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RESEARCH ARTICLE

EFFECT OF SOLUTION MOLARITY ON STRUCTURAL AND OPTICAL PROPERTIES OF NICKEL OXIDE THIN FILMS PREPARED BY CHEMICAL SPRAY PYROLYSIS TECHNIQUE

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ABSTRACT

In this work, NiO thin films at different molarities (0.05M, 0.1M, 0.15M and 0.2M) have been successfully deposited on glass substrates by chemical spray pyrolysis (CSP) technique at substrate temperature of (400 °C) and thickness of about 300 nm. The structural and optical properties of these films have been investigated using XRD, AFM, and UV-Visible spectroscopy. The XRD results showed that all films are polycrystalline in nature with cubic structure and preferred orientation along (111) plane. The crystallite size was calculated using Scherrer formula and it is found that the molarity 0.1M has maximum crystallite size (51.16nm). AFM images showed homogenous and smooth NiO thin films and the average grain size estimated from the AFM granularity report confirms the XRD results. The absorbance and transmittance spectra have been recorded in the wavelength range of (300-900) nm in order to study the optical properties. The optical energy gap for allowed direct electronic transition was calculated using Tauc equation. It is found that the band gap decreases when the molarity increases and the band gap values range between 3.71 eV and 3.59 eV for the prepared NiO thin films at different molarities. The Urbach energy increases as the molarity increases and the Urbach energy values range between 299 meV and 343 meV. The optical constants including (absorption coefficient, real and imaginary parts of dielectric constant) were also calculated as a function of photon energy. Refractive index and extinction coefficient for NiO thin films were estimated as a function of wavelength.

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INTRODUCTION

Nickel(II) oxide is the chemical compound with the formula NiO and it is the only well characterized oxide of nickel. The mineralogical form of NiO, bunsenite, is very rare. NiO can be prepared by multiple methods. Upon heating above 400 °C, nickel powder reacts with oxygen to give NiO. In some commercial processes, green nickel oxide is made by heating a mixture of nickel powder and water at 1000 °C, the rate for this reaction can be increased by the addition of NiO (Pradniak 2002). The simplest and most successful method of preparation is through pyrolysis of a nickel(II) compounds such as the hydroxide, nitrate, and carbonate, which yields a light green powder. Synthesis from the elements by heating the metal in oxygen can yield grey to black powders which indicates nonstoichiometry (Greenwood and Earnshaw 1984). NiO adopts the NaCl structure, with octahedral Ni(II) and O₂⁻. Nickel oxide (NiO) has a density of (6.67 g/cm³), molecular weight of (74.69 g/mol) and its melting point is (1955 °C) (Lascelles et al., 2005). Nickel oxide thin films have different applications such as, an antiferromagnetic material (Fujii et al., 1996), p-type transparent conducting films (Sato et al., 1993), electro catalysis, positive electrode in batteries, fuel cell, a mat-

erial for electro-chromic display devices, solar thermal absorbers, etc. (Cerc Korosec et al., 2003). Different techniques such as sol-gel, spray pyrolysis, ion beam sputtering, magnetic sputtering, and pulsed laser deposition have been used for deposition of NiO films (Giouroudiet et al., 2008). In the present paper, we report the effect of solution molarity on the structural and optical properties of NiO thin films prepared by chemical spray pyrolysis technique.

Experimental procedure

Chemical spray pyrolysis technique was used to deposit NiO thin films on glass substrates at temperature of (400 °C). In the preparation of NiO films, aqueous solution with different molarities (0.05M, 0.1M, 0.15M and 0.2M) of nickel nitrate Ni(NO₃)₂·6H₂O was mixed with distilled water by using magnetic stirrer for 30 minutes. The resultant solution was sprayed on glass substrates. Other deposition conditions such as spray nozzle substrate distance (30 cm), spray time (10 s), spray interval (2 minutes) and pressure of the carrier gas (1.5 bar) were kept constant for each concentration. The X-ray diffraction patterns for the prepared films were obtained in a (Shimadzu XRD-6000) goniometer using copper target (Cu K_α, 1.5418 Å) and Atomic Force Microscopy (AFM) micrographs were recorded by using scanning probe micro-

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scope type (SPM- AA3000), contact mode, supplied by Angstrom Advanced Inc. Optical properties in the wavelength range of (300-900) nm were investigated by using UV-Vis-NIR spectrophotometer (Shimadzu, UV-1800).

RESULTS AND DISCUSSION

Figure (1) shows the photo images of NiO thin films at different molarities (0.05M, 0.1M, 0.15M and 0.2M). It is reported that the correct stoichiometric NiO thin films are expected to have green color (Greenwood and Earnshaw1984); however, the NiO thin films deposited in the present study have black-grey color which can be attributed to the non-stoichiometry of the deposited material.

