

Growth of CdO films from CdO₂ films by chemical bath deposition: Influence of the concentration of cadmium precursor

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Cadmium peroxide films were grown by chemical bath deposition on glass slides at 50 °C using CdCl₂ as cadmium source. Films were deposited at different nominal cadmium concentrations. As-grown films were annealed in air at 300 °C for obtaining cadmium oxide thin films. The structural, morphological, optical and compositional properties of CdO films were analyzed in terms of the cadmium nominal composition and the annealing effect.

Keywords: CdO films; Cadmium peroxide; Chemical bath deposition; Heat treatment

1. Introduction

Transparent conducting oxide thin films have important applications in the opto-electronics field as transparent electrodes [1], liquid crystal displays, IR detectors, thin film solar cells [2], etc. Cadmium oxide is an *n*-type semiconductor with a high mobility at room temperature (~216 cm²V⁻¹s⁻¹) and a bandgap value calculated in 2.18 eV [3], properties that make this material ideal for solar cells applications. CdO films can be prepared by different techniques, such as sputtering, metal organic chemical vapor deposition, ion beam sputtering, sol-gel, spray pyrolysis, chemical bath deposition (CBD) among others. For synthesizing CdO films by CBD, first CdO₂ or Cd(OH)₂ films are obtained and subsequently are subjected to a heat treatment [2,4]. In this work, we report on the influence of the cadmium nominal concentration in the CdO₂ formation by CBD, and the formation of CdO by annealing in air.

2. Experimental details

2.1 Films growth

The CdO₂ films were deposited on glass substrates by CBD at a bath temperature of 50 °C for 1 h. Before growth, substrates were cleaned in ultrasonic bath for 5 min by

rinsing in successive steps in xylenes, ethanol, acetone and distilled water. The reaction solution was prepared mixing 40 ml of CdCl₂, 20 ml of ammonium hydroxide (NH₄OH) and 2 ml of H₂O₂. CdO₂ films were deposited varying the CdCl₂ concentration in: 0.030 M, 0.035 M and 0.040 M. DI water (18 MΩ) was used for the preparation of the solutions. The pH of bath was 11.5. After deposition, the films were rinsed in distilled water in ultrasonic bath and dried with nitrogen. Then, the as-grown films were heated at 300 °C in air by 1 h. As-grown CdO₂ films were labeled from low to high CdCl₂ concentration as: CD-01, CD-02 and CD-03 (see Table 1) whereas after the heat treatment samples were labeled CD-01-HT, CD-02-HT and CD-03-HT, respectively, (see Table 2).

2.2 Characterization

X-ray diffraction (XRD) patterns were obtained in a Rigaku Smartlab diffractometer, using the Cu-Kα line (1.5406 Å). Electron diffraction patterns from selected areas were obtained by transmission electron microscopy (TEM) using a JEOL JEM 2010 microscope operating at 200 kV. Film thicknesses were measured in a KLA Tencor P15 profilometer. The topography studies were performed by Atomic Force Microscopy (AFM), using a ThermoMicroscope Autoprobe CP (Veeco Instruments) in contact mode. A Perkin-Elmer Lambda 25 UV-Vis

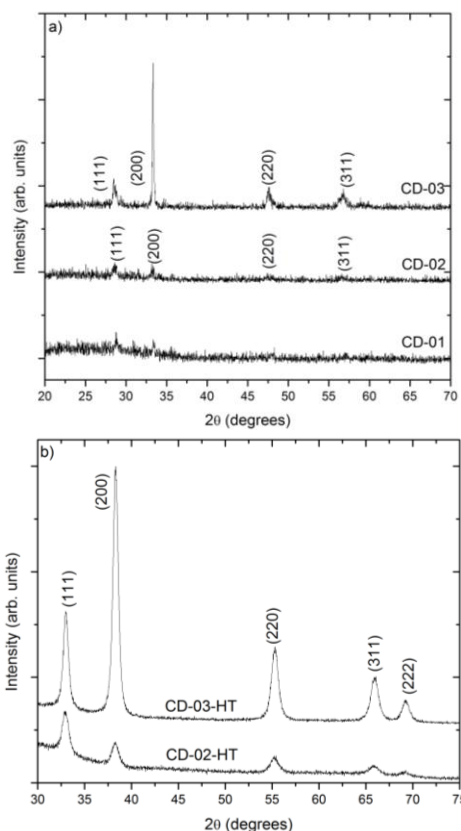


Figure 1. XRD patterns of a) CdO₂ films grown by CBD and b) CdO thin films, produced after annealing the CdO₂ films.

