

Effect of Aqueous Solution Molarity on Structural and Optical Properties of $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ Thin Films Prepared by Chemical Spray Pyrolysis Method

Nabeel A. Bakr*, Ziad T. Khodair and Ahmed M. Shano.

Department of Physics, College of Science, University of Diyala, Diyala, Iraq.

Received: 13 Dec. 2014, Revised: 6 Apr. 2015, Accepted: 7 Apr. 2015.

Published online: 1 May 2015.

Abstract: In this study, $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films with different molarities (0.05M, 0.1 M, 0.15M and 0.2 M) 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 studied 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 0.2M has maximum crystallite size (49.51nm). AFM results showed homogenous and smooth thin films. 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 and First derivative of absorbance with respect to energy of photon. It is found that the band gap decreases when the molarity increases and the band gap values ranges between 3.60 eV and 3.54 eV for the prepared thin films. The Urbach energy increases as the molarity increases and the Urbach energy values range between 439 meV and 680 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 the prepared thin films were estimated as a function of wavelength.

Keywords: $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films, Chemical Spray Pyrolysis, Aqueous Solution Molarity, Optical Properties, Structural Properties.

1 Introduction

NiO is a compound semiconductor of VIII-VI group which has a cubic structure [1]. Nickel oxide (NiO) is the most exhaustively investigated transition metal oxide. It adopts the NaCl - type antiferromagnetic oxide semiconductor [2], has a density of (6.67 g/cm³) and molecular weight of (74.69 g/mol). Its melting point is (1955 °C) [3]. It offers promising candidate for many applications such as solar thermal absorber, catalyst for O₂ evolution, photoelectrolysis and electrochromic devices. Nickel oxide is also a well-studied material as the positive electrode in batteries [2]. It can be used as a functional layer material for chemical sensors and it is considered to be a model semi-conductor with p-type conductivity due to its wide band-gap energy from (3.6 - 4) eV [1]. Different techniques such as sol-gel, spray pyrolysis, ion beam sputtering, magnetic sputtering, and pulsed laser deposition have been used for deposition of pure and Co doped NiO films [4]. Cobalt (Co) lies within the transition metals on the periodic table. The atomic number of Cobalt is 27 with an atomic mass of 58.933195 [5]. Cobalt is a sturdy, gray metal which resembles iron and nickel. Although cobalt is ductile it is

also somewhat malleable. Ductile means the metals ability to be drawn into thin wires. Malleable means the ability of being hammered into thin sheets [6]. In the present paper, we report the effect of aqueous solution molarity on the structural and optical properties of $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films prepared by chemical spray pyrolysis method.

2 Experimental Procedure

Chemical spray pyrolysis technique was used to deposit $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films with different molarities (0.05 M, 0.1 M, 0.15 M and 0.2 M) on glass substrates at temperature of (400 °C). In the preparation of Nickel-Cobalt Oxide films, aqueous solutions of nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with different molarities (0.05M, 0.1 M, 0.15M and 0.2 M) and appropriate volumes were mixed with distilled water by using magnetic stirrer for 30 minutes and the resultant solution was sprayed on glass substrates which were kept at temperature of 400 °C. The thickness of the prepared films was about 300 nm measured by gravimetric method. Other deposition conditions such as spray nozzle substrate

*Corresponding author e-mail: nabeelalibakr@yahoo.com

distance (30 cm), spray time (10 s), spray interval (2 min.) 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 microscope 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 spectroscopy (Shimadzu, UV-1800).

3 Result and Discussion

Figure (1) shows the photo images of (Ni_{0.92}Co_{0.08}O) thin films deposited at different molarities (0.05 M, 0.1 M, 0.15 M and 0.2 M). It is reported that the stoichiometrically correct NiO thin films are expected to have green color [7]. However, the thin films deposited in the present study tend to have black-orange color which can be attributed to non-stoichiometry of the deposited material. It can also be observed that the change in solution molarity is accompanied by a color change from black-orange to orange and the color density of the deposited films increases as the molarity increase.

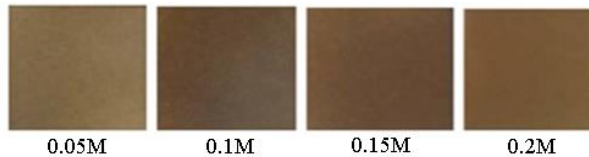


Figure 1: Photo images of (Ni_{0.92}Co_{0.08}O) thin films.

3.1. Structural analysis

XRD patterns of (Ni_{0.92}Co_{0.08}O) films are shown in figure (2).