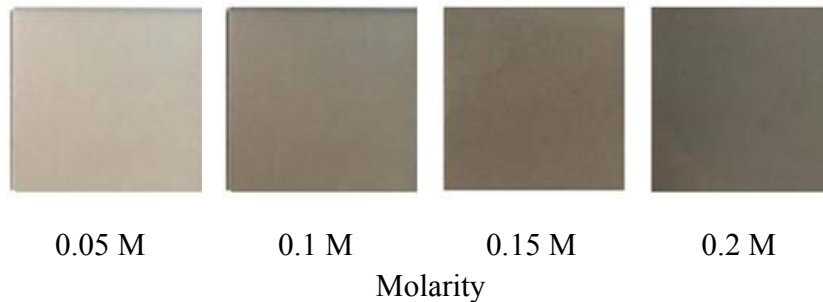


Figure 1. Photo images of NiO thin films at different molarities

Structural analysis

XRD patterns of the NiO films at different molarities are shown in Figure (2). It can be noticed that all the patterns exhibit diffraction peaks around (20~37°, 43° and 63°) referred to (111), (200) and (220) favorite directions respectively which is in agreement with the Joint Committee of Powder Diffraction Standards (JCPDS) card number 04-0835. The strongest peak occurs at 20~37° which is referred to (111) plane. The positions of the peaks and the presence of more than one diffraction peak lead to the conclusion that the films are polycrystalline in nature with a cubic crystalline structure, which is in agreement with other reports (Baluet et al.,2012; Ismail et al.,2013).

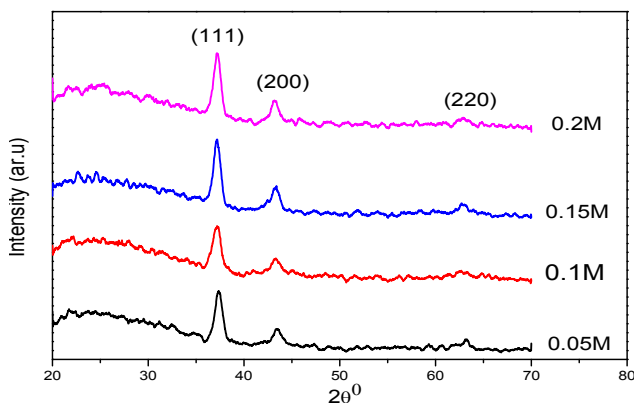


Figure 2. XRD patterns of NiO thin films at different molarities

It can be observed also that 2θ for (111) direction decreases with molarity increasing, which is in agreement with other studies (Baluet et al.,2012), as shown in Table (1). It can be seen

that the lattice constant (a_o) increases as the molarity increases as shown in table (1). It should be mentioned here that the standard a_o value for NiO is 4.176 Å which indicates that the film prepared at 0.1M has the nearest a_o value to the standard lattice constant. The average crystallite size for the films can be determined using Williamson-Hall (W-H) formula shown below (Moteet al.,2012).

$$\beta_{hkl} \cos \theta = \left(\frac{K \lambda}{D} \right) + 4 S \sin \theta \dots \dots \dots (1)$$

Where β_{hkl} is full width of half maximum, D is the average crystallite size, K is constant and was assumed to be equal to 0.9, λ is wavelength for Cu target for XRD instrument, θ is Bragg's angle for all peaks, and S is the microstrain in the film.

If β cos θ is plotted with respect to 4 sin θ for all peaks, strain and crystallite size can be calculated from the slope and y-intercept of the fitted line respectively as shown in Figure (3).

The average crystallite size for all films is also calculated for (111) direction by Scherrer formula by using the relation (11):

$$D_{av} = \frac{K \lambda}{\beta \cos \theta} \dots \dots \dots (2)$$

It is observed that the crystallite size for NiO thin films increases as the molarity increases from 0.05M to 0.1M to reach its maximum value of (51.16nm). The crystallite size then decreases as the molarity increases further to reach its minimum value of (10.84 nm) at 0.2M as shown in Figure (4). These results agree qualitatively with the results of crystallite size obtained by Williamson-Hall method as shown in Table (1). The microstrain in the films is induced during the growth of thin films by varying displacements of the atoms with respect to their reference lattice position (Saleh2013). All values of microstrain were negative which indicates the occurrence of compression in the lattice, as shown in Table (1).

The texture coefficient (T_c) represents the texture of a particular plane, in which greater than unity values imply that there are numerous of grains in that particular direction. The texture coefficients T_c(hkl) for all samples have been calculated from the X-ray data using the well-known formula (Barret and Massalki 1980):

$$T_c(hkl) = \frac{I(hkl)/I_0(hkl)}{N_r^{-1} \sum I(hkl)/I_0(hkl)} \dots \dots \dots (3)$$

Where $I(hkl)$ is the measured intensity, $I_0(hkl)$ the intensity values taken from the JCPDS data, (N_r) is the reflection number and (hkl) are Miller indices. The texture coefficient is calculated for crystal plane (111) of the NiO films. All values of texture coefficient were greater than 1 which indicates the abundance of grains in the (111) direction.

AFM Results

The 3D AFM micrographs of the NiO thin films are shown in Figure (5). The size of the scanned area was $(2 \times 2) \mu\text{m}^2$. The images show homogenous and smooth NiO thin films.

