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Effect of coumarin concentration on the physical properties of CdO nanostructures

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Abstract

In this work, nanostructured CdO films with different coumarin contents in the growth solution were fabricated on glass substrates by the SILAR method. The effects of coumarin content in the bath on optical, structural and morphological properties were studied by means of (UV–vis) spectrophotometer, SEM and XRD analysis. The analysis showed that the band gaps, surface morphologies and XRD peak intensities of the CdO films were found to change with coumarin content. A change in the band gap energy can be attributed to the improvement in crystallinity of the samples. XRD analysis showed that, the films have poly-crystalline structures with decent crystallinity levels.

Keywords: CdO; Nanostructured films; Band gap; SILAR; Coumarin effect

1. Introduction

Transparent conductive oxide (TCO) films have been extensively studied because of their use in semiconductor device technology [1–3]. Particularly, II–VI compound semiconductor oxide materials have attracted significant attention due to their potential applications in optoelectronics, ultraviolets light emitting devices, laser diodes, solar cells and optical communications [4,5]. However, among these compounds, cadmium oxide (CdO) films received less attention mainly due to their narrow band gap energies compared to other wide band gap oxides [6–8]. CdO exhibits high electrical conductivity and carrier concentration because of its inherent non-stoichiometry. CdO has also been used as heat mirrors due to high reflectance in the infrared region, together with a relatively high transparency in the visible region. The unique combination of high electrical conductivity, high carrier concentration and high transparency in the visible range of the electromagnetic spectrum has prompted its applications in solar cells [9]. The intensity of optical and electrical effects of CdO films depends on the deviations from the ideal CdO stoichiometry, as well as on the size and shape of the particles [10].

In general, additives are used in aqueous solution growth methods to control the surface morphology, the crystalline structure and to refine the grain size. The presence of additives also influences physical and mechanical properties of deposits such as grain size, brightness, internal stress, pitting, corrosion behavior and even chemical composition [11]. As an organic additive material, largely used in nickel plating industry, coumarin considerably refines the grain and makes the grains more uniform. Coumarins are attractive molecules due to their extended spectral range, high emission quantum yields and photostability [12]. Furthermore coumarin derivatives are frequently encountered as receptors and signaling units in sensors and biosensors as well as in advanced photophysical systems [13]. Coumarins exhibit fascinating and unique photophysical and spectroscopic properties; different derivatives can show different or even opposite behavior upon the same change in conditions. They show different absorption and fluorescence properties. Hence, they are interesting candidates not only from

