

Structural and optical properties of $Cd_xZn_{1-x}O$ Thin Film

Prepared by Chemical Bath Deposition Method

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Abstract

In the present work, $Cd_xZn_{1-x}O$ thin film with different Cd volume ratios in solution ($x=0, 0.3, 0.5, 0.7, \text{ and } 1$) have been deposited on glass substrate by chemical bath deposition method. The prepared films were characterized by using X-ray diffraction and UV-Vis spectroscopy measurements. The results show that the samples are polycrystalline and the crystallinity of the films enhanced with the increase of x value .The average transmittance of $Cd_xZn_{1-x}O$ films in the visible region was between (70–81%) with direct optical energy decreases from(3.34eV) to(2.38eV) when the value of x increases.

Keywords: $Cd_xZn_{1-x}O$ thin film, chemical bath deposition, different Cd volume , X-ray diffraction ,direct optical energy .

الخصائص التركيبية والبصرية للغشاء الرقيق $Cd_xZn_{1-x}O$ المحضر بطريقة الترسيب بالحمام الكيمائي

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الخلاصة

في هذا البحث تم ترسيب الغشاء الرقيق $Cd_xZn_{1-x}O$ عند نسب حجم متغيرة للكاديوم ($x=0,0.3,0.5,0.7$ and 1) على أرضيات زجاجية بطريقة ترسيب الحمام الكيميائي . خصائص الأغشية المحضرة شخّصت باستخدام حيود الأشعة السينية (XRD) وقياسات التحليل الطيفي للمنطقة فوق البنفسجية والمرئية. والنتائج بينت ان النماذج المحضرة متعددة التبلور (Polycrystalline) وتحسن الحالة البلورية مع زيادة قيمة x . ومعدل النفاذية لأغشية $CdZnO$ في المنطقة المرئية % 70-81 مع فجوة طاقة بصرية مباشرة تقل من 3.34 eV الى 2.38 eV مع الزيادة في قيمة x .

الكلمات المفتاحية: الغشاء الرقيق $Cd_xZn_{1-x}O$ ، ترسيب الحمام الكيميائي، نسب حجم متغيرة للكاديوم، حيود الأشعة السينية، فجوة طاقة بصرية مباشرة.

Introduction

In recent years, transparent conducting oxides are very promising materials for their numerous applications, such as sensor [1], phototransistor [2], diodes [3], and solar cells [4,5]. Among various transparent conducting oxides, zinc oxide (ZnO) and cadmium oxide (CdO) have attracted considerable attention because of their high electrical conductivity and optical transmittance [6,7]. Pure ZnO is an n-type semiconductor with a wide bandgap of (3.37 eV) [8]. The conductivity of undoped ZnO and CdO is due to the presence of Zn/Cd-interstitials and/or oxygen vacancies [9]. The CdO has optical bandgap of about (2.2 eV) [10]. The low bandgap of CdO could be modified by doping and growth conditions. A widening in the bandgap of CdO has been observed by titanium doping [11]. The bandgap increases to 3.0 eV by addition of (5%) titanium in CdO film.

Several techniques have been used to prepare CdO–ZnO alloy films such as sol–gel [12], spray pyrolysis [13,14], sputtering [15–17], chemical bath deposition [18], chemical vapor deposition [19,20], and pulsed laser deposition [21,22]. Among various techniques, chemical bath deposition offers many advantages such as low temperature processing, low cost, easy technology, and wide range of accessible shapes [23,24]. The product can be influenced by careful control of several reaction variations. The bandgap of nanostructure CdO can be tuned by copper doping [25] and co-doping with nickel and lithium ions [26]. The observed

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variation in the bandgap of the doped CdO was explained on the basis of quantum confinement.

In present paper, we report the preparation and characterization of $Cd_xZn_{1-x}O$ films. The main interest of the present work is to study the effect of different compositions on the optical properties of these films. The films were fabricated using chemical bath deposition method. The structural and optical properties of these films were studied in detail.