Table 1. Structural parameters of the NiO thin films at different molarities

Molarity (M)	0.05	0.1	0.15	0.2
2θ (deg)	37.3854	37.2539	37.2260	37.1826
hkl	(111)	(111)	(111)	(111)
d (Å)	2.40347	2.41167	2.41341	2.41613
(FWHM) (rad)	0.0136	0.0028	0.0118	0.0134
(D_{av}) nm Scherrer	10.76	51.16	12.33	10.84
(D_{av}) nm W-H	6.02	45.01	5	6.24
Micro strain $S \times 10^{-3}$ W-H	-8.57	-0.62	-11.87	-8.26
Lattice Constants a . (Å)	4.1629	4.1771	4.1802	4.1848
T_c	1.92	1.72	1.89	2.18

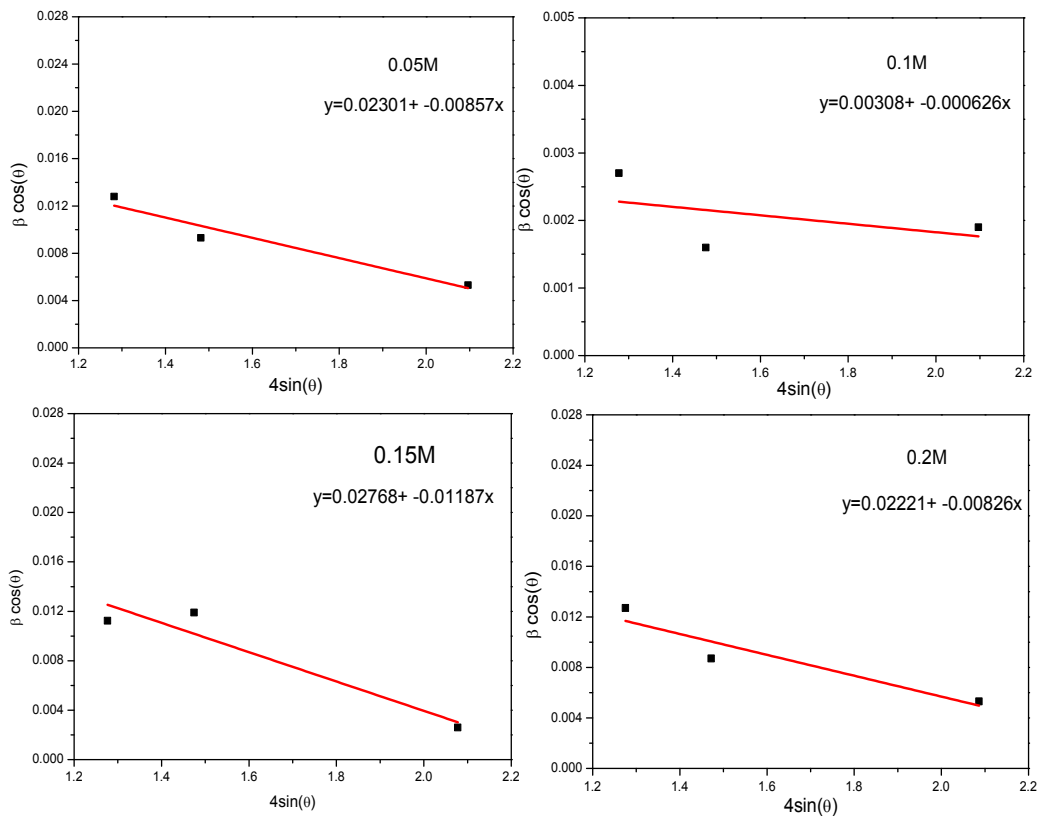


Figure 3. W-H analysis for NiO thin films at different molarities

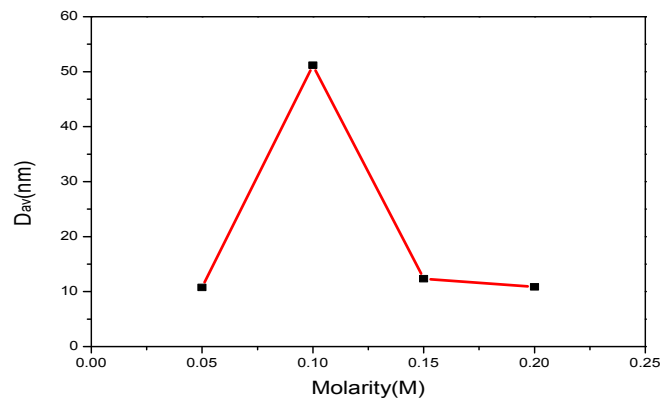


Figure 4. The crystallite size (D_{av}) for NiO thin films at different molarities

