Structural and Optical Properties of Boron Doped Cadmium Oxide

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Abstract: Thin films of transparent and conductive CdO and B1,3)w% doped cadmium oxide (CdO: B) (1 and 3) wt %, have been deposited using chemical spray pyrolysis (CSP)) technique on glass substrate temperature of 300°C. Microstructural analysis indicates that X-ray diffraction study shows that the obtained films were polycrystalline. The preferred orientation was along the direction (200) and that the average crystallite size increases with the increasing B content. Morphological properties were studied, by scanning electron microscope (SEM) and atomic force microscopy (AFM) which reveals that the grains have a similar column shape. UV-visible transmission spectroscopy reveal that the prepared thin films are transparent in the visible range, The value of the optical band gap obtained shows a slight increase in its values from 2.43 eV to 2.45 eV as B concentration increasing.

Key word: CdO: B, Thin films, Optical properties, Spray pyrolysis, photon energy graph, Grain size.

1. Introduction
Cadmium Oxide CdO is one of the most important materials in the semiconductor industry, according to the development of solid state devices [1]. Cadmium oxide is a transparent in the visible, ultraviolet and near infrared regions of the electromagnetic spectrum [2]. Cadmium oxide is considered to be a semiconductor of n type charge carriers and a direct energy band gap near 2.22 eV. It has, which can be increased by doping[3]. In general, the undoped and non-stoichiometry cadmium oxide is considered to have little resistance because it contains a small amount of oxygen vacancies and interstitial defects [4]. It transitions from transparent materials in the region of 450 nm of the electromagnetic spectrum [5]. Synthesis of CdO films with different types of doping elements such as Cu [6], Ga [7], F [8], Li-Ni [9], Bi [10], Fe [11], In [12] confirms the possibility of tuning their material properties to be developed in new applications in optoelectronic devices and sensors, by approving electrical conductivity in pure cadmium oxides to the existence of oxygen vacancies [13]. It is possible to control electrical conductivity by producing thin films of cadmium Oxide is doped with metallic ions [14]. And cadmium oxide can be doped with many materials such as phosphorus tin and boron, which can shift the optical energy gap to the visible region [15]. Cadmium Oxide doping in the tin and prepared by sputtering can be used in pressure monitoring applications in the atmosphere [16]. Cadmium oxide can be prepared in the form of chemical evaporation. The optical, electrical, and structural properties can be affected by partial pressure and the substrate temperature, the thickness and the annealing can be obtained with a resistance of 14-17 Ω/ square unit and for pure cadmium oxides of thickness 120-150 nm [17]. Explained that there is a direct and indirect electronic transmission of the type of package to its package and associated with three and two and a half electron volts [18]. The aim of this work is to prepare B doped CdO by the simple and low cost spray pyrolysis technique in order to study their structural and optical properties.

2. Materials and Methods

The CdO thin films were prepared from O.1 M of CdCl₂ (provide by Sigma-Aldrich – German) that dissolved in 1:1 deionized water and ethanol. The doping agent was Boron trichloride (BCl₃) (provide by PubChem India) dissolved in deionized water, few drops of HCl were added to the solution in order to get clear solution. Chemical spray pyrolysis was used to prepare B-doped CdO film deposited on glass slide substrate. The preparation conditions are: Substrate temperature 300 °C, distance between the nozzle and the substrate was 27 cm,
spraying period 7 s lasted by 60s to avoid cooling, spray rate was 4ml/min, and Nitrogen gas was used as a carrier gas.

The film thickness was measured using the gravimetric method to be 300 ± 30 nm. The XRD (SHIMADZU XRD-6000), SEM (Jeol JSM 6335F), and AFM (AA3000 SPM) were used to determine the structure and the morphology of the films. UV-Visible spectrophotometer (UV SPECTROPHOTOMETER SHIMADZU MODEL UV-1800) that used to record the absorbance spectra in the wavelength range 300-900 nm.