It can be noticed that all the patterns exhibit diffraction peaks around (2 θ ~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 2 θ ~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 [8, 9]. It can be noticed that 2 θ for (111) direction and the lattice constant (a_0) decrease with molarity increasing, as shown in table (1). It should be mentioned here that the standard a_0 value for NiO is 4.176 Å which indicates that the film prepared at 0.15 M has the nearest a_0 value to the standard lattice constant. The average crystallite size for the films can be determined using Williamson-Hall formula [10] shown below:

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

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 of the film. Figure (3) shows the Williamson-Hall analysis of all samples. The average crystallite size of all films is also calculated for (111) direction by Scherrer formula given below [11].

$$D_{av} = \frac{k\lambda}{\beta\cos\theta} \quad (2)$$

It is observed that the crystallite size of (Ni_{0.92}Co_{0.08}O) thin films increases with molarity increasing and 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 [12]. 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 the 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 [13]:

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

Where $I(hkl)$ is the measured intensity, $I_0(hkl)$ taken from the JCPDS data, (N_r) is the reflection number and (hkl) is Miller indices. The texture coefficient is calculated for crystal plane (111) of (Ni_{0.92}Co_{0.08}O) thin films at different molarities (0.05 M, 0.1 M, 0.15 M and 0.2 M). All values of texture coefficient were greater than 1 which indicates the abundance of grains in the (111) direction.

The crystallites are preferentially oriented along the (111) direction for all thin films. All these results are shown in table (1).

3.2. Results of Atomic Force Microscope (AFM)

The morphological investigation of (Ni_{0.92}Co_{0.08}O) thin films at different molarities (0.05M, 0.1 M, 0.15M and 0.2M) is shown in figure (5). The size of the scanned area was (2x2) μm^2 . AFM results showed homogenous and smooth (Ni_{0.92}Co_{0.08}O) thin films. The average grain size, average roughness and root mean square (RMS) roughness for (Ni_{0.92}Co_{0.08}O) thin films estimated from AFM, are given in Table (2). The sample prepared with solution molarity of 0.2M has highest average grain size, average roughness and RMS roughness of the film. The increase of the crystallite size may be caused by columnar grain growth in the structure which is in agreement with other studies [9].

Table 1. Structural parameters of $(\text{Ni}_{0.92}\text{Co}_{0.08}\text{O})$ thin films at different molarities.

Molarity (M)	0.05	0.1	0.15	0.2
2θ (deg)	37.1760	37.1810	37.236	37.4265
hkl	(111)	(111)	(111)	(111)
d (Å)	2.41655	2.41623	2.41579	2.41438
(FWHM) (rad)	0.0167	0.0144	0.0052	0.003
D(nm) Scherrer	8.75	10.1	27.97	49.51
D(nm) W-H	1.52	5.46	1.52	5.48
Micro strain $S * 10^{-3}$	-58.74	-11.9	44.81	-0.57
Lattice Constants a_c (Å)	4.1855	4.1850	4.1788	4.1585
T_c	1.8	2.18	1.08	1.93

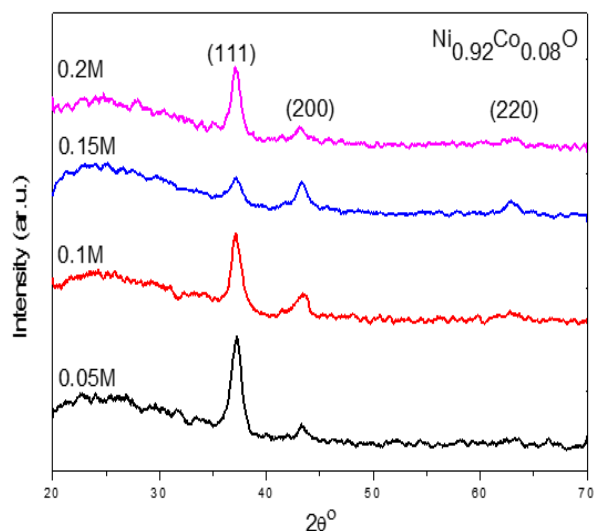


Figure 2: XRD pattern of $(\text{Ni}_{0.92}\text{Co}_{0.08}\text{O})$ thin films at different molarities.

3.3. Optical analysis

Optical absorption spectra of the films in spectral range of (300-900 nm) were recorded by using UV-visible 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 gaps of the films [14]. Figure (6) shows the relation between transmittance and wavelength for $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films at different molarities. It can be noticed that the transmittance increases rapidly as the wavelength increases in the range of (300 - 350 nm), and then increases slowly at higher wavelengths.