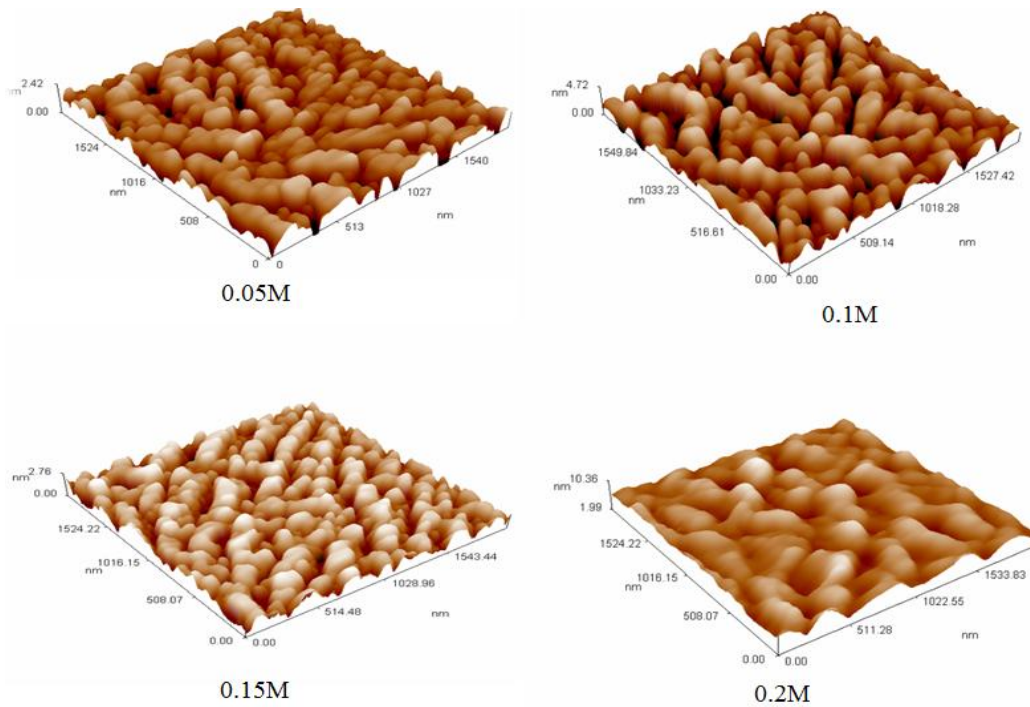


Figure 5. 3D AFM images of NiO thin films at different molarities

Table 2. Surface roughness, root mean square (RMS) and grain size for NiO thin films at different molarities

Molarity(M)	Surface roughness (nm)	RMS (nm)	Grainsize (nm)
0.05	0.378	0.459	83.84
0.1	0.89	1.05	133.8
0.15	0.517	0.615	98.77
0.2	0.864	1.1	98

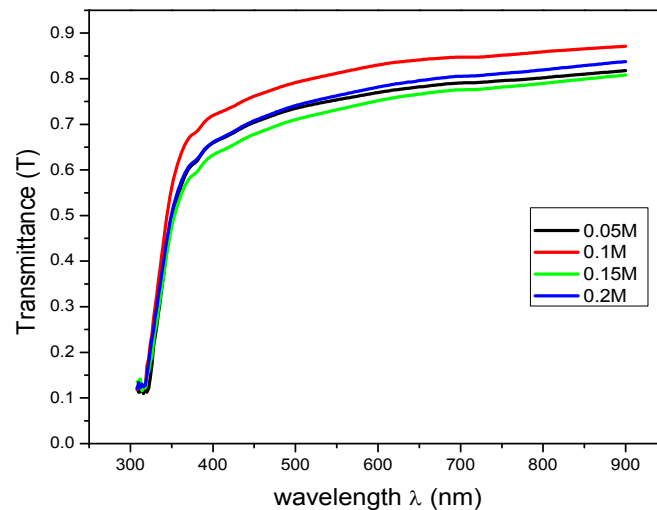


Figure 6. Transmittance (T) versus wavelength (λ) of NiO thin films at different molarities

The average grain size, average roughness and root mean square (RMS) roughness for all samples are given in Table (2). The sample prepared with solution molarity of 0.1M has highest average grain size, average roughness and RMS roughness of the film. The increase of the crystallite size maybe caused by columnar grain growth in the structure which is in agreement with other studies (Ismail et al., 2013).

Optical analysis

Optical absorption spectra of the films in spectral range of (300-900 nm) were recorded by using UV-Vis spectrophotometer. The analysis of the dependence of absorption coefficient on photon energy in the high absorption regions is performed to obtain the detailed information about the energy band gap of the films (Sahinet al., 2014). Figure (6)

shows the relation between transmittance and wavelength for NiO thin films at different molarities. It is clear that the transmittance for all samples increases rapidly as the wavelength increases in the range of (300- 350 nm), and then increases slowly at higher wavelengths. The spectra show high transmittance in the visible and infrared regions, and low in the ultraviolet region. It can be noticed also that the fundamental absorption edge is sharp in the visible region of the spectrum. The maximum transmittance observed of NiO thin films was about 85% at 0.1M.

Figure (7) shows the relation between absorbance (A) and wavelength for NiO thin films at different molarities. The absorbance decreases rapidly at short wavelengths corresponding to the energy gap of the film (when the incident photon has an energy equal or more than the energy gap value). This evident increase of energy is due to the interaction of the material electrons with the incident photons which have enough energy for the occurrence of electron transitions. It is observed that the absorbance is slightly affected by solution molarity and we can notice slightly higher absorbance at 0.15M.

The absorption coefficient can be estimated from the absorbance using the well-known formula (Pankove 1971):

$$\alpha = (2.303 \times A) / t \dots \dots \dots (4)$$

Where A is the absorbance, t is the thickness and α is the absorption coefficient. It has been noticed that all the prepared thin films have high absorption coefficient in visible range of solar spectrum, and this could be seen in Figure (8). The absorption coefficient increases with increase in photon energy ($h\nu$). The absorption coefficient of NiO thin films at different molarities have values of ($\alpha > 10^4 \text{ cm}^{-1}$) which implies the increase of the probability of the occurrence of direct transitions. The optical energy band gap (E_g) is given by the classical relation (Pankove 1971):

$$\alpha h\nu = A(h\nu - E_g)^r \dots \dots \dots (5)$$

Where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap, A is a constant which does not depend on photon energy and r has four numeric values (1/2) for allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions.

