Structural and optical properties of CdO-ZnO thin films synthesized by sol-gel spin coating method

A Nfissi1, M Belhajji1, L Mrharrab1,2, Y Ababou1,3 and S Sayouri1

1 LPAIS, Faculty of Sciences-DM, USMBA, B.P. 1796, Fez-Atlas, Morocco
2 ERMAM, FP, Ouarzazate, Morocco
3 Corresponding author: ababouyahya@hotmail.com

Abstract. CdO-ZnO thin films with volume ratio of (Cd: Zn) of (1: 0), (0.75: 0.25), (0.5: 0.5) and (0: 1) were prepared using the sol-gel spin coating method. The as-coated films were annealed at 550 °C for 1h and their structural and optical properties investigated. From structural investigations, it was observed that ZnO phase is present in the composites. The crystallite size values decreased with increasing the Zn content, and the dislocation density increased from 0.77 to 0.988 (10^{15} \text{lines/m}^2). The optical properties were examined by a ultraviolet-Visible spectroscopy, which indicated that the optical transmission increases in the visible region, and the band gap is found to be blue shift from 2.26 to 3.24 eV with the increase of ZnO content.

1. Introduction
Cadmium oxide (CdO) is an n-type semiconductor with a cubic NaCl-type crystal structure, possesses a direct band gap of 2.2-2.7 eV [1-3]. In addition, CdO films shows high transparency especially in the NIR spectral region, and have been used for many applications such as transparent conducting oxide (TCO), optical communications, photovoltaic solar cells, photo transistors, gas sensors devices and thin-film resistors [4-8]. CdO thin films can be synthesized by different chemical and physical deposition methods such as sol-gel [9], spray pyrolysis [10], magnetron sputtering [11], chemical bath deposition [12], pulsed laser deposition [13] and electrodeposition [14].

Zinc oxide (ZnO) is an n-type semiconductor with a wide band gap in the near ultraviolet of 3.3 eV [15]. In addition, ZnO shows interesting properties such as good transparency, high thermal conductivity and high electron mobility. Besides that, ZnO have been used in light-emitting diodes (LED), solar cells, photodetectors and piezoelectric devices [16-18].

Optical properties of nanostructured Zn and Cd oxides mixture films can be controlled by the oxides content ratio [19]. Caglar et al. [20] prepared CdZnO films with various compositional ratios using the sol-gel method and have found that the optical transmission increased with the increase of Zn concentration.

In the present work, we report elaboration and characterization of CdO-ZnO thin films. The main interest is to study the effect of ZnO content on the structural and optical properties of CdO thin films.

2. Experiment
The following precursors were needed to elaborate the CdO-ZnO thin films: cadmium acetate dihydrate (Cd(CH₃COO)₂.2H₂O) and zinc acetate dihydrate (Zn(CH₃COO)₂.2H₂O). During the
preparation process monoethanolamine (C$_2$H$_7$NO, MEA) and 2-methoxyethanol (C$_3$H$_8$O$_2$) were used as a stabilizer and solvent.

CdO and ZnO solutions of 0.5M were synthesized separately: at first, cadmium acetate dihydrate was dissolved in 2-methoxyethanol, then, MEA was added to the solution and the resulting mixture was stirred at 60°C for 3h. ZnO solution was synthesized by the same method (stirred at 70°C for 3h). The resulting CdO and ZnO solutions were mixed in various volume ratios of (Cd: Zn) of (1: 0), (0.75: 0.25), (0.5: 0.5) and (0: 1). These CdO-ZnO Composites were denoted S$_0$, S$_{25}$, S$_{50}$ and S$_{100}$ respectively, and were stirred at 60°C for 30 min. The final solutions were deposited on the glass substrates, and then rotated at 3000 rpm for 20 s using a spin coater, the films were pre-heated at 300 °C for 10 min in order to evaporate the solvent, these operations were repeated 10 times in order to increase the thickness of the thin films. Finally, the prepared CdO-ZnO thin films were annealed at 550 °C for 1h in a tube furnace in air ambiance.

The structural and optical characterizations of the samples were performed using an X-ray diffraction (XPERT-PRO diffractometer) with Cu-Ka radiation ($\lambda$=1.540598 Å), ultraviolet-Visible (UV-Vis) spectroscopy was used at room temperature in the wavelength range from 300 to 700 nm, respectively.

3. Results and discussion

3.1. Structural analysis

The room temperature X-ray diffraction (XRD) patterns of CdO-ZnO thin films with different Cd: Zn ratios are plotted in figure 1. For the CdO sample (S$_0$) exhibits (111), (200), (220), (311) and (222) characteristic peaks of cubic NaCl-type structure, and the calculated lattice parameter is 4.69 Å, this is in good agreement with the result reported [21]. The characteristic peaks (100), (002) and (101) of the ZnO sample (S$_{100}$) were indexed to hexagonal wurtzite structure, and the calculated lattice parameters are a=3.20 Å, c=5.22 Å. For S$_{25}$ and S$_{50}$ samples, peaks of CdO and ZnO are present.

![Figure 1. XRD patterns of CdO–ZnO thin films with different Cd:Zn ratios: S$_0$, S$_{25}$, S$_{50}$ and S$_{100}$.](image)

The crystallite size (D) of CdO-ZnO thin films was estimated from the peak (111), using Scherrer’s equation:

$$D = \frac{0.9 \lambda}{\beta \cos(\theta)}$$

(1)
where $\beta$ is the full-width-at-half-maximum (FWHM) of a characteristic diffraction peak, $\theta$ is the diffraction angle and $\lambda=1.5406$ Å.