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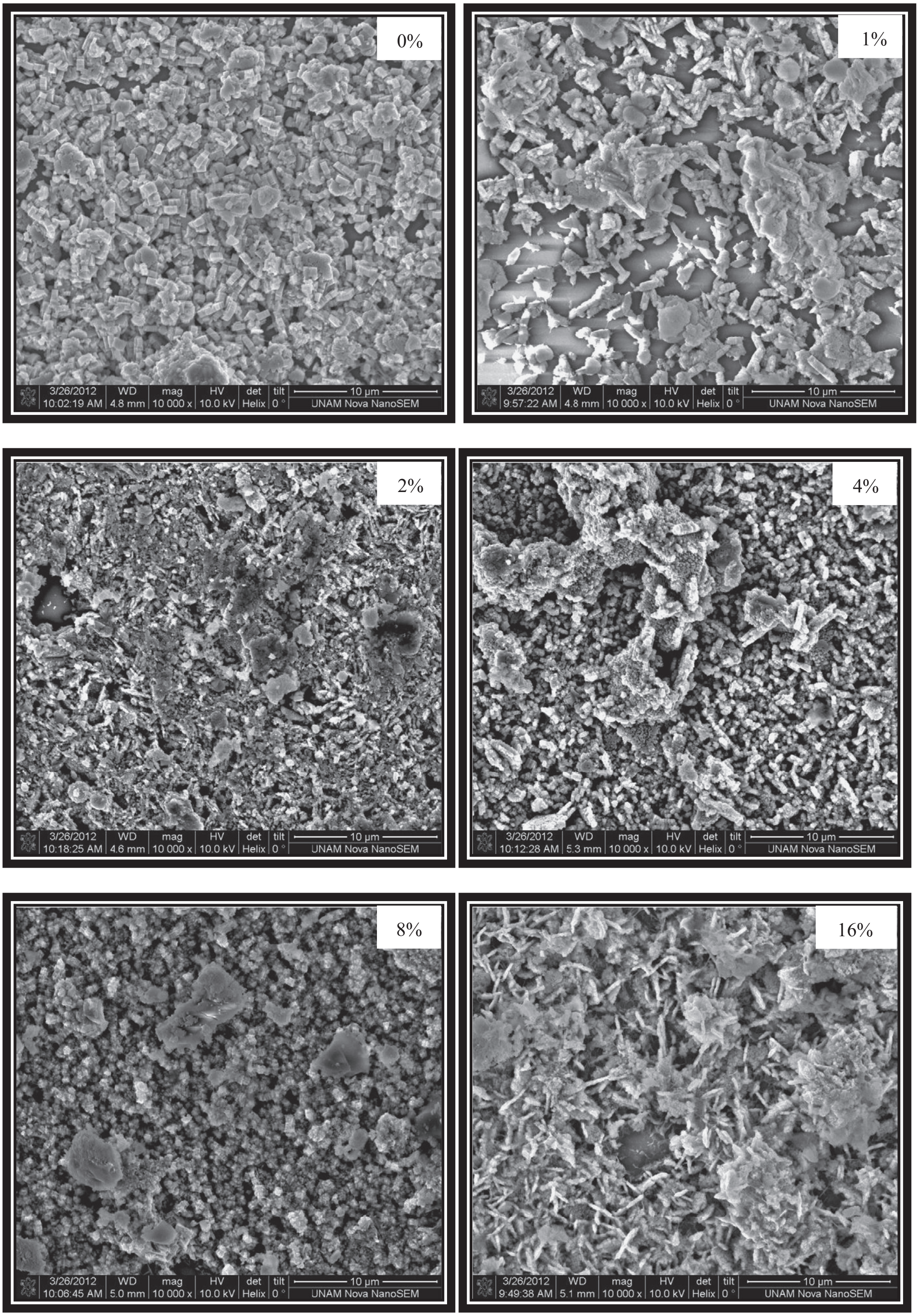

Fig. 1. SEM images of CdO films which were growth in pure and coumarin added (coumarin content: 1%, 2%, 4%, 8% and 16%) baths.

the view of applications, but also with respect to an understanding of absorption and emission mechanisms [14].

Additives are generally added to the synthesis baths which are the main parts of the chemical-based growth techniques like electrochemical deposition (ECD), chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR) etc. Among them SILAR is a relatively new liquid-phase chemical deposition method. As compared to other liquid-phase synthesis methods, SILAR has various advantages including well suitability, good reproducibility, layer-by-layer growth feature and separation of the precursors for anionic and cationic solutions. This method is capable of producing metal oxide films (CdO, ZnO, CuO etc.) at relatively low temperatures and is widely used to deposit metal chalcogenides (CdS, ZnS, CdSe etc.) multilayer and epitaxial films [15,16].

As-grown films that are synthesized at low temperatures might contain high number of defects. Annealing of these films reduces the defect density and removes the possible hydroxide phases [6]. Accordingly, to obtain CdO films without traces of hydroxide and oxide vacancies, certain thermal annealing recipes are applied for example they are annealed at 450 °C for 1 h in oxygen atmosphere.

Literature survey reveals that there is no report on the effect of coumarin content on the properties of CdO films growth by the SILAR method or any other methods. In the present work, preparation and characterization of CdO films growth by the SILAR method is studied and the effect of coumarin content on the structural, morphological and optical film properties have been discussed.

