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November 5, 2019

Effect of Bismuth addition on thin films of ZnO on Structure and Optical Properties

Ali Mohammed Jabbar¹, Akeel Shakir Alkelaby², Reem Sami Ali¹, Nadir Fadhil Habubi³, Khalid Haneen Abass⁴, Sami Salman Chiad^{3*}

¹Department of Physics, College of Science, Mustansiriyah University, Iraq, alimohammed@uomustansiriyah.edu.iq, reemphy81@uomustansiriyah.edu.iq.

²The General Directorate of Education in Babil, Ministry of Education in Iraq, Iraq, akeelshakir@gmail.com.

³Department of Physics, College of Education, Mustansiriyah University, Baghdad, Iraq, nadirfadhil@uomustansiriyah.edu.iq, dr.sami@uomustansiriyah.edu.iq.

⁴Department of Physics, College of Education for Pure Sciences, University of Babylon, Iraq, Pure.khalid.haneen@uobabylon.edu.iq .

*Corresponding author E-mail : dr.sami@uomustansiriyah.edu.iq

Abstract

thin films of pure Zinc Oxide (ZnO) and Bismuth doped ZnO (1, 3 wt.%) were synthesized via the technique of chemical spray pyrolysis CSP. From using X-Ray diffraction (XRD) pattern, all the prepared films have hexagonal wurtzite structure. Transmittance and absorbance were estimated via Uv-Visible spectrophotometer. Parameters of optical (energy gap, absorption coefficient, refractive index, extinction coefficient, real and imaginary parts of dielectric constant) were calculated from recording absorption spectrum. The energy gap of (ZnO) films had been seen as decreased with increasing concentration of bismuth.

Keyword: (ZnO:Bi) films, chemical pyrolysis technique, XRD, optical constants.

Introduction

ZnO is main place in new technologies and offers a vast area of scientific in many applications [1]. Its II-VI compound semiconductor and ionicity exist at the boundary between ionic and covalent semiconductors [2]. ZnO is an n-type semiconductor [3] and has bandgap energy of 3.37 eV [4], melting point is 2248 K and a wider binding energy 60 meV [5,6]. ZnO is used for different applications such as short wavelength semiconductor diode lasers(SDLs) [7], gas sensors [8], solar cells [9]. Thin films of (ZnO) have been made with a different of deposition technique include atomic layer deposition [10], pulsed laser deposition (PLD) [11], thermal evaporation [12], novel DC plasma reactor [13], electrodeposition [14], sol-gel [15], pulsed filtered cathodic vacuum arc deposition (PFCVAD) [16], and chemical spray pyrolysis

[17]. In this paper, the method used to make all films is chemical spray pyrolysis and investigated from optical properties and structural.

Experimental

Pure Zinc Oxide(ZnO) and Bismuth(Bi) doped ZnO were mixed at various doping percentage of Bismuth (1, 3wt. %) and deposited this mixing on a glass substrate preheated at 450 °C via CSP method. The properties of structural for all films were studied via X-Ray Diffractometer, Cu:K α radiations($\lambda=1.54059\text{\AA}$) and scans are made between 2θ values of 20°and 70°. At room temperature the optical absorption spectra are recorded between 380 to 800 nm wavelength via Shimadzu UV-visible Spectrophotometer.

Results and discussion

At room temperature, the crystal structure was studied via X-ray diffraction pattern were determined from Fig.(1) for all films. This figure shows that films are polycrystalline and its structure is hexagonal wurtzite [18]. The synthesized of all films shows an XRD reflecting major peak detected at $2\theta = 34.4^\circ$, pointing a (002) direction. The pure ZnO and ZnO:Bi major peaks having also determined at 31.8° and 36.2° , identical to the lattice planes (100) and (101), respectively .The results in this work agree with that reported via Keskenler et al. [19]. The intensity of the (100) and (101) peaks decreases with increasing the concentration of Bi, while the (002) peak increased with increasing Bi concentration. This is the fact that all prepared films have good crystallization.