The crystallite size values decreased from 36.01 nm to 31.81 nm, with increasing the Zn content from 0 to 50%. This can be ascribed to the smaller ionic radius of $\text{Zn}^{2+}$ (0.74 Å) than that of $\text{Cd}^{2+}$ (0.95 Å). The dislocation density ($\delta$) of CdO-ZnO thin films was calculated from the crystallite size using the equation:

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

The small dislocation density ($0.7711 \times 10^{15}$ lines/m$^2$) for pure CdO means that the crystallization of this thin films is better. It is also seen that the $\delta$ value of CdO-ZnO thin films is increased with increasing the Zn content from 0 to 50%. This means that ZnO increases the defects in the CdO thin films. This behavior was also observed in Al doped CdO films [22].

The full-width-at-half-maximum (FWHM), the crystallite size (D) and the dislocation density ($\delta$) of CdO-ZnO thin films were shown in Table 1.

| Sample | FWHM of (111) peak (°) | D (nm) | $\delta$ $(10^{15}$ lines/m$^2$) |
|--------|------------------------|--------|---------------------------------|
| S$_0$  | 0.2299                 | 36.01  | 0.7711                          |
| S$_{25}$ | 0.2457               | 33.70  | 0.8052                          |
| S$_{50}$ | 0.2603               | 31.81  | 0.9882                          |

### 3.2. UV-Vis analysis

The room temperature UV-Vis transmittance spectra of CdO-ZnO thin films with different Cd: Zn ratios are plotted in figure 2. It is evident that the transmittance increases with Zn content to reach its maximum value at Cd 0: Zn 1 (i.e. S$_{100}$ sample), then pure ZnO shows high transparency in the visible spectral region in contrast to the pure CdO. This can be explained by the higher value of the surface roughness of the pure CdO thin film due to the increased optical scattering of light incident on the film mince surface [23].

![Figure 2. UV-Vis transmittance curves of CdO--ZnO thin films.](image-url)
The absorbance (A) spectra of CdO-ZnO thin films was calculated from the measured transmittance (T) spectra using the relation:

\[ A = \log_{10} \left( \frac{T}{100} \right) \]

The wavelength of the gap energy was extracted by extrapolating the linear part of the curve absorbance, and an illustration of such determination for all the sample is shown on figure 3.

![Figure 3](image)

**Figure 3.** Determination of the wavelength of the gap energy from the absorbance, for CdO–ZnO thin films with different Cd:Zn ratios: (a) S₀, (b) S₂₅, (c) S₅₀ and (d) S₁₀₀.

The optical band gaps of all the sample were calculated from the wavelength using the equation:

\[ E_g = \frac{1240}{\lambda} \]

where \( \lambda \) is the wavelength determined from the absorbance spectra.
Table 2 gathers $E_g$ values of all the compositions studied which show an increase with an increase in Zn content. The recorded values of this parameter for $S_0$ sample belong to the interval of values known for the pure CdO which lay between 2.2 and 2.7. For $S_{100}$ sample a band gap energy of 3.24 eV was obtained, which is in good agreement with reported values of pure ZnO by Singh et al. [24]. A. A. Ziabari et al. [25] prepared CdO-ZnO composite films with volume ratio of (Cd:Zn) of (0:1), (1/4:3/4), (1/2:1/2), (3/4:1/4) and (1:0) via the sol-gel dip coating method, and have obtained the following $E_g$ values 3.28 eV, 3.03 eV, 2.50 eV, 2.44 eV and 2.23 eV, respectively.

| Sample | $E_g$ (eV) |
|--------|------------|
| $S_0$  | 2.26       |
| $S_{25}$| 2.51       |
| $S_{50}$| 2.74       |
| $S_{100}$| 3.24       |

It is observed from figure 4 that $E_g$ increases linearly as a function of Zn content. Hence, the band gap energy exhibits a blue shift with the rise of Zn content from 0 to 100%, which shows the strong influence of the ZnO on the band gap of the CdO thin films. Moreover, the parameter $E_g$ decrease with increasing crystallite size. This behavior was also observed in CdO-ZnO composite films [25].

![Figure 4. Band gap energy of CdO–ZnO thin films as a function of Zn content.](image)

4. Conclusion
CdO-ZnO thin films were successfully prepared on glass substrates using the sol gel method at a temperature of calcination 550 °C for 1 h. Structural analysis showed that pure CdO and ZnO crystallize in the cubic NaCl-type and hexagonal wurtzite structures, respectively. The crystallite size values decreased with increasing the Zn content from 0 to 50%, and the small dislocation density for pure CdO means that the crystallization of this thin film is good. The transmittance increases with increasing the Zn content from 0 to 100% in the visible spectral region. The obtained values of the
band gap energy from absorbance spectra shifted to the higher energy as a result of the increasing of Zn content in the thin film.

**Nomenclature**

| Symbol | Description                   |
|--------|-------------------------------|
| a, c   | Lattice parameters            |
| D      | Crystallite size              |
| δ      | Dislocation density          |
| T      | Transmittance                 |
| A      | Absorbance                    |
| λ      | Wavelength                    |
| $E_g$  | Band gap energy               |
| FWHM   | Full-width-at-half-maximum    |
| NIR    | Near-infrared                 |
| UV-Vis | Ultraviolet-Visible          |
| TCO    | Transparent conducting oxide  |
| LED    | Light-emitting diodes         |
| MEA    | Monoethanolamine              |

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