2. Experimental details

All the chemical reagents used in the experiments were analytical grade, purchased from Sigma-Aldrich Company and Merck KGaA. Cleaning process of the substrates (microscope glass slides) consisted of three steps which were cleaning in dilute sulfuric acid solution (H_2SO_4:H_2O, 1:5 by volume), in acetone and in double distilled water for 5 min each in ultrasonic bath [17]. Synthesis of the films was described as follows: 2.66 g cadmium acetate was weighted and mixed with 100 ml double distilled water (18.2 $M\Omega\,cm^{-2}$) to obtain 0.1 M cadmium acetate solution. Then the solution was stirred in a magnetic stirrer at the room temperature for 1 h in order to get a transparent and well-dissolved solution. After stirring, the pH value of the solution was increased to ≈ 12.0 by adding ammonium hydroxide (NH_4OH). The solution was heated up to 85 °C. The substrates were dipped into the solution and kept for 30 s. Then they were dipped into hot water (85 °C) for another 30 s. This cycle was applied for 30 times. To investigate the effects of coumarin content to the films, six series of samples were produced. Coumarins are a very large group of 1,2-benzopyrones derivatives that are largely distributed in a variety of natural plant sources [18]. We added coumarin 4 ($C_{10}H_8O_3$) organic dye. Coumarin 4 was chosen as a organic dye because of its high fluorescence efficiency, chemical and photo stability [19,20].

As a result, we have obtained $Cd(OH)_2$ nanostructured films. The first bath was pure (i.e. contains only cadmium acetate, water and ammonium hydroxide). The other baths contained 1%, 2%, 4%, 8%, 16% coumarin, respectively. Then $Cd(OH)_2$ films were annealed at 450 °C for 1 h in a PROTHERM PTF 12/50/450 tube furnace in a controlled oxygen ambient in order to convert $Cd(OH)_2$ into CdO.

3. Results and discussion

3.1. Morphological analysis

The morphology and microstructure of the CdO samples were examined by scanning electron microscopy (SEM). Fig. 1 shows CdO nanoparticles growth in pure and coumarin added (coumarin content: 1%, 2%, 4%, 8% and 16%) baths on glass substrates. It can be seen that all the substrates are fully covered by CdO nanoparticles. The distribution of grains is heterogeneous and their diameters range from 26 to 19 nm. It is observed that the pure CdO films are the most homogeneous one with the uniform grain size. The surface morphology and grain size of CdO films were changed considerably as a function of coumarin content that is in agreement with the studies by Mouanga et al. [21]. This organic molecule of high molecular weight is adsorbed preferentially on active sites precisely those of cadmium. It equalizes growth speeds in the crystals and contributes to a finer alloy and more regular structure. Fig.2 shows the cross-sectional image of CdO films. Thicknesses of films were found to change from 2.20 to 2.90 μm with the increase of Coumarin concentration.

3.2. Structural analysis

XRD analyses were employed to study the crystal structures of the CdO films. Fig. 2 shows the typical XRD patterns of the films that have different coumarin concentrations in the growth solution. All diffraction peaks can be clearly indexed to cubic CdO phases (JCPDS Card no.: 05-0640 for CdO). Fig. 3(a) shows the pure and 1%, 2%, coumarin content and it exhibits decent crystallinity. But the intensities of (111) and (200) peaks in the 4%, 8%, 16% samples were found to be slightly