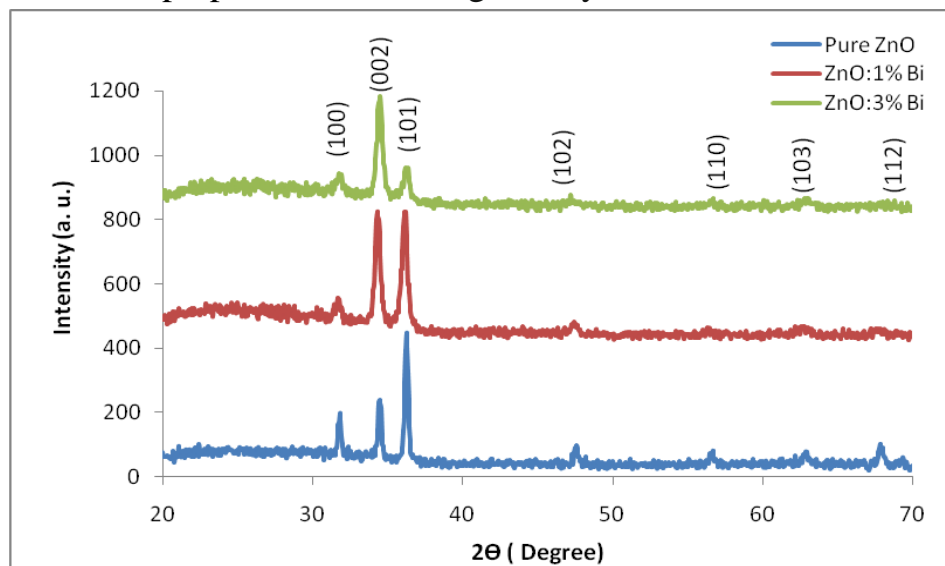


Fig.(1): XRD pattern of prepared films with diverse concentration of Bi.

The crystallite size(D) of the films can be estimated via the Scherer's relationship [20,21] :

$$D = 0.9\lambda / \beta \cos\theta$$

where λ is wavelength(\AA) of X- ray, θ is Bragg diffraction angle of the XRD peak (degree), β FWHM) (radian). The size of crystallite for the prepared films increased from 43.08 nm to 63.48 nm with increasing Bi concentration. The crystallite size of films is changed depending on the difference in the ion radius (Zn^{2+} $r = 0.88 \text{\AA}$ and Bi^{3+} $r = 1.17 \text{\AA}$) of the dopant element. The crystallite size is shown in Table(1).

Table (1): The crystallite size of XRD for all prepared films at diverse concentrations for (002) plane.

Film	Bi (wt.%)	Crystallite size (nm)
ZnO	0	43.08
ZnO:Bi	1	52.45
ZnO:Bi	3	63.48

The absorbance spectra for the prepared films with different concentration of Bi were illustrated in Fig. (2), the absorbance has increased when concentration of Bi films increased and decreased when the wavelength increased as in Fig. (2).

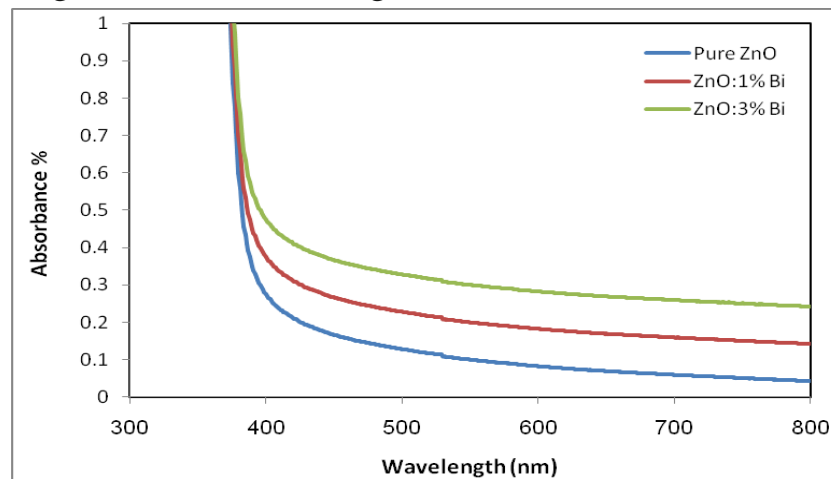


Fig.(2): The absorbance spectra with wavelength of Bi-doped ZnO films.

The spectra of optical transmittance for films illustrated in Fig.(3). Figure shows that the transmittance decreased when concentration of Bi increasing. This might be according to the free carriers coupling to the electric field; therefore the reflection increase [22].