Table 1. Physical properties of as-grown CdO₂ films.

Sample	[CdCl ₂] (M)	Thickness (nm)	E _g (eV)
CD-01	0.030	136	3.98
CD-02	0.035	386	3.95
CD-03	0.040	573	3.82

Table 2. Physical properties of CdO films (annealed films).

Sample	[CdCl ₂] (M)	Thickness (nm)	Thickness evaporated (nm)	E _g (eV)
CD-01- HT	0.030	0	136	-
CD-02- HT	0.035	130	256	2.38
CD-03- HT	0.040	291	282	2.59

spectrophotometer was used to obtain optical transmittance. Atomic concentration measurements of films were determined by Energy Dispersive Spectrometry (EDS) with a Bruker 5010 XFlash detector installed in a Jeol JSM-6300 scanning electron microscope.

3. Results and discussion

3.1 Structural characterization

XRD patterns of as-grown films are shown in Fig. 1a). The CD-01 and CD-02 samples have two diffraction peaks of low intensity at 28.46° and 33.32°. The CD-03 sample presents four diffraction peaks at 28.46°, 33.32°, 47.66° and 56.76°. These peaks correspond to the cubic CdO₂ (cadmium peroxide) phase and the diffraction planes are (111), (200), (220) and (311), respectively. The peaks were indexed using the powder diffraction files 39-1221 (PDF#39-1221). From Fig. 1a) it is noted that the crystalline quality improves as the CdCl₂ concentration increases in the bath, indicating that the increase of the CdCl₂ concentration promotes the formation of the CdO₂ compound.

Fig. 1b) shows the XRD patterns of films after the heat treatment at 300 °C in air. Five diffraction peaks at 32.98°, 38.34°, 55.32°, 66.06° and 69.22° are distinguished, whose diffraction planes are (111), (200), (220), (311) and (222), respectively. These diffraction planes correspond to the cubic CdO. The peaks were indexed using the PDF#01-1049. It is important to mention that during the annealing, the CD-01 sample was totally evaporated. This indicates that an important amount of material evaporates during the annealing. Fig. 2 shows the transmission electron diffraction patterns of CD-03 sample before and after annealing. The electron beam incides into the [011] zone axis. The diffraction planes are indicated in Fig. 2. The electron diffraction patterns confirm that the CD-03 and

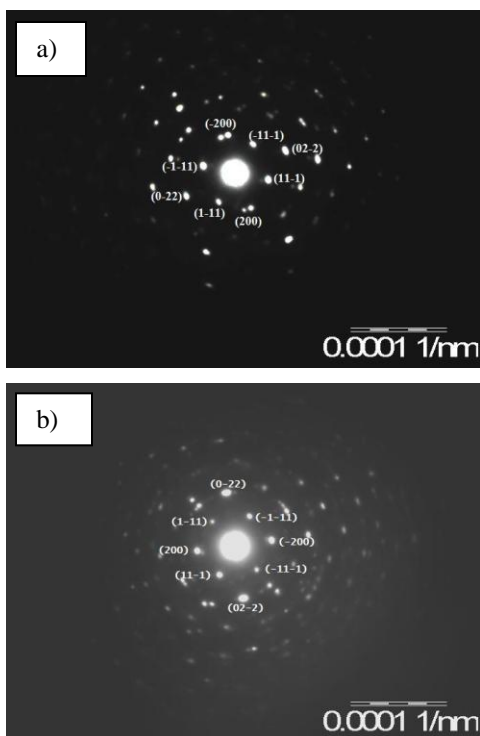


Figure 2. Diffraction patterns of a film deposited with a 0.040M CdCl₂ concentration; a) CdO₂ as-grown sample and b) after annealing.

CD-03-HT samples have a cubic structure; in fact, these samples have an fcc crystalline structure.

As mentioned before, heat treatment desorbs the films surface. In order to know the evaporation rates, thickness measurements were performed. Table 1 shows the thickness of as-grown CdO_2 films. The film thickness increases with the CdCl_2 concentration, suggesting that the increase of the Cd nominal concentration promotes the formation of material, in agreement with XRD analysis in Fig. 1a). Table 2 displays the thickness of the samples. The CD-01 sample was evaporated during the annealing so that the thickness of the CD-01-HT film was zero. Note from Tables 1 and 2 that during the heat treatment a great amount of material evaporates. The thicknesses evaporated (summarized in Table 2), from CD-01, CD-02 and CD-03 were 136 nm, 256 nm and 282 nm, respectively.