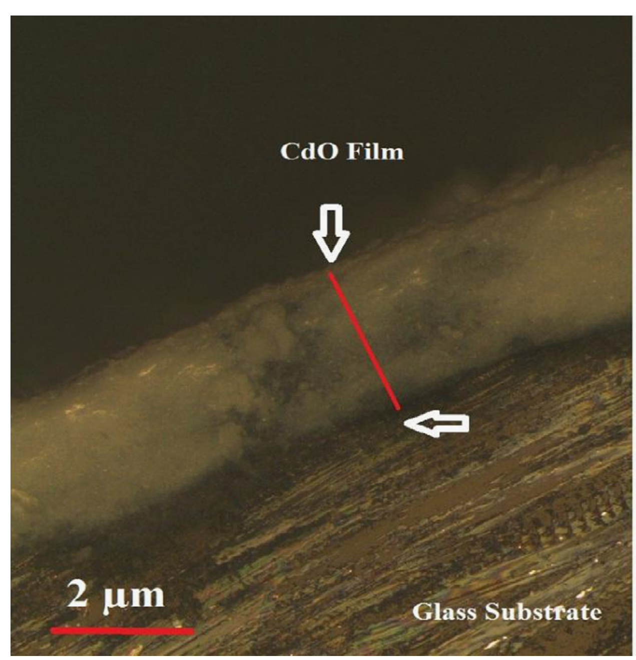

Fig. 2. Crossectional image of the CdO film.

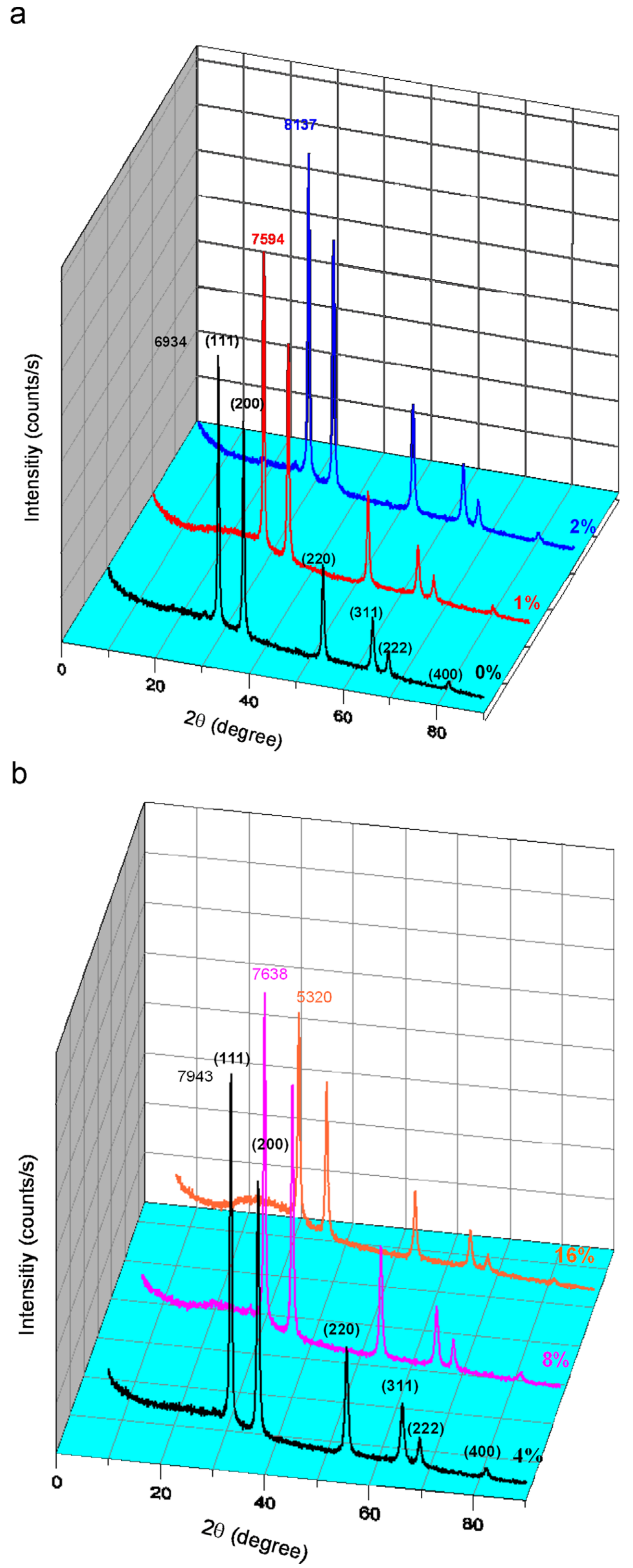

Fig. 3. XRD patterns of the films. (a) pure, 1%, 2% and (b) 4%, 8%, 16% coumarin content.