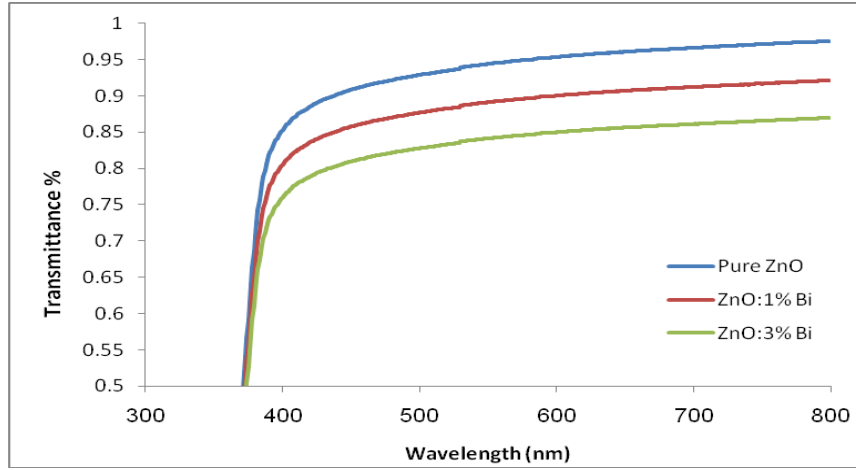


Fig.(3): Transmittance spectra with wavelength of Bi-doped ZnO films.

The absorption coefficient(α) can be studied via the relationship [23, 24]:

$$\alpha = 2.303A/d$$

where A and d represent absorbance and thickness respectively.

The absorption coefficient for all prepared films was illustrated in Fig.(4). where we see that the absorption coefficient increased when the concentration of Bi increase. Its value is larger than (10^4 cm^{-1}), which confirm the possibility of direct transitions [25].

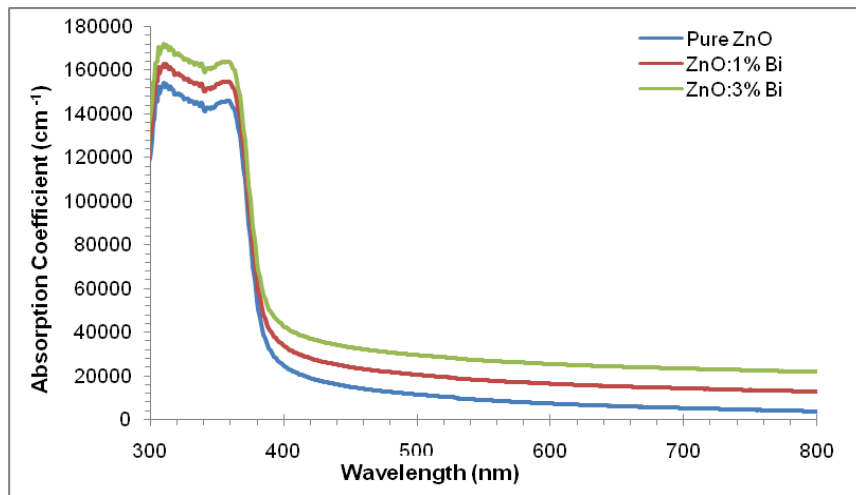


Fig.4: The absorption coefficient with wavelength of Bi-doped ZnO films.

The optical band gap (E_g) is found via the following relationship [26]:

$$(\alpha h\nu) = A[h\nu - E_g]^n$$

where A and $h\nu$ represent a constant and the photon energy respectively, $n = 1/2$ for direct allows transition,. E_g of ZnO:Bi thin films extracted

from the plot of $(\alpha h\nu)^2$ versus $h\nu$ curve. Fig.(5) explains the plot between $(\alpha h\nu)^{1/2}$ and $h\nu$ for films with concentration of Bi. The energy gap for all prepared films decreased when concentration of Bi increase. This due to that the increase of impurities ratio within the material (ZnO) increase the probability of Bi^{+3} to occupy the Zn^{+2} site and this will lead to creation of acceptor levels within the energy gap near the valence band [27], which takes place according to the improvement of crystallinity in samples [28]. The band gap energies are tabulated in Table (2).