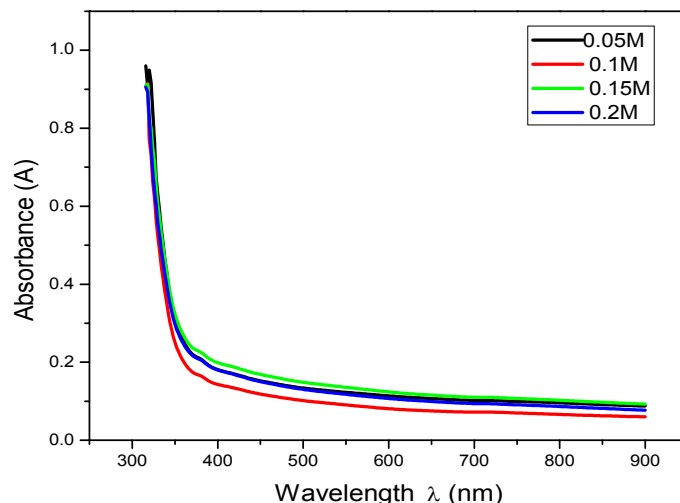


Figure 7. Absorbance (A) versus wavelength(λ) for NiO thin films at different molarities

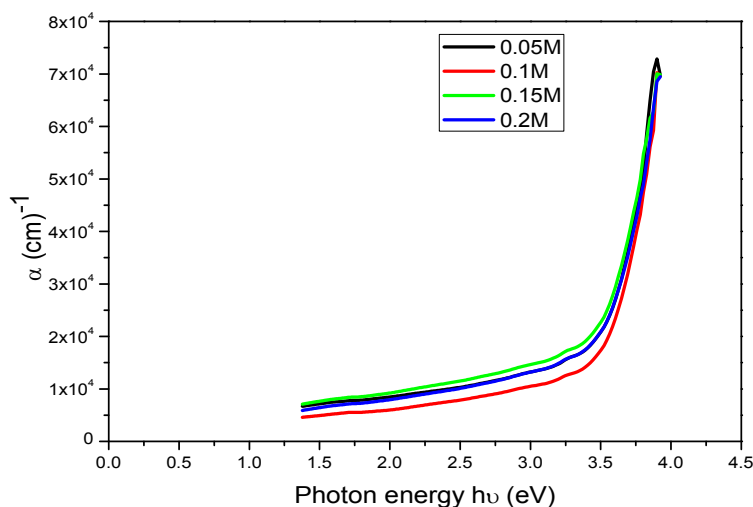


Figure 8. Absorption coefficient versus photon energy for NiO thin films at different molarities

In this work, direct band gap was determined by plotting a graph between $(\alpha h\nu)^2$ and $(h\nu)$ in eV. The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ gives value of the direct band gap of the material, and this could be seen in Figure (9). We notice that the band gap value decreases when the molarity increases, which is in agreement with other reports (Thayumanavan et al., 2011; Patilet et al., 2011). The allowed direct band gap values range between 3.71 eV and 3.59 eV.

absorption edge. Figure (10) shows the variation of $(\ln\alpha)$ versus photon energy for the films. The E_t values were calculated as the reciprocal of the straight line slopes shown in the figure. Urbach energy increases as the molarity increasing.

The refractive index has been calculated using the relation (Al-Shammary et al., 2010):