decreased as seen in Fig. 3(b). The reason for this may be, up to 2% content, coumarin ions replace the oxygen ions in the CdO lattice. However, at higher coumarin percentages, apart from replacing the oxygen ions, coumarin ions might occupy the interstitial positions in the CdO lattice. When the coumarin content in the bath further increases, the intensities of the (111) and (200) peak decrease evidently. Therefore, it can be concluded that the film formation mechanism and hence the crystallinity change with coumarin concentration [22].

The average grain sizes (D) of the CdO structures was calculated from the full-width at the half maximum (β) of a peak, using the Debye–Scherrer's equation [23]

$$D = \frac{0.90\lambda}{\beta \cos \theta}$$

where λ is the wavelength of X-ray radiation and θ is the Bragg's angle of the corresponding peak. Each X-ray diffraction peak obtained in a diffractometer is broadened due to instrumental and physical factors (grain size and lattice strains). The calculated average grain sizes of the structures are given in Table 1. As seen from the table grain sizes of the structures were increased with coumarin content up to 2%, and decreased for higher coumarin concentrations. This result is in good agreement with the SEM measurements. The measured grain size values are plotted as a function of coumarin concentration in Fig. 4. The dislocation density (δ) defined as the length of dislocation lines per unit volume of the crystal can be estimated from the following relation using the simple approach of Williamson and Smallman [24].

$$\delta = \frac{1}{D^2}$$

Table 1
Band gap and structural parameters of CdO films.

Coumarin content in the growth solution %	E_g (eV)	Average grain size (D) (nm)	Dislocation density x 10^{15} / m^2
0	1.86	26.0	1.47
1	1.89	27.0	1.37
2	1.90	28.8	1.20
4	1.92	27.2	1.35
8	1.96	26.5	1.42
16	2.06	19.0	2.77

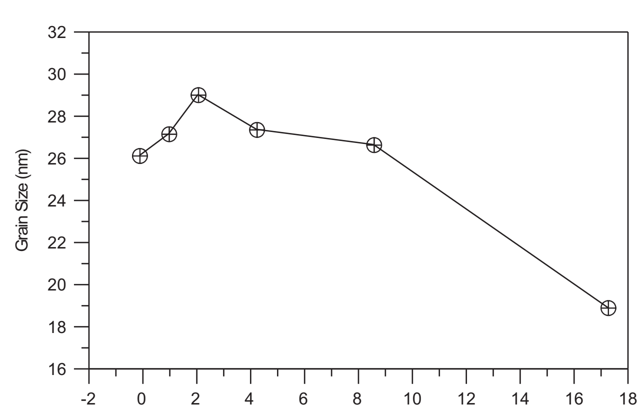

Fig. 4. Effect of coumarin concentration on the grain size.

where D is average grain size of crystal. Dislocations play an important role in surface properties. Both morphological and optical properties of thin films depend strongly defect concentration. Moreover, controlling and minimizing the density of defects or dislocations becomes also important to realize useful devices based on transparent conducting oxides (TCOs) and transparent oxide semiconductors (TOSs). Therefore, understanding the interactions between dislocations and structural properties is a significant scientific interest and has an practical importance in materials design [25,26]. Dislocation density values of the CdO nanostructures depending on coumarin content are listed in Table 1.

3.3. Optical analysis

Optical absorption spectra of the films in spectral range of 190–1100 nm was determined by using UV–visible spectrophotometer (Thermo Scientific Genesys 10 S UV–vis). The analysis of the dependence of absorption coefficient on photon energy in the high absorption regions is performed to obtain the detailed information about the energy band gaps of the films. The optical band gap energy values of the films were determined by using the following relation [27].

$$(\alpha h\nu) = C(h\nu - E_g)^m$$

where C is an energy-independent constant, E_g is the optical band gap and m is an index that characterizes the optical absorption process which is theoretically equal to 2 and 1/2 for indirect and direct allowed transitions, respectively. According to the previous theoretical and experimental results CdO exhibit direct inter band transitions [28]. Thus m can be chosen as 1/2. The band gap value can be determined by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs. $(h\nu)$ plot.