Experimental

For the synthesis of $Cd_xZn_{1-x}O$ films, analytical grade zinc nitrate salt [$Zn(NO_3)_2 \cdot 6H_2O$] (Fluka), cadmium nitrate salt [$Cd(NO_3)_2 \cdot 4H_2O$] (Fluka) and ammonia solution (NH_4OH) (30 %)(Aldrich) were used. At first, zinc nitrate dihydrate and cadmium nitrate dihydrate of 0.5 M were prepared separately. In order to prepare ZnO precursor solution, the zinc nitrate was dissolved in (200 ml) at constant stirring, an excess ammonium hydroxide solution (NH_4OH) was added slowly until a transparent solution was obtained. CdO solution was prepared in the same manner. The resulting mixture was stirred at room temperature for (4 hr). The obtained solutions were mixed in different volume ratios ($x=0,0.3,0.5,0.7$ and 1) at room temperature. Commercial quality microscope glass slides with dimensions, $75mm \times 26mm \times 1mm$, were used as the substrates. In order to remove macroscopic contaminations, the substrates were cleaned ultrasonically in a mixture of ethanol and acetone (each of 50% in volume) for (15 min). The latter operation was repeated in deionized water. Finally, the substrates were immersed in acetone and rinsed with deionized water and dried with nitrogen.

The glass substrate was dipped in the solution for (24 hr). After that, the samples were dried at (80 °C) for (10)min to evaporate the solvent and remove organic residuals in an oven, then naturally cooled to room temperature. This procedure was repeated (10 times), and finally the resulting thin films were annealed at (400 °C) in air for (1 hr) using a furnace (model Yamato FM 27).

Film thickness was measured by laser interferometer. The X-ray diffraction(XRD) analysis was carried out using X-ray 6000(Shimadzu) diffractometer with CuK_{α} radiation

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($\lambda=1.541 \text{ \AA}$) at (40 kV) and (30 mA) .The optical transmission spectra were investigated by UV-Visible Spectrophotometer (Cintra 5) GBC-Astrural).

Results and discussion

1-X-Ray Diffraction

Fig. 1 shows the XRD patterns of the $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ thin films. It can be distinguished from Fig. 1 that all samples are polycrystalline. The diffraction peaks in the XRD pattern consist of the diffraction peaks of ZnO and CdO. The observed diffraction peaks (100), (002) and (101) for ZnO and (111), (200) and (220) for CdO are in good agreement with the reported data [27,28]. It is also illustrating that the $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ thin films are a binary mixture composed of a NaCl cubic structure (CdO) and a hexagonal wurtzite structure (ZnO) with small preferential orientation in the planes (111) and (002), respectively. It is also important to mention that when the concentration x of cadmium increases from 0 to 1 (with a step of 0.3) the intensity of the characteristic peaks of ZnO decreases, whereas the full width at half maximum (FWHM) of the related peaks increases. The fact that the FWHM decreases is the manifestation of the deterioration of the crystalline quality.

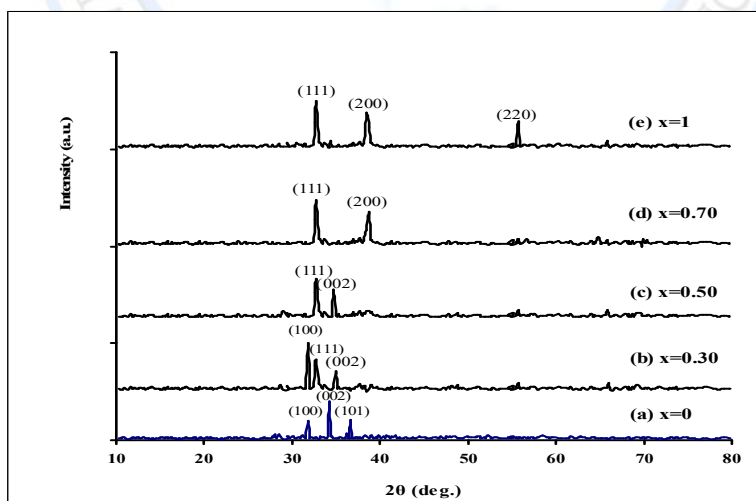


Fig. 1. X-ray diffraction patterns of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ thin films with various x values.

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The average grain sizes were calculated by using Sherrer's formula [29] .

$$D = \frac{k\lambda}{\beta\cos\theta} \dots\dots\dots (1)$$

Where (k) is a constant taken to be 0.94, (λ) is the X-ray wavelength, (β) is the full-width at half-maximum (FWHM) of the peak, and (θ) is the reflection angle[21]. The grain sizes of the CdS films increase from (18 nm) to (58 nm) , when x increases, as shown in figure (2) where increasing cadmium ion concentration causes to increasing in grain size and the results are given in Table 1. Several authors have reported the nature of the films having such grain sizes [30–34].

