Effect of Zn Doping on Structural and Some Optical Studies of Nano NiO Films Prepared by Sol–Gel Technique

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ABSTRACT. This research deals with the study of the structural and optical properties of NiO and Zn doped NiO nano films with different ratios (0.01, 0.05, 0.1 mol %). NiO nano films in thickness 100 nm were deposited on a glass substrate using sol-gel spin coating technique. XRD results indicated that the films are polycrystalline and have cubic structure with a preferred orientation along (111). The average grain sizes of the crystallites estimated from XRD data was found to lie in the range of 19.11 – 25.05 nm. Data of AFM indicate that the surface of films is smooth. The optical transmittance value of nano NiO film reaches to 94% in the VIS and NIR regions, while it is value of films deposited with 0.1 mol% Zn reaches to (91)% which is important for its applications as window layers in solar cells. The values of optical energy gap of NiO and Zn doping by 0.01, 0.05, and 0.1 mol % were equal to 3.73, and 3.58, 3.42, 3.41 eV respectively.

1. INTRODUCTION

NiO is an important antiferromagnetic p-type of semiconductor and is a promising candidature for many applications such as lithium ion batteries, solar cells, antiferromagnetic layer, electrochemical capacitors, chemical sensors, and electrochromic coatings [1]. Stoichiometric NiO at R.T is an insulator with a resistivity of $10^{13} \Omega \text{ cm}$. The electrical conductivity of NiO can be manipulated by changing the concentration of Ni ion during doping [2]. Nickel oxide has demonstrated excellent properties such as catalytic [3], magnetic, electrochromic, optical and electrochemical properties [4]. Zinc is a first transition element in group 2. It has a hexagonal crystal system and the structure type of hexagonal close packed with $a=0.22 \text{ nm}$ and $c=0.49 \text{ nm}$ and has an electron configuration of $[\text{Ar}] (1s^2 4s^2)$. Zinc is hard and brittle at most temperature, but malleable at 100 to 150°C, above 210°C becomes brittle again [5]. On the other hand, it's a fair conductor of electricity, and burns in air at high red heat with evolution of white clouds of the oxide. It is employed to form numerous alloy with other metals, also large quantities of zinc are used to produce die casting, used extensively by the automotive, electrical and hardware industries [6]. We have prepared thin films from undoped NiO and Zn-doped NiO using sol-gel spin coating technique. The effects of Zn doping on the structure and some optical properties of NiO films were studied.

2. EXPERIMENTAL WORK

2.1 Preparation of films

Nickel oxide solution were prepared from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with purity 98%. 9.5 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with 0.4 M was dissolved into 100 ml of ethanol, mixed slowly for 1 hr by using magnetic stirrer device, and then added glycerine at a rate 10 V/V%, to obtain homogeneous solution, mixed it slowly for 6 hr until we get way a green solution. The completed preparation of the solution by adding 0.01 M of ZnCl_2 solution for different concentrations as shown in the Table (1).

Table 1: The rastes and concentrations of doped nickel oxide solution

Rank	NiCl ₂ 6H ₂ O (ml)	NiCl ₂ 6H ₂ O (M)	ZnCl ₂ (ml)	ZnCl ₂ (M)	Zn (mol%)
1	5	0.4	0.02	0.01	0.01
2	5	0.4	0.1	0.01	0.05
3	5	0.4	0.2	0.01	0.1

he spin coater device was used to prepare the films under the conditions of speed 3000 rpm and time 60 sec. 100 μ l from the solution dropped on the substrate to get a films , then dried it in electrical oven at 200 $^{\circ}$ C for 5 min in order to remove the effect of the solvent (Ethanol). . The samples were annealed at 500 $^{\circ}$ C for 2hr in a furnace. Fig.1 showsflow chart of NiO:Zn synthesis and the structural and optical measurements.

Fig. 1: Flow chart of NiO:Zn synthesis and the structural and optical measurements.

The film crystallinity was examined by X-ray diffraction 6000 of 1.54 $\text{\AA}$ from Cu- α , the XRD patterns of samples were recorded in the range $2\theta=20-80^{\circ}$. Surface morphologies were analyzed by an atomic force microscope AFM (AA3000, Angstrom Advanced IncUSA). We measured spectral

absorbance and transmittance over the spectral range of 300-800 nm by using UV-Visible–NIR spectrophotometer supplied by Shimadzu company .

