Structural, Morphological and Optical Properties of \( \text{Zn}(1-x)\text{Cd}_x\text{O} \) thin films grown on a glass substrate by spray pyrolysis method.

K. Bouzid a, A. Abdelhak a, A. Serrar a, A. Roustila a,

a Laboratory of microstructures and material defects, university p-of constantine 1. Agleria

Abstract

Method on the glass substrate at 450°C. For Cd doping, various concentrations of cadmium nitrate \( \text{Cd(NO}_3\text{)}_2 \) (2–8 wt%) was used in the spraying precursor solution. The structural, Zinc oxide (ZnO) and ZnxCd1-xO thin films were deposited using a low cost spray pyrolysis morphological, and optical properties of ZnO and Cd:ZnO films were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), atomic force microscope (AFM), UV–vis. X-ray diffraction study reveals that the ZnO and Cd:ZnO films are possessing hexagonal wurtzite structure. SEM and AFM studies reveal that the grain size and roughness of the films are decreased with increasing Cd doping concentration. Optical transmittance spectra of the CdO film decreases with increasing doping concentration of cadmium. The optical band gap of the films decreases from 3.25 eV to 2.90 eV with increasing concentration of cadmium. On increasing Cd concentration in ZnO binary system, the absorption edge of the films showed the red shifting.

Keywords (Cd-doped ZnO, Spray pyrolysis, X-ray diffraction, Optical properties)

I. INTRODUCTION

Zinc oxide (ZnO) is a II-VI compound semiconductor with a stable wurtzite structure and a direct wide bandgap (3.37 eV) and high excitonic binding energy (60 meV) at room temperature [1]. It has attracted much attention due to its excellent structural, optical and electrical properties, which are very useful in transparent electronics, thin films photovoltaics, window layers and many other optoelectronic devices [1–2]. It could be used as a light-emitting diode (LED), diode laser and radiation resistance. ZnO has unique and diverse properties comparable to other wide bandgap semiconducting materials, such as piezoelectricity, chemical stability, optical transparency exceeding 90% in the visible region of solar spectrum.

Generally, various dopants such as Al, Cd, In, K, Mg, etc. have been used for improving the optical gap and electrical conductivity of the ZnO to be used as a potential TCO material in optoelectronics [3–4]. The cadmium (Cd) is a material of interest as it reduces the bandgap of ZnO with an improvement in other useful properties. The main aim of this work is to tailor optical properties of ZnO thin films for optoelectronic applications, by doping transition metal elements. On incorporation of Cd into ZnO lattice, Cd+2 ions can uniformly substitute Zn+2 or interstitial sites inside ZnO lattice [4]. The radii of zinc and cadmium ions are 0.074 nm and 0.097 nm, respectively. Cd ion has larger radius than that of zinc ion hence, lattice distortion may occur in ZnO lattice system. This may lead to the narrowing of electronic structure of ZnO binary system and as a result, to some decrease in the band gap of ZnO thin film.

In the present work, ZnO and Cd doped ZnO thin films with different concentrations of Cd were deposited on glass substrates by spray pyrolysis method. The influence of Cd doping on structural, optical and properties of ZnO thin films was investigated in details.

II. EXPERIMENTAL DETAILS

Pure and Cd doped ZnO thin films were deposited on the glass substrates using the spray pyrolysis technique. In the preparation of ZnO films, 0.1M zinc acetate Zn (CH3(COO)2) was used as a source material of Cd. Water and methanol was used as the solvent. A small amount of acetic acid was added to aqueous solutions to adjust the pH value to about 4.8 to prevent the formation of hydroxides. To achieve Cd doping, an aqueous solution of cadmium nitrate with various concentrations, mixed with the precursor solution. The optimised deposition parameters such as substrate-spray nozzle distance (5 cm), carrier gas pressure (compressed air 40 kg/cm2) and the flow rate of the solution (about 0.1 ml/min) were kept constant. ZnO and Cd doped ZnO thin films were deposited onto microscope cover glass substrates (30 x 12 x 1.2 mm3). The temperature and the deposition time have fixed at 30 min for all films. The film morphology was examined using a (Tescan Vega TS5130MM) scanning electron microscope (SEM). The structural analysis of all thin films is done by powder X-ray diffraction (XRD) data collected on XRD Panalytical EMPYREAN diffractometer using Cu Kα radiation. Surface roughness was elucidated using atomic force microscope (AFM - A100SGS). The thickness of the pure and Cd doped ZnO films was measured by stylus profilometer. Optical transmittance spectrum was recorded in the wavelength range of 200–800 nm using UV–vis spectrometer (UV-3101 PC-SHIMADZU).

III. RESULTS AND DISCUSSIONS

A. structural studies

Fig.1 shows the X-ray diffraction pattern of ZnO and cadmium doped ZnO thin films deposited by spray pyrolysis method as a function of various cadmium concentrations.

![XRD patterns of Cd doped ZnO thin films.](image-url)
The XRD pattern of Fig. 1 reveals that all films are polycrystalline and retained a hexagonal structure type wurtzite. The diffraction peaks are easily indexed on the basis of the hexagonal structure of ZnO (P63mc, a = 3.249 Å, and c = 5.205 Å, JCPDS 36-1451) and the cubic structure of CdO (a = 0.3253 nm and c = 0.5213 nm, ICDD PDF#89-1379).