Due to the high amount of material evaporated, the topography of samples after heat treatment must change drastically. In order to know the topography of the films AFM measurements were carried out. The surface morphology of films is shown in Fig. 3. AFM images corresponding to the as-grown CdO_2 films are displayed in the left column, whereas those of CdO films (annealed films) are placed in the right column. The surface of the CD-01 sample (Fig.3 a) shows holes, which indicates that for a 0.030 M CdCl_2 concentration the formation of the CdO_2 film begins. The surface morphology of CD-02 sample is shown in Fig. 3b). This sample has large clusters of around 500 nm. Comparing images CD-02 and CD-HT-02 (Figs. 3b and 3d) there is no significant difference between the two surfaces. However, differences between the surfaces of the CD-03 and CD-HT-03 samples are notable. Fig. 3c) displays the surface of the CD-03 sample, showing grains of irregular shape, distributed in a periodic array. These grains decrease in dimensions after heating the sample as corroborated in Fig. 3e). The optical properties of the CdO samples are strongly related to the size of these grains. In the following paragraphs, we will further discuss this idea.

Fig. 4a) shows the transmittance spectra of as-grown CdO_2 films. The CD-01 and CD-02 samples present absorption of light in the wavelength region ≥ 400 nm, which can be attributed to crystalline defects, that are responsible of the reduction of transmittance [5]. The CD-03 sample has a high transmittance in the visible region ($>70\%$) and the spectrum presents an absorption edge practically vertical, indicating a good crystalline quality of the sample (in agreement with the XRD results). The transmittance spectra of films with heat treatment are shown in Fig. 4b). Note that the heat treatment reduces the transmittance of films and shifts the absorption edge towards the yellow. From these spectra the absorption coefficient (α) was calculated by the relation: $T=(1-R)^2\exp(-\alpha d)$, where T is the transmittance, R the reflectance and d the film thickness [5]. The absorption coefficient was used to determine the bandgap (E_g) of