3. Results and discussion:

Figure (1) shows the pattern of reflection of X-ray and note that all the films of the pure precipitate and barium-doped with a pattern of reflection of multi-crystallization and that all reflections are identical to the international card of CdO No. 05-0640 [19]. And the preferred reflection is (200) plane, which are associated with angle 2θ =38.22°, which we note that the intensity of reflection decrease with the increase of B doping up to 4 wt% ,which may be attributed to the deformation in the CdO lattice induced by the size difference between Cd and B ions and also due to the segregation of B2+ ions in the grain boundaries of the host CdO lattice [20]. The crystallite size decreases with the increase of doping concentration from 34.20 nm to 32.40 nm according to the calculation by Sherrer equation (1) and is shown in Figure (1-a). Figure (1) shows a number of secondary reflections (111), (220), (311) and (222), which are associated with angles 2θ = 32.74°, 55.26°, 65.88° and 69.14° which vary in intensity with increasing the doping concentration. A shift in Bragg angle was noticed according to the ICDD, this shift could be attributed to the existence of B. The Microstrain (ε) could be calculated by equation (2) [21] and the dislocation density (δ) by equation (3) [21]. The relationship between microstrain and the dislocation density was represented as a function of the deflection concentration as in Fig (1-b and c).

\[
D = \frac{k \lambda}{\beta \cos \theta} \quad (1)
\]

\[
\varepsilon = \frac{\beta \cos \theta}{4} \quad (2)
\]

\[
\delta = \frac{1}{D^2} \quad (3)
\]
Figures (2, 3 and 4) show the SEM images and the topographic images represented by AFM powered by a graph showing the accumulation distribution chart of the particle clusters on the surface of undoped and doped cadmium oxide. The SEM images show that the surface became more homogenous with the increase in doping concentration. The AFM images show more clearly the growth of nanoparticles on the film surface by the height 32.65 nm and the radius (50-70) nm and the average particle size (40-80) nm in the pure sample as in Table 1. With the increase of doping concentration up to 3 weight % as in fig. (4), we notice that the number of columns is decreasing and the height is about 2.66 nm and the average particle size (20–40) nm (Table 1). These results were in good agreement with the results obtained by XRD.
Table 1. Average particle size, Average roughness, R.M.S and Radius for pure and B doped CdO.

| Sample  | Average particle size (nm) | Average roughness (nm) | R.M.S | Radius (nm) |
|---------|---------------------------|------------------------|-------|-------------|
| Pure    | 40- 80                    | 8.32                   | 9.57  | 50- 70      |
| 1 w%    | 60- 70                    | 6.01                   | 7.09  | 40-70       |
| 3 w%    | 20- 40                    | 5.04                   | 6.15  | 60- 80      |

Figure 2. (a) SEM image and the inset image of, (b) AFM and (c) Accumulation distribution chart of pure CdO.
Figure 3. (a) SEM image and the inset image of (b) AFM and (c) Accumulation distribution chart of (1w%) B doped CdO.

Figure 4. (a) SEM image and the inset image of (b) AFM and (c) Accumulation distribution chart of (3 w%) B doped CdO.
The measurements of transmittance of the pure CdO and B doped samples showed that high transmittance is located in the visible region at the limits of (60 - 80) the doping concentration increasing up to 3 wt % due to the improvement in crystallization and an increase in the roughness of the surface by increasing the diameter of the developing columns on the surface, Figure (5) represents the spectrum of pure and B doped CdO films. The absorption coefficient (\( \alpha \)) can be calculated according to Tauc formula [22]:

\[
\alpha = 2.303 \left( \frac{A}{t} \right) \quad (4)
\]

Here, “t” represents the thickness of the films. The direct transition was estimated through the following relation[23]:

\[
(\alpha h\theta) = b(h\theta - E_g)^{1/2} \quad (5)
\]

Where \( h\theta \) is the photon energy, \( n \) is an index related to the density of state (\( n=1/2 \) for direct transition and \( n=2 \) for indirect transition) and \( E_g \) is the optical band gap of the semiconductor films. Figure (6) shows the plot of \((\alpha h\theta)^2\) vs photon energy, the extrapolation of straight line portion of the graphs were used to evaluate the band gap of pure and B doped CdO films. Their values were decreased from 2.32 eV for the pure sample to 2.17 eV for B doped with 4 wt %. This can be attributed to the localized energy levels created in the forbidden band [24].

![Figure 5. Transmittance as against wavelength graph for pure and B doped CdO films](image-url)
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Figure 6. \((\alpha h\nu)^2\) versus photon energy graph for pure and B doped CdO films

4. Conclusions

CdO and B doped CdO was successfully prepared utilizing the most cheap and inexpensive chemical spray pyrolysis technique. The most important results were the decrease in crystallite size with the increase of doping concentration, the effect of doping was noticed clearly in the increase in the optical energy gap.

Acknowledgments

The authors would like to thank the mustansityah university (www.mustansiryah.edu.iq) Baghdad- Iraq for its support of this work.

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