2.2 Basic relations

The lattice constant(a) are estimated from the relation[7]:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (1)$$

The average grain size dimension (D),can be estimated using Scherrer's formula [8].

$$D_{av} = \frac{0.94\lambda}{B \cos \theta} \quad (2)$$

Where: θ is the Bragg diffraction angle, B is the full width of the diffraction line at half –maximum intensity (FWHM, radian).

From the crystallite size calculations calculated the dislocation density (δ) by using the relation [9]:

$$\delta = 1/D_{av}^2 \text{ (line/cm}^2\text{)} \quad (3)$$

The number of crystallites per unit area (N) of the films was determined by the using formula [10]:

$$N = t/D_{av}^3 \quad (4)$$

At the absorption edge, the absorption coefficient (α) can be calculated using the expression [11]:

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \quad (5)$$

Where d is the samples thickness .

The optical energy gap (E_g^{opt}) was calculated using the Tauc relation which is given by the formula [12]:

$$\alpha h\nu = A (h\nu - E_g^{opt})^n \quad (6)$$

Where n is an integer depending on the nature of electronic transitions. For the direct allowed transitions n has a value of $1/2$, while for the indirect allowed transitions $n = 2$, and A is energy dependent constant. h is Plank's constant and $h\nu$ is the energy of the incident photon, ν is the frequency.

3. RESULTS AND DISCUSSION

3.1 Structural studies

XRD patterns of the films deposited at a glass substrate temperature 298K, and thicknesses consistently around 100 nm are shown in Fig.2. NiO and Zn doped NiO nano films were found to be polycrystalline in nature with two diffraction peaks along with (111) and (200) planes of cubic NiO phase (ASTM card 04-0835). The XRD data showed the dominating peak is (111), which is found to be in agreement with the researchers Anwer, Hao and Khansaa [13,14,15]. The average grain sizes of the crystallites for major reflex(111) increase gradually with the increase of Zn

concentrations. It is found to be 19.11nm, 23.51 nm, 24.79nm, and 25.05nm for doping concentrations (0, 0.01, 0.05, and 0.1 mol)% of Zn respectively.

Having no reflection peaks in the spectrum of XRD which indicate the presence of Zn. The diffraction peaks of samples NiO doped with concentration 0.01,0.05, and 0.1 mol % of Zn are slightly shifted towards lower 2θ values (diffraction peaks of (111) emerged at 2θ degree of 37.43 and 37.31, 37.28, 37.27 for pure NiO and 0.01 ,0.05, and 0.1 mol % of Zn-doped NiO respectively) in comparison with peaks for NiO as shown in Fig.2, resulting from the distortion (in the form of swelling) that has plagued the basic lattice attributed to the ionic radius of Zn (0.083 nm) compared with that values of Ni(0.078 nm) [16].

The lattice parameters, dislocation density and number of crystallites per unit area of undoped NiO and Zn doping by 0.01,0.05 and 0.1 mol %, were calculated using equation (1,3,4).

Table 2: Values of lattice constant, dislocation density and the no. of crystallite per unit area

	Rank	Lattice constant a (nm)	Dislocation density δ lines/ cm ²	Number of crystallites unit area (N)
0.4171	0	0.4171	2.70985	1.4106455
0.4175	1	0.4175	1.809234	7.695593
0.4177	2	0.4177	1.627222	6.639014
0.4181	3	0.4181	1.593619	6.361753

Fig. 2: XRD patterns of NiO and NiO: Zn doped thin films at different concentration

3.2 Surface Morphological Studies

The surface morphology of undoped NiO and Zn doping by 0.01, 0.05 and 0.1 mol %, was studied measured at thickness of 100 nm. It was observed with AFM micrographs as shown in Fig. 3. It can be noticed that a root mean square (RMS) roughness ranged of 6.06-4.82 nm, and a maximum peak to peak height, Sz (ten point height) ranged of 23.9 -20.4 nm. Data above indicate that the surface of films is highly smooth as can be seen from the results listed in Table 3.

Fig. 3: AFM images for undoped NiO and various Zn –doped NiO films. (-1- for 2D, & -2- for 3D)

Table 3: AFM data for undoped NiO and various Zn –doped NiO films measured at thickness of 100 nm films .