Fig. 5(a) illustrates the plots of $(\alpha h\nu)^2$vs. $h\nu$ of CdO films. The E_g values were found to be 1.86, 1.89, 1.90, 1.92, 1.96 and 2.06 eV for the films which are pure and 1%, 2%, 4%, 8%, 16% coumarin contents, respectively. As a result, the optical band gap of the CdO film can be controlled by coumarin concentration. Optical band gap values of the samples indicate a regular trend depending on the coumarin rate. With various contents of coumarin, the band gap of CdO can be modulated with coumarin concentration during the film growth stage. As summarized in Table 1, the shift in the optical band gap of the CdO films can be explained by the coumarin rate and grain size [29]. It was found that the particle sizes changes with coumarin rate. With the increase in coumarin rate from 0% to 16%, the optical absorption edge shifted towards longer wavelengths (1.86–2.06 eV) which might be attributed to change in grain size [30,31]. The effect of coumarin ratio on the optical band gap is shown in Fig. 5(b).

The transmittance spectra as a function of coumarin concentration recorded in the wavelength range of 200–1200 nm are shown in Fig. 6. The pure CdO film has the highest transmittance (11%) at longer wavelengths. The transmittance decreased rapidly with increasing coumarin concentration. As the coumarin concentration reaches 8 at% and beyond, the transmittance decreases under 3%. This result is usually attributed by a partial coverage of the substrate by additives which block the active sites, change the nucleation rate and as a result change the film structure [11,21]. These findings are in good agreement with our previous results on coumarin added CuO nanostructures [32], in which coumarin content did affected the transmittance with descending direction. As a result, film properties changes with increase in the coumarin content. We can say that film properties are a key factor which enhances the structural and optical characteristics in optoelectronic materials.