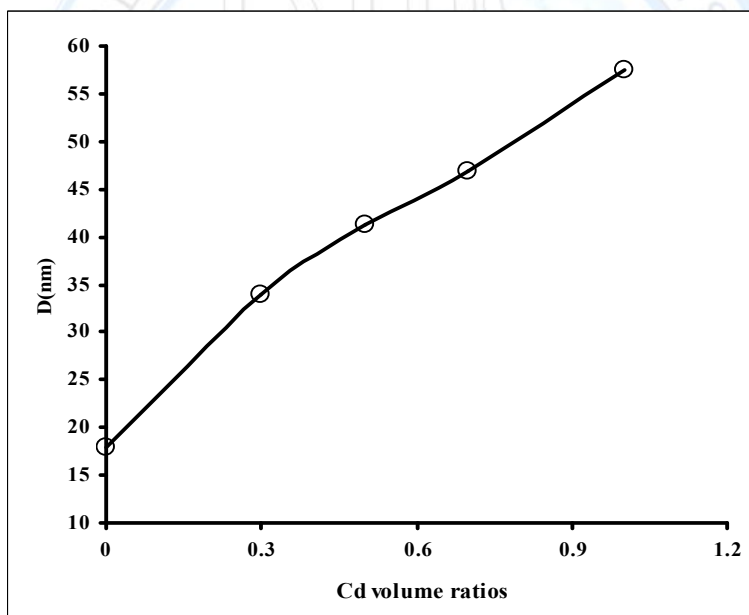


Figure (2): Variation of crystallite size with the increasing cadmium ion.

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Table (1):The thickness and grain size values of CdZnO thin films.

Sample	Thickness (nm)	Grain size (nm)
ZnO	180	18
Cd _{0.30} Zn _{0.70} O	176	28
Cd _{0.50} Zn _{0.50} O	170	36
Cd _{0.70} Zn _{0.30} O	154	47
CdO	140	58

Optical Properties

The optical transmission spectra of the films were measured at room temperature in air over (200 to 800 nm) (Fig. 3). The main three features of the transmission spectra are as follows: **1.** the transmission of the films in the visible and near-IR regions decreases with x (from 81% to less than 70%); **2.** except ZnO and Cd_{0.30}Zn_{0.70}O films, the other investigated samples have no sharp principal absorption edge; it may be attributed to Urbach's effect [35]; **3.** the optical transmission spectra also show the shifting of the band edge to lower energy (red shift) as Cd concentration increases. This may be due to the modulation of band gap caused by Cd substitution [36]. The optical direct band gap E_g of the films can be estimated by extrapolation of the linear portion of $(\alpha h\nu)^2$ vs. $h\nu$ plots using the Tauc relation [37]

$$(\alpha h\nu) = B(h\nu - E_g)^{1/2} \dots\dots\dots(2)$$

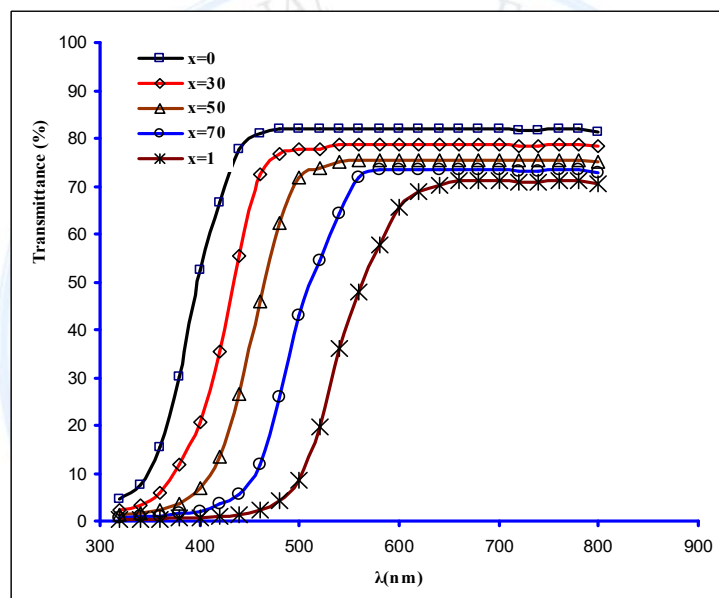
Where (α) is the absorption coefficient, $(h\nu)$ is the photon energy and (A) is the band edge constant. The corresponding plots are shown in Fig.4. The optical band gap value decreases from (3.34) to (2.38) eV as Cd concentration increases. To explain this trend, we firstly focus