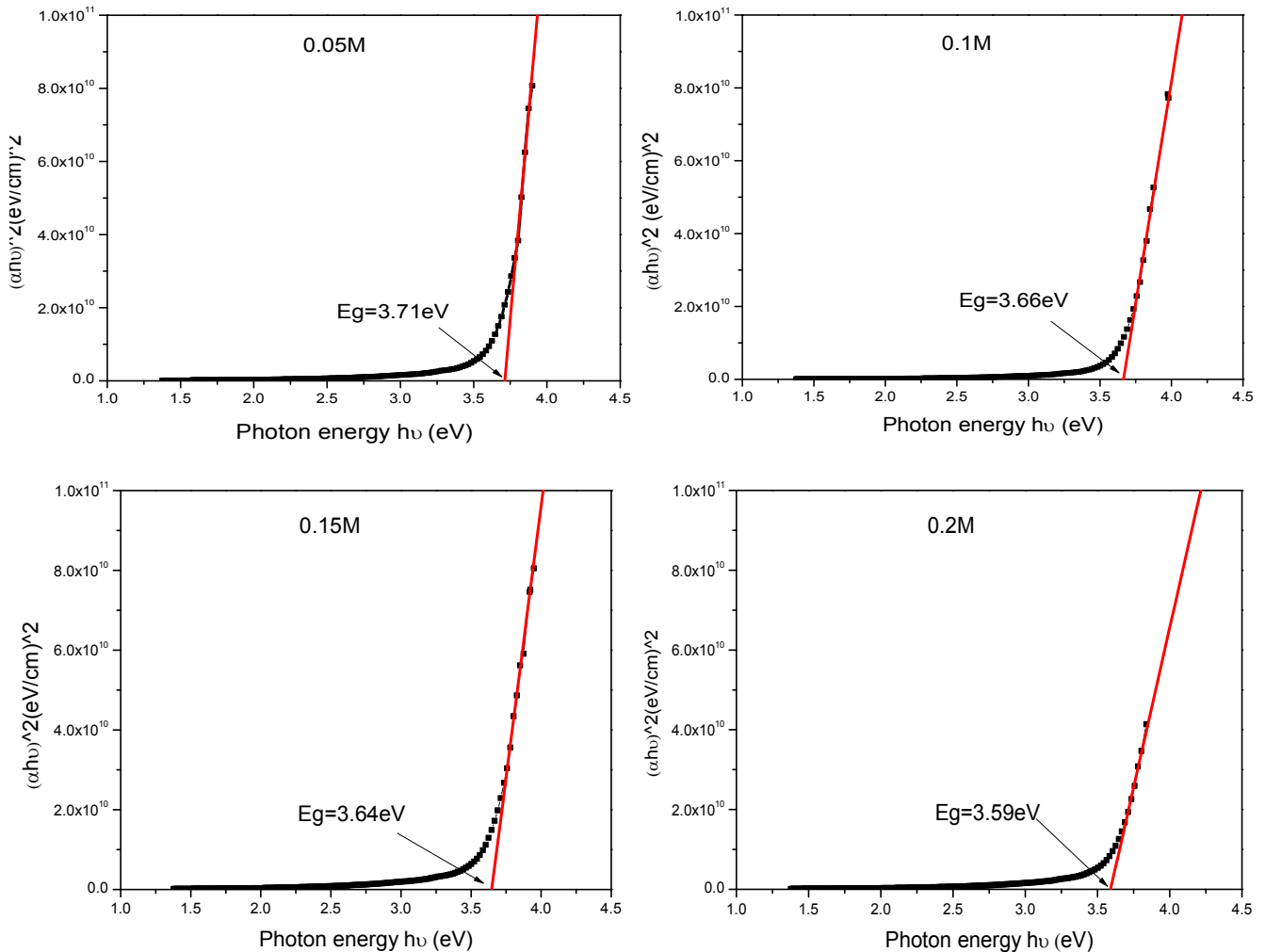


Figure 9. The relation between $(\alpha h\nu)^2$ and $(h\nu)$ for NiO thin films at different molarities

The width of the localized states available in the optical band gap of the films affects the optical band gap structure and optical transitions and it is called as Urbach tail, which is related directly to a similar exponential tail for the density of states of either one of the two band edges. The Urbach tail of the films can be determined by the following relation (Lingshirn 1997):

$$\alpha = \alpha_o \exp \left(\frac{h\nu}{E_t} \right) \dots \dots \dots (6)$$

Where E is the photon energy, α_o is constant, and E_t is the Urbach energy which refers to the width of the exponential

$$n = \left[\frac{(1+R)^2}{(1-R)^2} - (k_o^2 - 1) \right]^{1/2} + \frac{(1+R)}{(1-R)} \dots \dots \dots (8)$$

Where n is the refractive index, R is the reflectance and k_o is the extinction coefficient. The relation between refractive index and wavelength for NiO thin films at different molarities is shown in Figure (11). It can be seen that the refractive index of the prepared films have values in the range of (1.71-2.63) which is in agreement with other reports (Al-Shammary 2010; Venter and Botha 2011).

Where k_o is the extinction coefficient and λ is the wavelength of incident photon. The relation between extinction coefficient and

wavelength for NiO thin films at different molarities is shown in Figure (12).