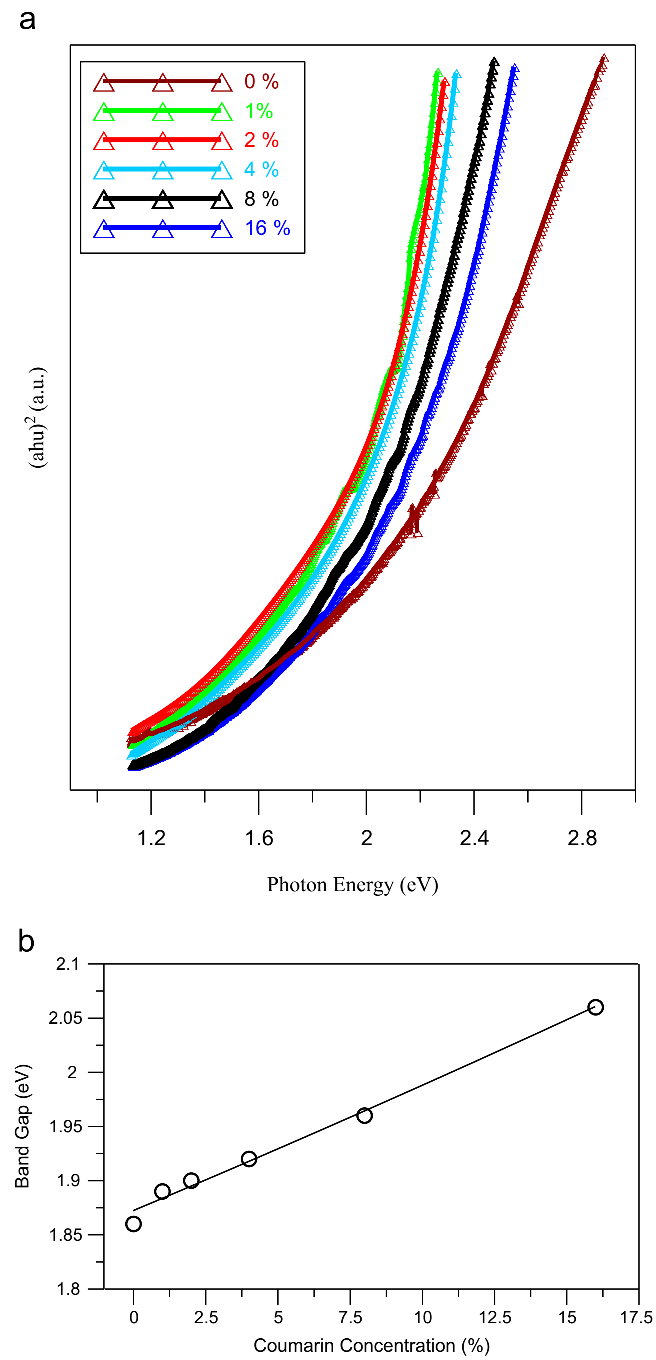

Fig. 5. (a) $(\alpha h\upsilon)^2$ vs. photon energy plots of the films: pure, 1%, 2%, 4%, 8% and 16% coumarin content (b) effect of coumarin concentrations on the optical band gap.

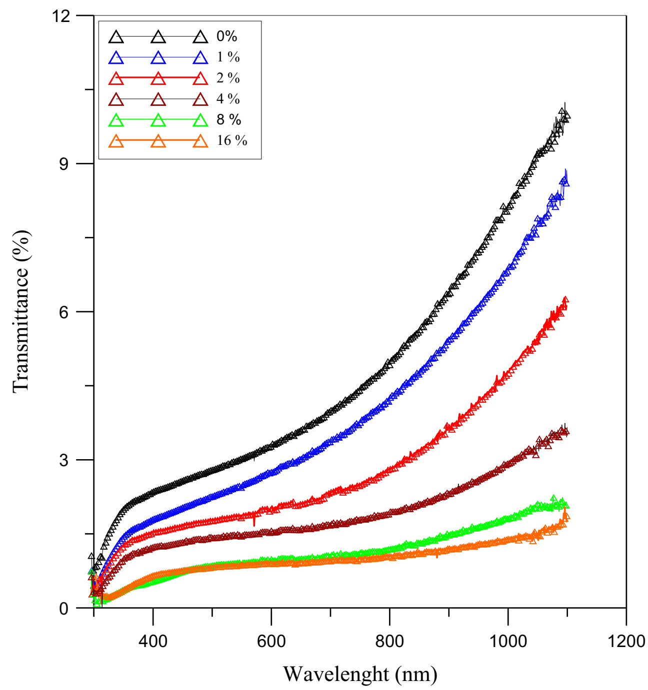

Fig. 6. Transmittance spectra of CdO films as a function of coumarin concentration.

4. Conclusion

The influence of coumarin content to the structural, morphological and optical properties of CdO films synthesized by SILAR method have been investigated. The CdO films were found to be polycrystalline with cubic structure. Coumarin addition to the growth bath caused an initial increase (up to 2%) in the intensities of (111) and (200) peaks but eventually decrease for higher coumarin content levels (more than 4%). It is observed from the SEM images and XRD patterns that the grain sizes of the structures were increased with coumarin content up to 2%, which then also decreased for the higher levels. The optical band gaps of the pure and 1%, 2%, 4%, 8%, 16% coumarin content CdO films were determined to be 1.86, 1.89, 1.90, 1.92, 1.96 and 2.06 eV, respectively. Both optical band gap and morphological properties could be controlled and calibrated by adjusting the coumarin concentrations. This controlling mechanism might be instrumental for different optoelectronic device applications where tunable material properties including band gap and crystalline quality are of critical importance. We believe that our proposed SILAR-based nanostructured CdO film growth technique is promising for tunable optoelectronic materials synthesis.

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