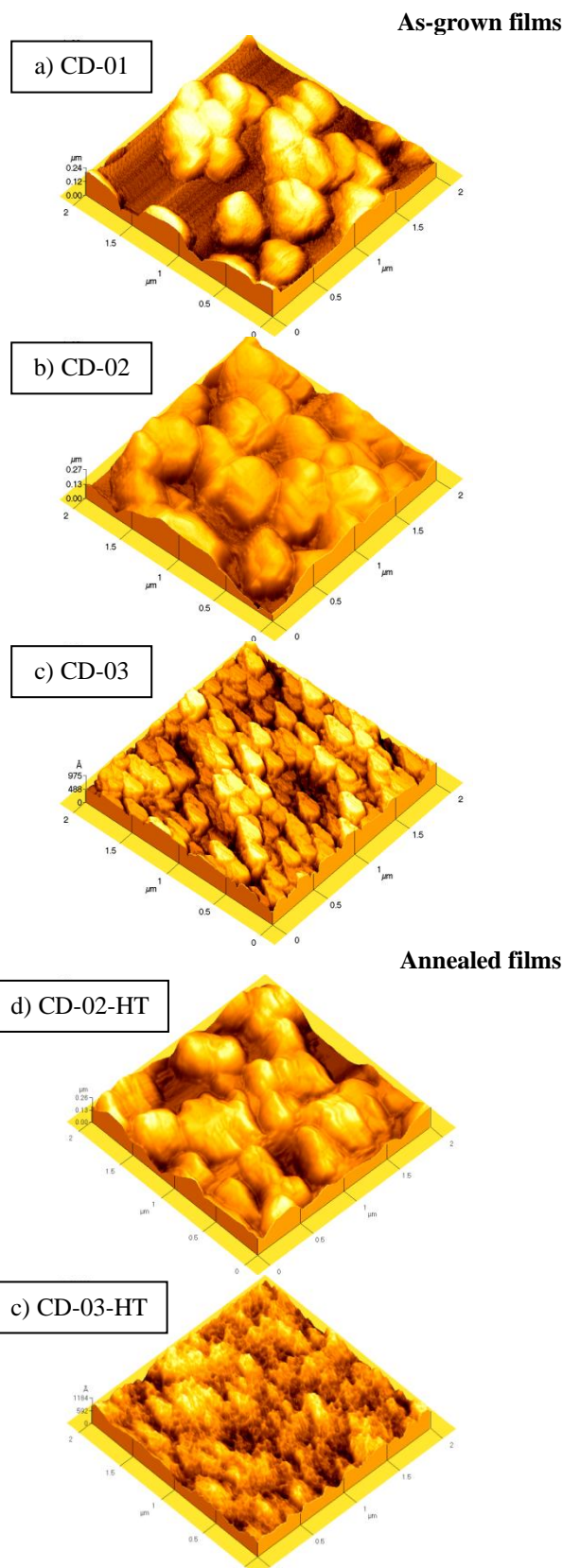


Figure 3. AFM images of as-grown CdO_2 (a, b, c) and annealed (CdO) (d, e) films, respectively.

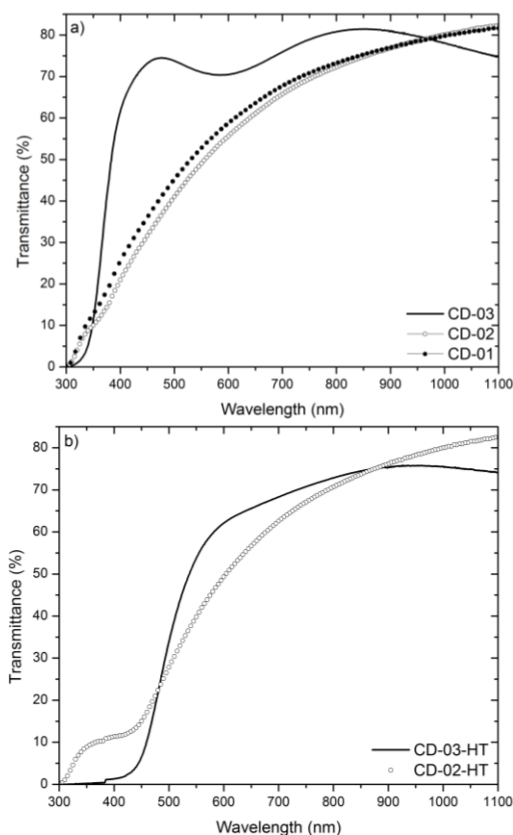


Figure 4. Transmittance spectra of a) as-grown CdO₂ and b) CdO films.

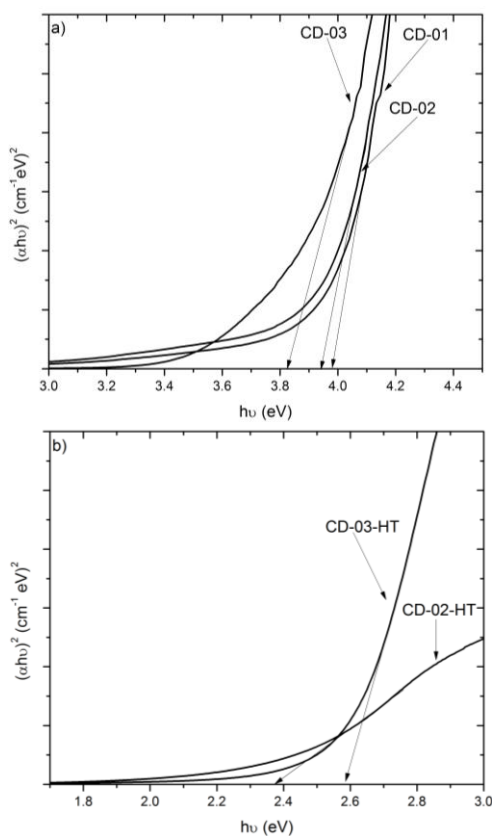


Figure 5. Bandgap calculations of a) CdO₂ films and b) CdO films.