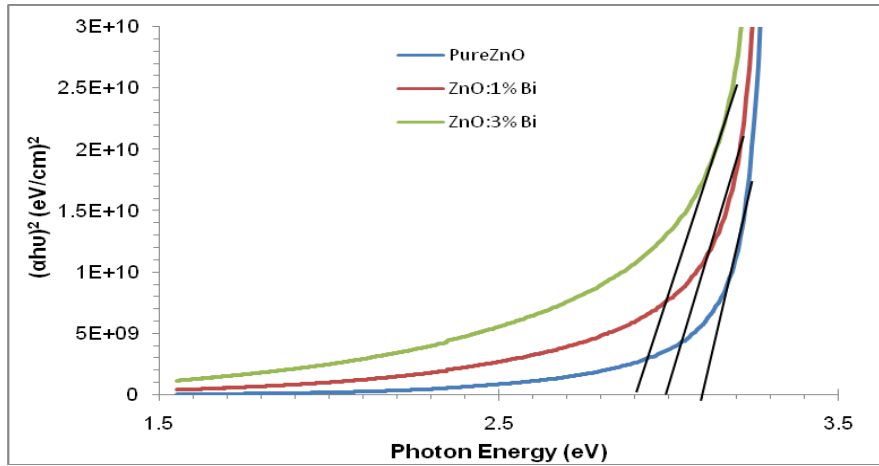


Fig.(5) A plots of $(\alpha h\nu)^2$ verses $(h\nu)$ of Bi-doped ZnO films with various concentration of Bi.

Table 2: The optical energy gap of Bi-doped ZnO films.

Film	(wt.%)	E_g (eV)
ZnO	0	3.1
ZnO:Bi	1	3
ZnO:Bi	3	2.9

The refractive index (n) have been determined via using the relationship [29,30]:

$$n = \left(\frac{4R}{(R-1)^2} - k^2 \right)^{1/2} + \frac{(R+1)}{(R-1)}$$

and can be determined by the extinction coefficient(k) via the relationship [31]:

$$k = \frac{\alpha\lambda}{4\pi}$$

Figs.(6,7) show (n) and (k) as a functions of wavelength. It can be noticed from figures, that (n) and (k) increased when concentration of Bi increase.

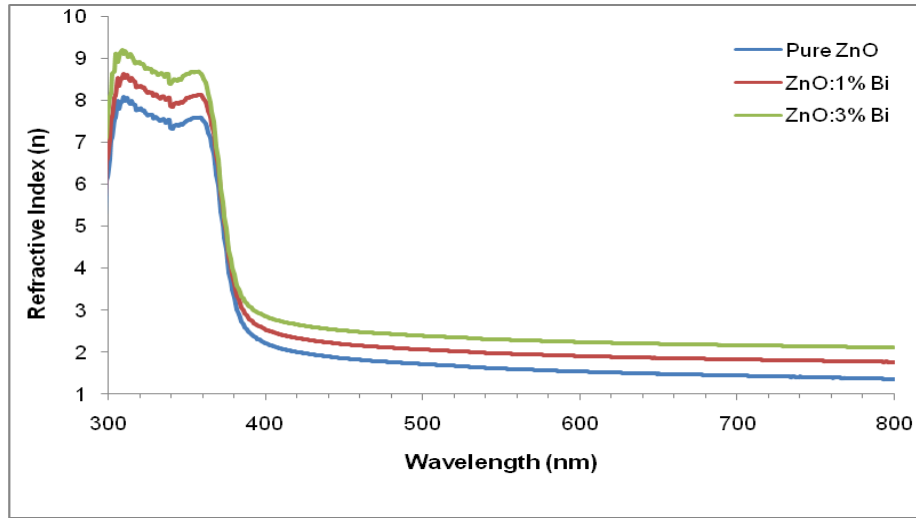


Fig.(6) Variant of (n) with wavelength of Bi-doped ZnO films.

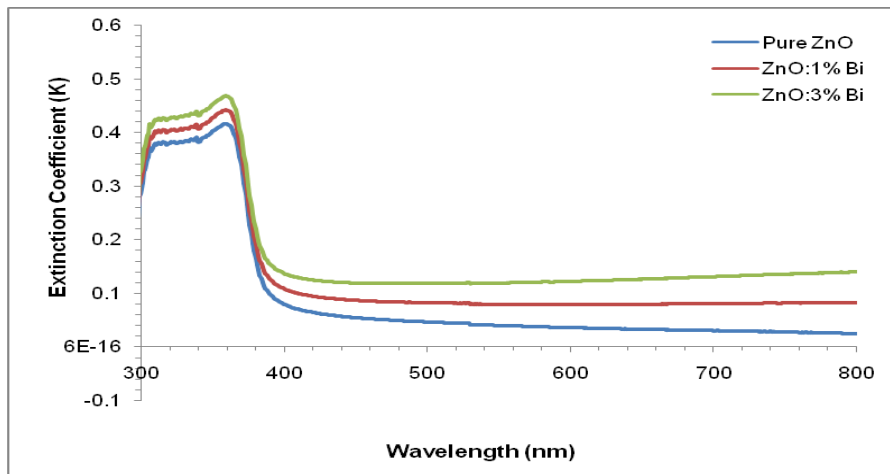


Fig.(7) Variant of (k) with wavelength of Bi-doped ZnO films.

