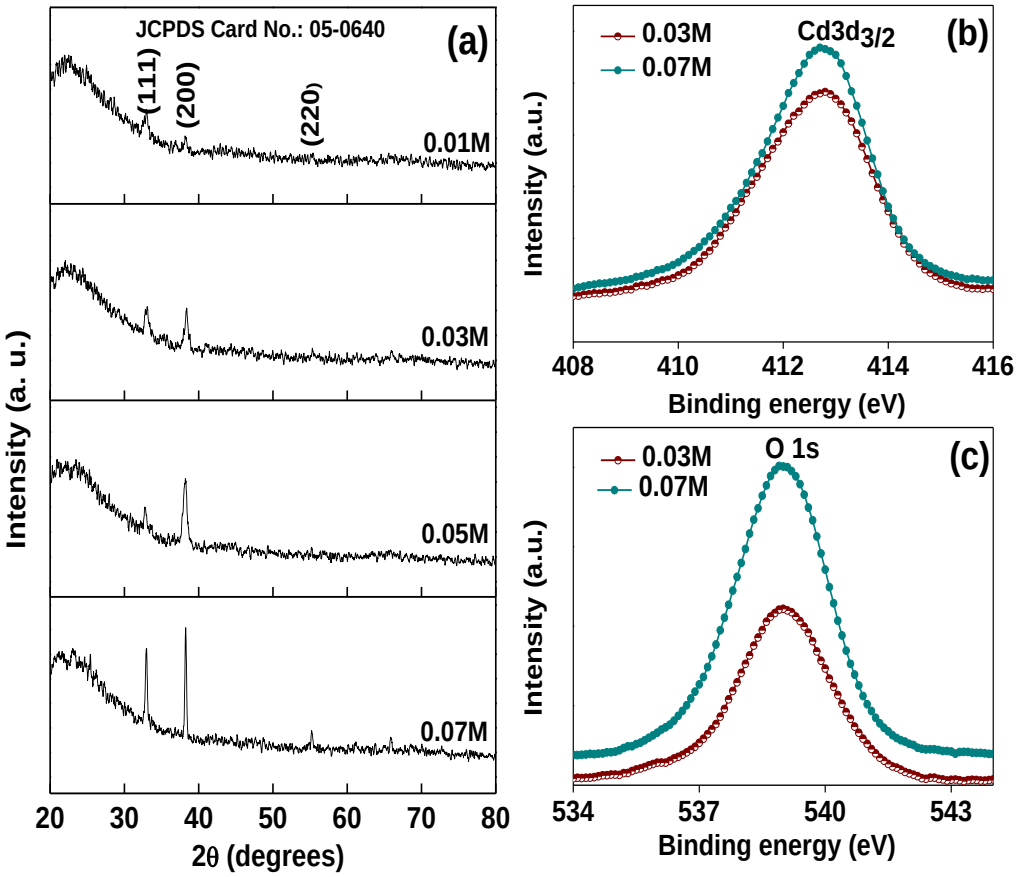

Fig. 1. (a) X-ray diffraction patterns of CdO films with various molar concentrations. XPS spectra of CdO films corresponding to (b) Cd3d, and (c) O1s.