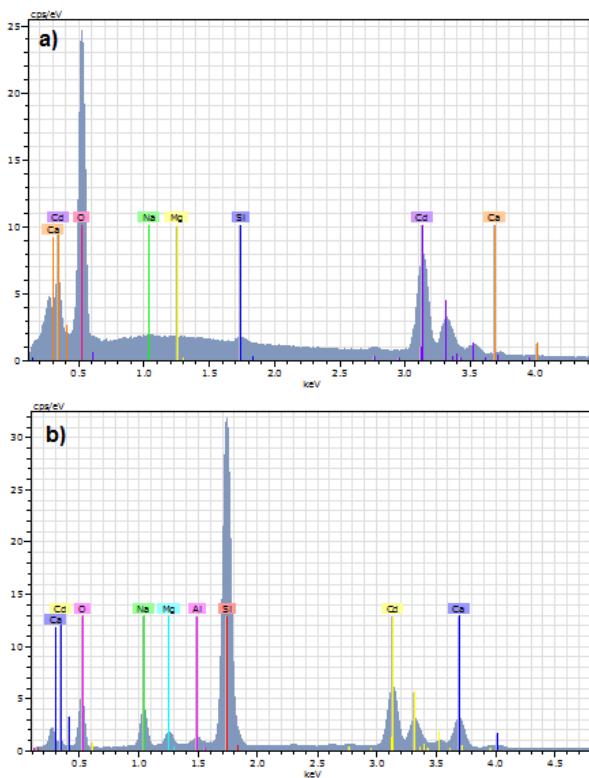


Figure 6. EDS spectra of CD-03 and CD-03-HT samples deposited with a 0.040 M CdCl₂ concentration: a) as-grown CdO₂ film and b) CdO thin film.

films, using the relation $\alpha h\nu = (h\nu - E_g)^{1/2}$, where $h\nu$ is the photon energy [1,5]. Fig 5 shows the graphic of $(\alpha h\nu)^2$ vs $h\nu$, the E_g was determined by fitting the lineal part of the curve. The bandgap values of the as-grown CdO₂ films are compiled in Table 1, the bandgap value decreases from 3.98 eV to 3.82 eV as the CdCl₂ concentration in the bath increases. The E_g value calculated for CdO films; CD-02-HT and CD-03-HT, was 2.38 eV and 2.59 eV (see Table 2), respectively, in agreement with the bandgap values reported in the literature [6]. Pan et al. [7] reported that the grain size decrease in CdO samples produces an increase in their bandgap. Encompassing the same consideration the AFM images of Figs. 3d) and 3e) show that CdO surface grains decrease from sample CD-02-HT to CD-03-HT. We infer that the grain decrease observed by AFM is responsible of the bandgap widening in our samples synthesized with the highest concentration of CdCl₂, suggesting that the molar concentration has strong influence in the grain size. This result will be subject of another publication concerning electrical properties of the samples. The increase in the bandgap has been explained in terms of the Burstein-Moss effect as long as the intrinsic physical properties of CdO samples [7,8].

Fig. 6a) and Fig. 6b) show the EDS spectra of CD-03 and CD-03-HT samples, respectively. Peaks associated to cadmium (Cd), oxygen (O), sodium (Na), magnesium (Mg), silicon (Si) and calcium (Ca) are indicated.

In Fig. 6a) peaks corresponding to Ca, Si, Mg and Na are of low intensity, while those associated to Cd and O are of high intensity. Peaks of low intensity are due to substrate, whereas detected peaks of Cd and O correspond to the CdO₂ compound formation. The oxygen peak is about three times more intense than that corresponding to cadmium; this is because a fraction of the oxygen detected corresponds to the substrate. Fig. 6b) shows the spectrum of CD-03-HT. After annealing the intensity of peaks corresponding to the substrate increases, due to the reduction of film thickness by evaporation. In spite the intensity of cadmium and oxygen peaks decreases after annealing, Fig. 6b) shows Cd and O signals are similar in intensity, suggesting the CdO compound formation.

4. Conclusions

Cadmium peroxide (CdO₂) films were obtained by CBD using CdCl₂ as cadmium source. The physical properties were analyzed as a function of CdCl₂ concentration. X-ray diffraction showed that CdO₂ films have the cubic stable phase. The structural, morphological and compositional characterization showed that the increase of the CdCl₂ concentration promotes the formation of CdO₂ compound. For a 0.040 M CdCl₂ concentration CdO₂ films with a high crystalline quality were obtained. CdO₂ films were annealed in air at 300 °C for obtaining CdO films. The structural characterization of the annealed films showed that CdO samples have cubic structure. Bandgap values of 2.38 and 2.59 eV were estimated from optical characterization. This widening in the bandgap was explained in terms of the Burstein-Moss effect.

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