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on thickness variations due to Cd alloying. As the Cd ratio increases in the solution, the thickness of the films increases (Table 1). According to references [38,39] with thickness the value of E_g decreases due to energy spread of the localized states increasing. However, due to low difference between thickness values the thickness dependence of the Urbach tail does not seem just the case. The optical band gap of the $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ thin films changed with increasing cadmium ion concentration, as shown in Figure 5. These show that with increasing cadmium ion concentration, values of obtained optical band gap decreased.

**Fig.3. UV-vis spectra of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ thin films.**

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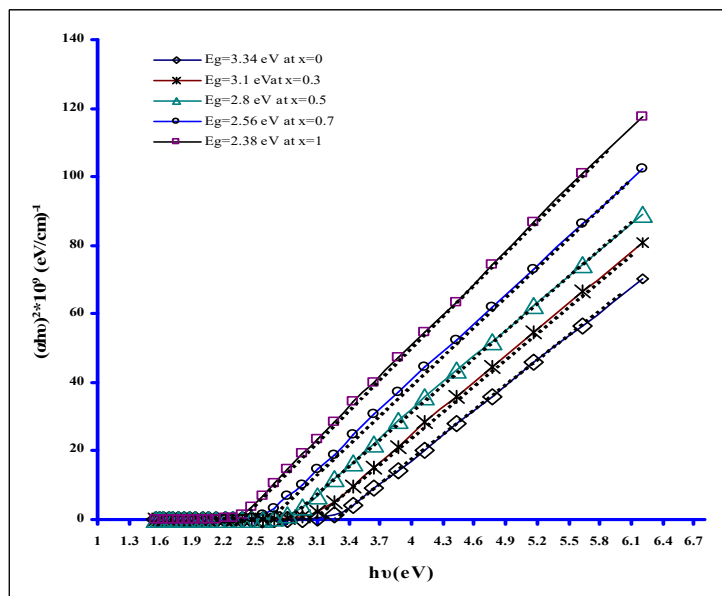


Fig. 4 The plots of $(\alpha hv)^2$ vs. $h\nu$ for Cd_xZn_{1-x}O thin films.

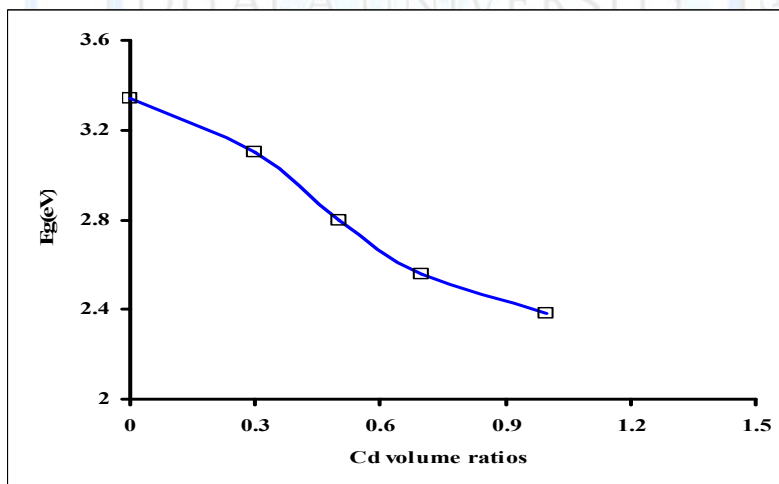


Figure (5): Variation optical band gap of Cd_xZn_{1-x}O thin films with the increasing cadmium ion.

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From the obtained results, we can conclude the following. The deposition rate increases with increasing cadmium ion concentration. The X-ray diffraction studies showed that the films are polycrystalline in nature with a mixture of hexagonal and cubic phases. Grain size increase with the increasing cadmium ion concentration. The optical transmission spectra also show the shifting of the band edge to lower energy (red shift) as Cd concentration increases with the presence of direct band gaps decrease with increasing cadmium ion concentration.

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