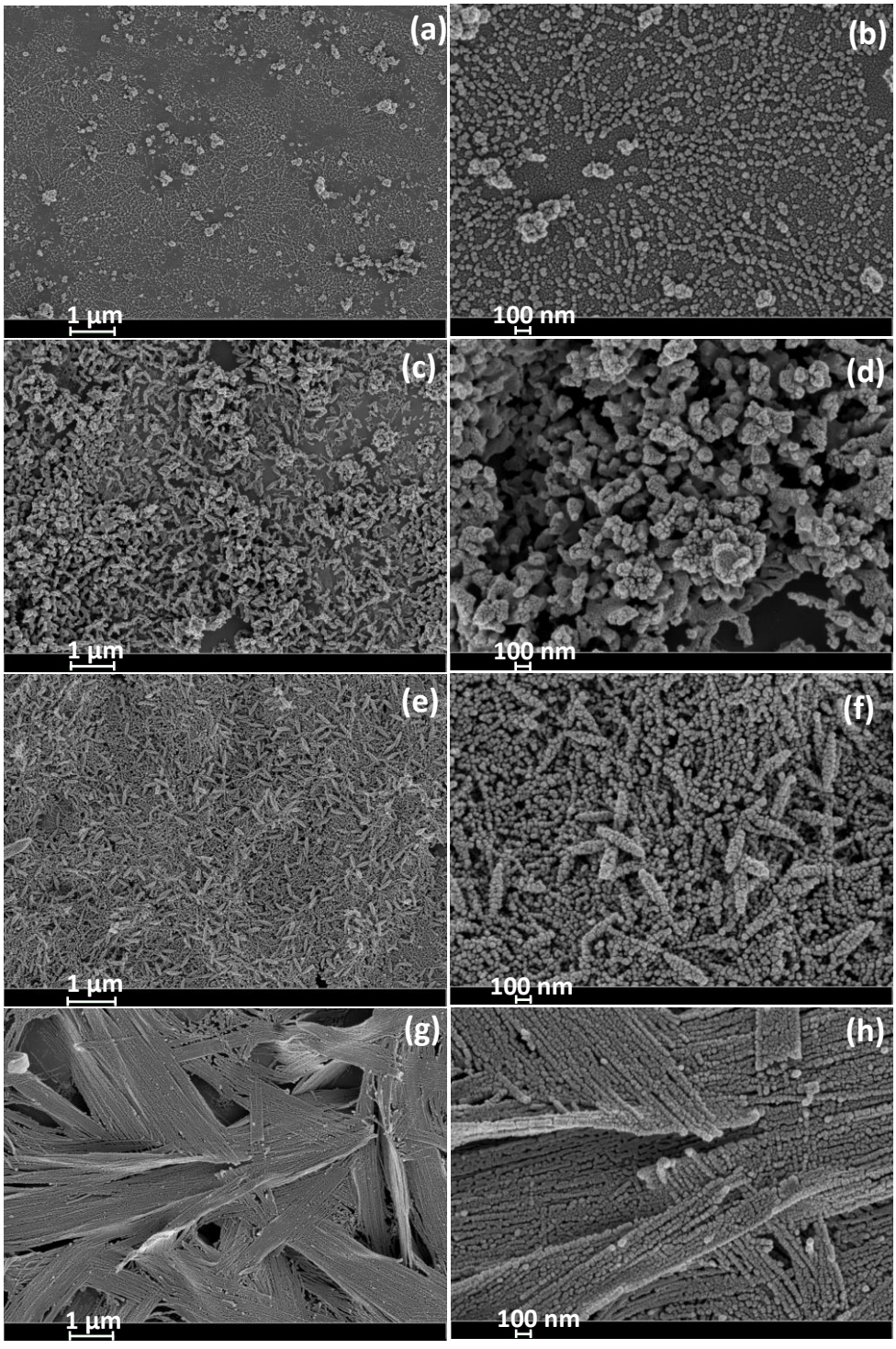

Fig. 2. FESEM images of CdO films at two different magnifications. (a, b) 0.01M, (c, d) 0.03M, (e, f) 0.05M and (g, h) 0.07M.

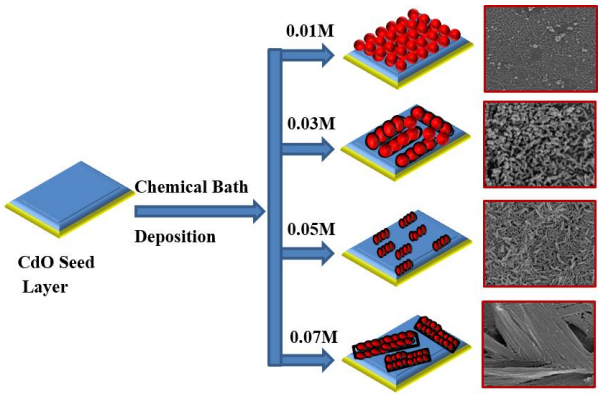

Fig. 3. The schematic diagram of the possible growth process of CdO nanostructures