Concentration Of Zn(%)	Roughness average Sa(nm)	Root mean square Sq(nm)	Ten point height Sz(nm)
0	5.24	6.06	23.9
0.01	4.67	5.31	10
0.05	3.99	4.59	9.2
0.1	4.22	4.82	20.4

3.3 Some Optical Studies

3.3.1 Absorbance

Fig.4 shows the dependence of absorbance on the wavelength (λ) in the spectral range 300-800 nm for NiO and Zn -doped NiO nano films measured at thicknesses consistently around 100 nm. It is clear that the absorption edges shift to longer wavelength (red shift), which is indicating a decrease in the optical band gap value, with respect to the increasing of Zn concentration. This is attributed to the presence of intra band transitions at localized states in the energy gap. The sharp

absorption edge; corresponding to the band gap confirms the good quality of grown films. The films show higher absorption on the shorter wavelength side (UV region), and low absorption on the higher wavelength side (VIS region). This behavior can be explained as follows: at high wavelength, the incident photon does not have enough energy to interact with atoms, thus the photon will be transmitted, while at low wavelength region, the incoming photons have sufficient energy to excite electrons from the valence band to the conduction band, and thus these photons are eventually absorbed within the material.

Fig. 4: Optical absorbance VS. wavelength for NiO and various Zn-doped NiO nano films.

3.3.2 Transmittance

Fig.5 shows the dependence of the optical transmittance on the wavelength (λ) in the spectra range 300-800 nm for NiO and Zn-doped NiO nano films. The optical transmittance value of nano NiO film reaches to 94% in the VIS and NIR regions, while it is value films deposited with 0.1mol%Zn reaches to (91)% which is important for its applications as window layers in solar cells. This behavior may be attributed to microstructural features of prepared films, as the photon scattering increases by crystal defects [17]

Fig. 5: Optical transmittance spectra VS wavelength for NiO and various Zn-doped NiO nano films.

3.3.3 Optical absorption coefficient

Fig.6 shows the dependence of optical absorption coefficient (α) on the photon energy ($h\nu$) for NiO and Zn-doped NiO nano films. The optical absorption coefficient values increases with the increase of Zn-concentration, based on the fact that a small increase in the values of absorbance was found when increasing the dopant. In the high absorption region all films have value of $\alpha > 10^4 \text{ cm}^{-1}$, which caused the increase of the probability of the occurrence of direct transition.

Fig 6: The absorption coefficient for NiO and various Zn-doped NiO nanofilms .

3.3.4 Optical energy gap (E_g^{opt})

The experimental values of $(\alpha h\nu)^2$ plotted against $(h\nu)$ of pure NiO and NiO: 0.01, 0.05, and 0.1 mol % Zn concentration deposited at 298 K for 60 sec and thickness consistently around 100 nm are shown in Fig. (4.7, a, b, c, and d). The band gap energy is determined from the extrapolated straight line portion of the plot to the x axis, $(\alpha h\nu)^2 = 0$. The linear nature of the plots at the absorption edge confirmed that all deposited nano films NiO and NiO:Zn are a semiconductor with direct band gap. The values of optical energy gap, which have been obtained by extrapolating the curves to $(\alpha h\nu)^2 = 0$ for NiO and NiO 0.01, 0.05, 0.1 mol % Zn films were equal to 3.73, and 3.58, 3.42, 3.41 eV respectively. Change in the optical band gap energy with concentration may be attributed to the changes in homogeneity and density of the localized states, which increases with increasing concentration of Zn in the deposited films.

Fig. (7,a): Plot of $(\alpha h\nu)^2$ VS. photon energy ($h\nu$) for NiO film

Fig. (7,b): Plot of $(\alpha h\nu)^2$ VS. photon energy ($h\nu$) for 0.01 mol % Zn- doped NiO film .

Fig. (7,d): Plot of $(\alpha h\nu)^2$ VS. photon energy ($h\nu$) for 0.1 mol % Zn- doped NiO films.

Fig. (7,c): Plot of $(\alpha h\nu)^2$ VS. photon energy ($h\nu$) for NiO 0.05mol % Zn- doped NiO film.

4. CONCLUSIONS

The XRD results revealed that NiO and NiO:0.01,0.05, and 0.1 mol %Zn nano films were found to be polycrystalline and have cubic structure. The XRD data showed the dominating peak is (111). The AFM results revealed that the surface of films is highly smooth. With increase Zn content the roughness of film surface decreases. The transmittance value of undoped NiO film reaches to 94% in the visible and NIR range, which is important for its applications as window layers in solar cells. The optical energy gap of NiO with concentration (0,0.01,0.05, and 0.1) % of Zn thin films were equal to 3.73, 3.58, 3.42, and 3.41 eV.

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