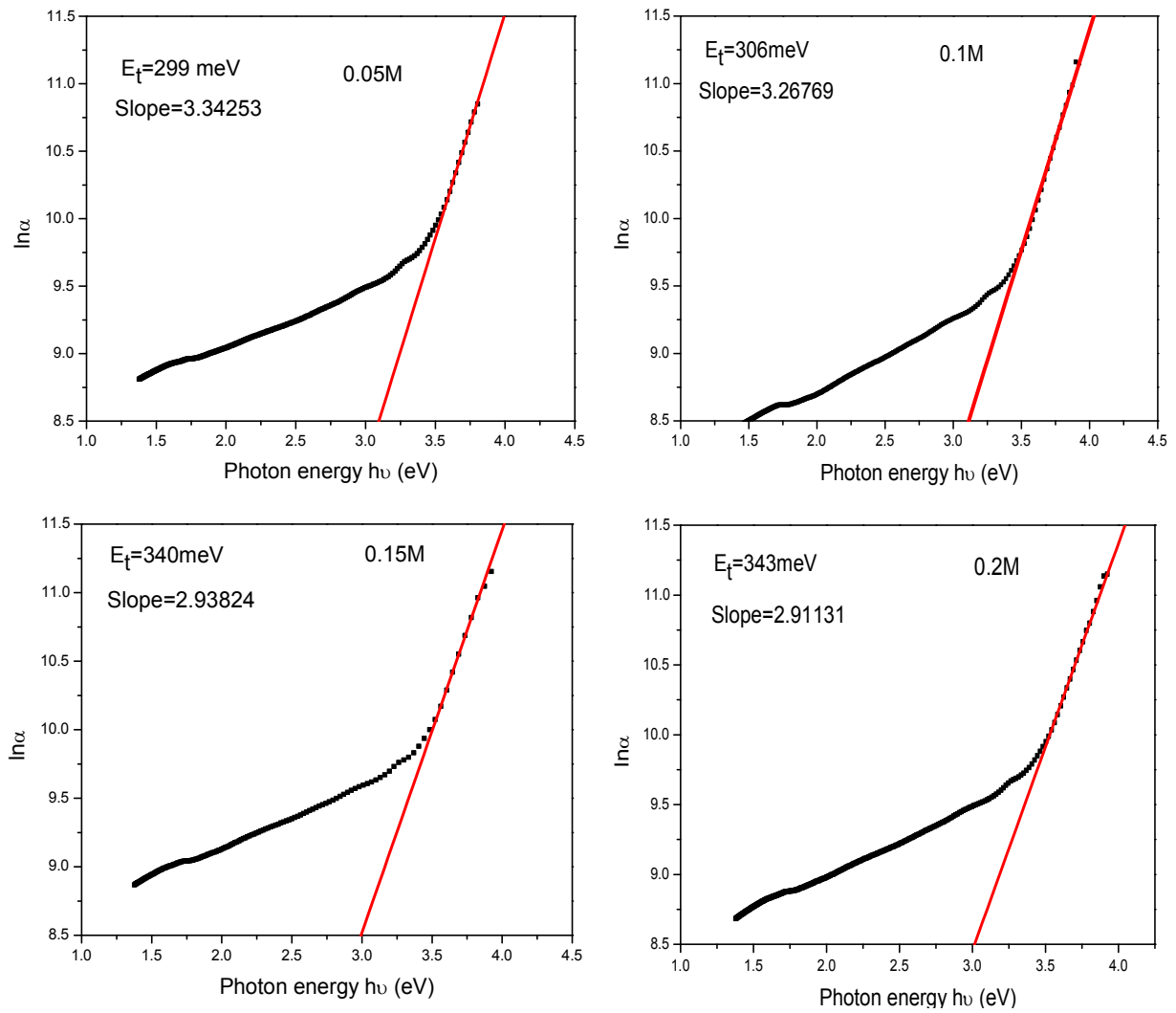


Figure 10. The Urbach plots of NiO thin films at different molarities

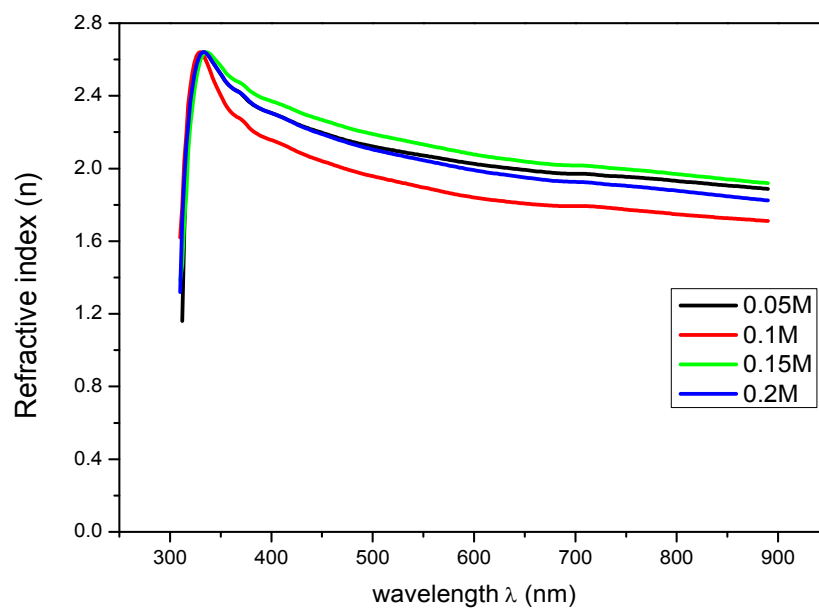


Figure 11. Refractive index versus wavelength for NiO thin films at different molarities

The extinction coefficient (k_o) was calculated using relatio..... (9)
 The extinction coefficient(k_o) decreases rapidly at short wavelengths (300-400)nm and after that the value of (k_o) remains almost constant. The rise and fall in the value of (k_o) is directly related to the absorption of light. The lower value of (k_o) in the wavelength range (400–900) nm implies that these films absorb light in this region very easily. Results show that the extinction coefficient values of NiO thin films are in the range of (0.024-0.18) which is in agreement with other report(Baluet al.,2012).

dielectric constant in its two parts one can use the following expressions:

$$\epsilon_1 = n^2 - K_o^2 \dots\dots\dots (11)$$

$$\epsilon_2 = 2nK_o \dots\dots\dots (12)$$

Real and imaginary parts of dielectric constant as a function of photon energy for NiO thin films are show in Figure (13).