XRD patterns of Pure Zinc Oxide showed that formation was polycrystalline. The peaks were found in basically 7 directions [100, 002, 101, 110, 103, and 112]. The doping of ZnO with Cd such that the numbers of doped atoms are up to 8% does not forms a new phase. Cd doped ZnO thin films the intensity of the (002) peaks decreased and the intensity of (101) peak is increased. The rest of the crystalline planes appear at the positions corresponding to the wurtzite phase but with different relative intensities. There are not formation new phases in all samples. We did not detect any phase that could be attributed to the Cd ions present in the film, although there might be amorphous regions.

The reason for the change in growth orientation is substitution of Cd ions into the Zn lattice sites. The diffraction angle of (101) and (002) planes lightly shifted to smaller (2θ) angle due to the shrinkage of the lattice parameter. The increase of lattice constant is due to the increase in interatomic spacing which results of substitution of higher Cd ions (0.95Å) into smaller Zinc ions (0.60Å) [5]. The cell parameter ‘c’ of ZnO and Cd doped ZnO was found between 5.194Å and 5.201 Å (shown in table.1) [6]. The increase of lattice constant is due to the increase in interatomic spacing which results of substitution of larger Cd+2 ions (0.95Å) into smaller Zinc ions (0.60Å) [7].

<table>
<thead>
<tr>
<th>%Cd</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C)(Å)</td>
<td>5.194</td>
<td>5.195</td>
<td>5.197</td>
<td>5.199</td>
<td>5.201</td>
</tr>
</tbody>
</table>

Table 1 Values of lattice parameters for CZO films

crystallites size of the CZn thin films with different concentrations was estimated using Scherrer’s relation. Where D is the crystallite size, λ is the wavelength of the X-ray (1.54059 Å), β is the broadening of diffraction line measured at the half of its maximum intensity in radians, and θ is the diffraction angle.

The microstructures of the undoped and doped samples have been investigated in detail by scanning electron microscope (SEM). For low x (x ≤ 0.02) the nanostructures are formed predominantly pyramidal shaped nanocrystals. As an example we show in figure 2 the particle size distribution of the undoped ZnO sample. The nanostructures are predominantly pyramidal in shape and the average sizes ~20-25 nm. The pyramidal shape of the nanostructures no longer persists as soon as significant Cd incorporation starts. This is shown in figure 2. For x = 0.08, the formation of nanorods can be seen as marked in the figure. The rods have typical diameter of ~ 30-36 nm and length 150-200 nm.

Fig.3 shows the AFM images of spray deposited ZnO and Cd doped ZnO thin films for scanning area of 5x5 μm². Root mean square surface roughness was estimated from the AFM data and it was found to be 23 nm for pure ZnO and 7 nm for higher concentration of Cd doped ZnO thin film (8%). From the AFM images, it is observed that the grains possess different shapes, sizes and roughness. Thus, the surface morphology of the ZnO is modified by Cd doping.

B. Optical properties

The transmission spectra of ZnO and Cd doped ZnO thin films deposited on glass substrate in the range of 200 to 800 nm are shown in Fig.4.
High transmittance of 75 to 83 % in the visible region of solar spectrum is observed in the figure. The significant red shift can be observed in the band edge with the increase in Cd concentration. The variation of the absorption coefficient ($\alpha$) with the photon energy ($h\nu$) is related by the relation (1) [9, 10]:

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

(1)

where $A$ is a constant, $E_g$ is the optical gap and $m$ is the exponent whose value varies between $\frac{1}{2}$ to 2 and determines the nature of transitions, its value is taken as $\frac{1}{2}$ for the case of direct bandgap semiconductors. From Equation (1)

$$(\alpha h \nu)^2 = A (h \nu - E_g)$$

The variation of $(\alpha h \nu)^2$ versus photon energy ($h\nu$) for all the CZO samples is shown in Figure 4. The energy band gap in case of a film is evaluated from the intercept of the linear portion of each curve on the $x$-axis [10, 11]. The calculated optical band gaps of thin films showed shift from 3.25eV to 2.90 eV (table 2) [12, 13]. Similar result on Cd doped ZnO thin films was also reported by A. Singh et al. [14]. When Cd content increases in a ZnO binary system, a contraction of the band gap of the thin film is observed. It may be due to the Zn ions replacement with the Cd ions in the ZnO lattice site.

<table>
<thead>
<tr>
<th>Teneur Cd(%)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$ (eV)</td>
<td>3.25</td>
<td>3.23</td>
<td>3.21</td>
<td>3.12</td>
<td>2.90</td>
</tr>
</tbody>
</table>

Table 2. Optical band gaps of thin of ZnO and Zn-1-xCd$_x$O thin films.

IV. CONCLUSIONS

The structural and optical properties of ZnO and Cd doped ZnO thin films grown by spray pyrolysis method on glass substrates have been investigated in this work. XRD patterns showed the growth of thin films along the (101) plane with hexagonal wurzite structure. There are not formation new phases in all samples. We did not detect any phase that could be attributed to the Cd ions present in the film. The average crystallite sizes of the films were found to be in the range of 20 -25 nm for ($x \leq 2\%$). The rods have typical diameter of ~ 30-36 nm and length 150 -200 nm. The transmittance of the films was found to be high, ranging from 75 to 83 % in the visible region. The band gap of the films decreased with increasing Cd content in ZnO lattice. On increasing Cd concentration in ZnO, the absorption edge of the films showed the red shifting. The surface morphologies of the films showed nano pyramidal and nano spherical shaped particles, uniformly distributed over the surface.

References