The real (\mathcal{E}_r) and the imaginary (\mathcal{E}_i) parts of the dielectric constant for films were calculated by following relationship [32,33].

$$\mathcal{E}_r = n^2 - k^2$$

$$\mathcal{E}_i = 2nk$$

Figs.(8,9) shows the dielectric constant (\mathcal{E}_r and \mathcal{E}_i) parts for the films as a performance of wavelength, from this figure, we note \mathcal{E}_r and \mathcal{E}_i increased when concentration of Bi increase.

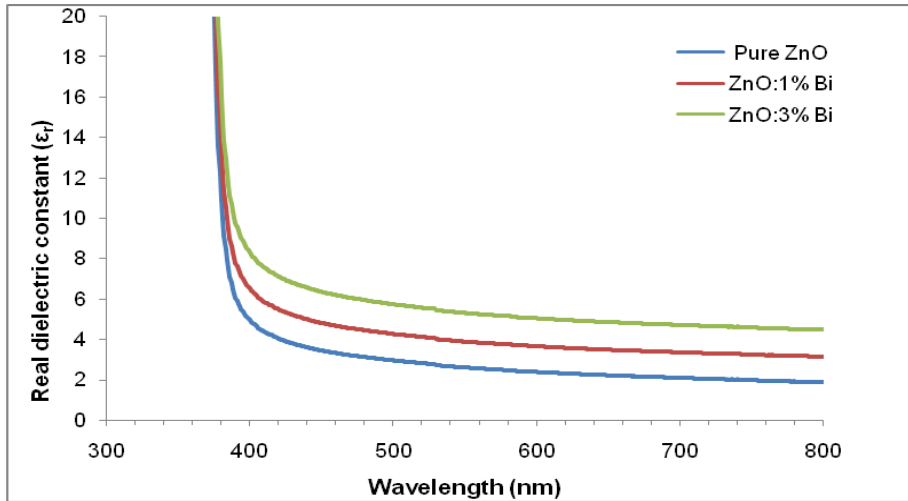


Fig.(8) Variant of ϵ_r with wavelength of Bi-doped ZnO films.

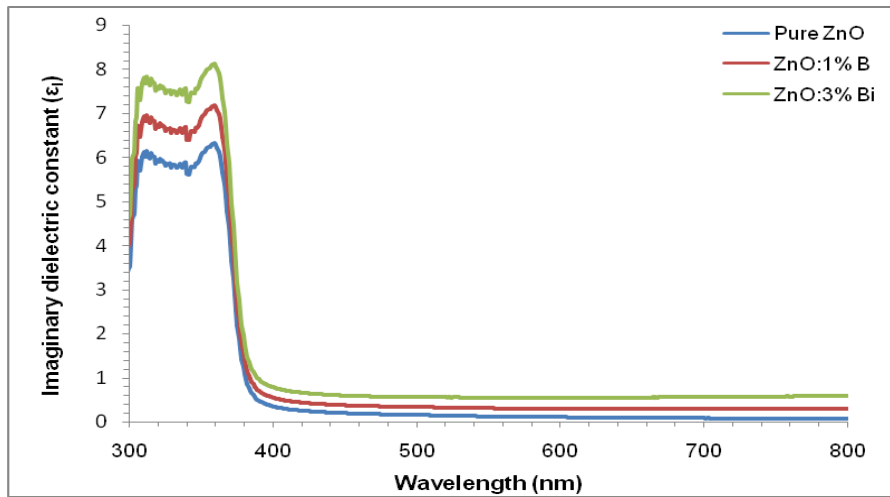


Fig.(9) Variant of ϵ_i with wavelength of Bi-doped ZnO films.

Conclusions

All prepared films were made via chemical spray pyrolysis technique. In XRD analysis, films prepared are hexagonal wurtzite polycrystalline with a preferred orientation along (002) plane and size of crystallite increased when concentration of Bi increase, which increased from 43.08nm to 63.48nm. In the UV-visible analysis, the transmittance is decreased when concentration of Bi for all prepared films increases, while the absorbance increased when concentration of Bi for all samples increases. The E_g energy of films has allowed direct energy gap (E_g) that decreased when concentration of Bi increase, which decreased from 3.1eV to 2.9eV. The (α , n , k and ϵ_r and ϵ_i parts) increased when concentration of Bi. Increase.

Acknowledgments

The author would thank Mustansiriyah University for their support in this work.

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