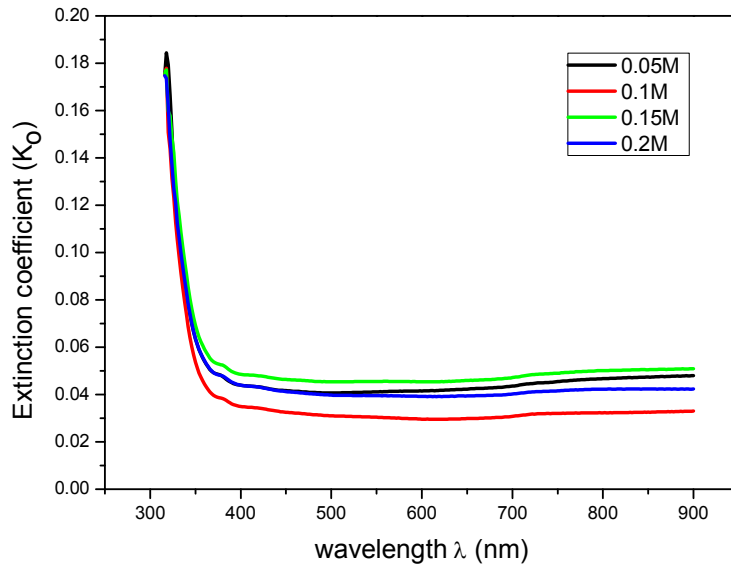


Figure 12. Extinction coefficient versus wavelength for NiO thin films at different molarities

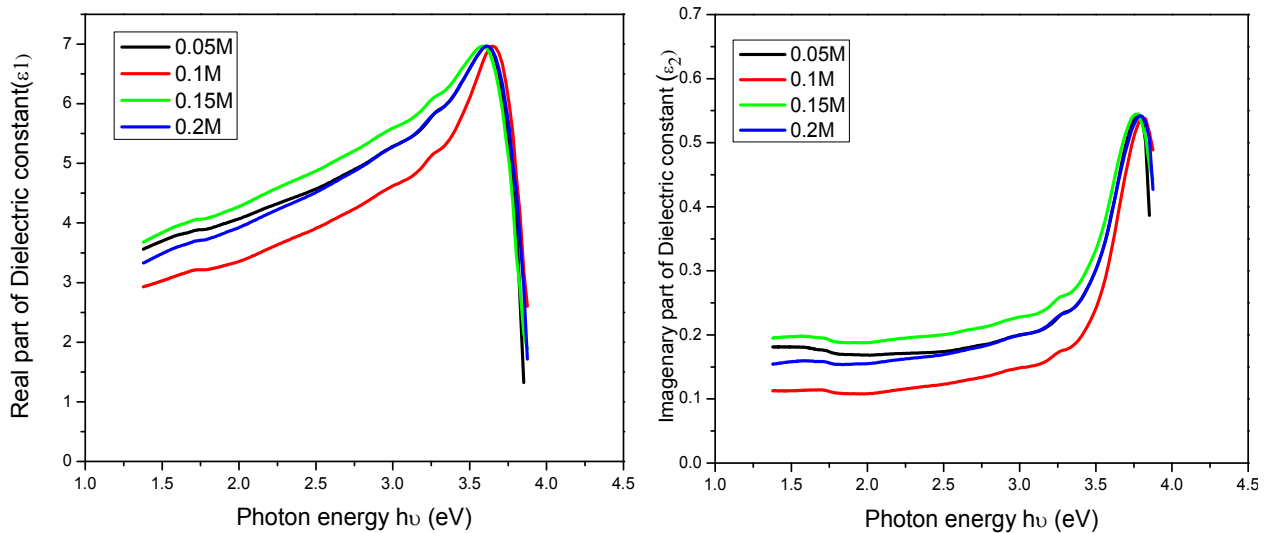


Figure 13. Real and imaginary parts of dielectric constant versus photon energy for NiO thin films at different molarities

The dielectric constant can be represented by the flowing equation (Ahmed et al.,2014):

$$\epsilon = \epsilon_1 - i \epsilon_2 \dots\dots\dots (10)$$

Where ϵ_1 is the real part of the complex dielectric constant and ϵ_2 is the imaginary part of it. For the calculation of the

It can be seen that both the real and imaginary parts of the dielectric constant increase as photon energy increases in the range of (1.25-3.5)eV and after that, the values of the real and imaginary parts decrease as the photon energy increases.

Conclusion

In this study (NiO) thin films at different solution molarities were successfully deposited on glass substrates at (400 °C) by chemical spray pyrolysis technique using Nickel nitrate as the Ni source. The NiO thin films deposited in the present study have black-grey color which can be attributed to the non-stoichiometry of the deposited material. XRD patterns of the NiO thin films indicate that all films are polycrystalline with cubic face centered crystal structure. The main characteristic peaks are assigned to the (111), (200) and (220) planes. It is confirmed that the film prepared at 0.1M has the nearest a_0 value to the standard lattice constant. The microstrain in the films is induced during the growth of thin films by varying displacements of the atoms with respect to their reference lattice position. All values of microstrain were negative which indicates the occurrence of compression in the lattice. All values of texture coefficient were greater than 1 which indicates the abundance of grains in the (111) direction. AFM results show homogenous and smooth NiO thin films. The sample prepared with molarity solution of 0.1M has the highest grain size, average roughness and RMS roughness. The band gap decreases when the molarity increases and the band gap values range between 3.71 eV and 3.59 eV. The Urbach energy increases as the molarity increases and the Urbach energy values range between 299 meV and 343 meV.

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