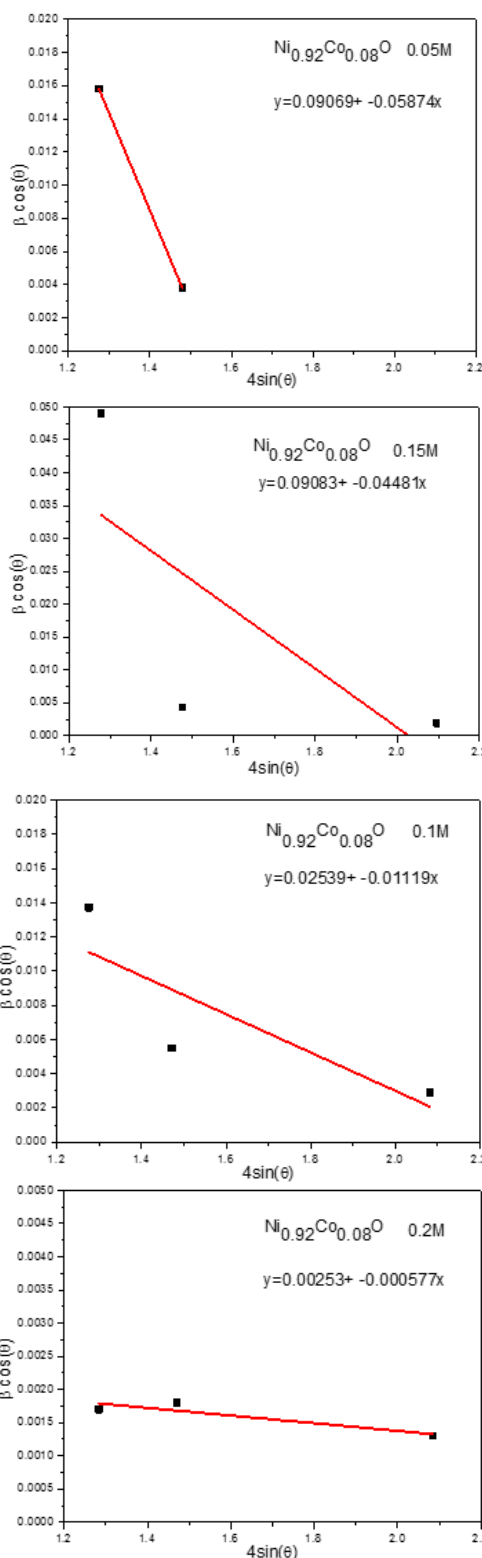


Figure 3: The W-H analysis of $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films at different molarities.

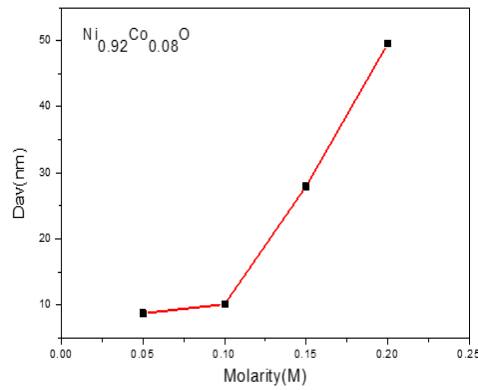


Figure 4: The crystallite size (D_{av}) of $Ni_{0.92}Co_{0.08}O$ thin films at different molarities.

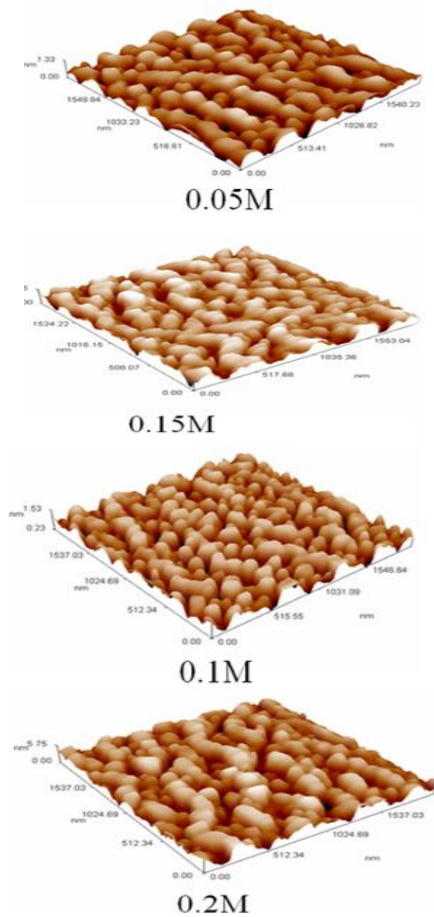


Figure 5: 3D AFM images of $Ni_{0.92}Co_{0.08}O$ thin films at different molarities.

The spectrum shows high transmittance in the visible and infrared regions, and low in the ultraviolet region is high. It can also be observed that the fundamental absorption edge (absorption edge which separates between the high

absorption region and the low absorption region or the window region) is sharp in the visible region at the wavelength (680 nm) of the spectrum. The transmittance increases with increase in the molarity of the solution and the molarity 0.2 M has a maximum transmittance of nearly equal to 85%.

Table 2. Surface roughness, root mean square (RMS) and grain size of $Ni_{0.92}Co_{0.08}O$ thin films at different molarities.

Molarity (M)	Surface roughness (nm)	RMS (nm)	Grain Size (nm)
0.05	0.243	0.29	85.23
0.1	0.247	0.293	88.84
0.15	0.63	0.756	96
0.2	1	1.21	111.18

Figure (7) shows the relation between absorbance (A) and wavelength for $Ni_{0.92}Co_{0.08}O$ thin films at different molarities thin films. The absorbance decreases rapidly at short wavelengths (high energies) 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 decreases as the molarity increases.

The absorption coefficient can be estimated from the absorbance using the formula [15]:

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

Where A is the absorbance, t is the thickness and ($\alpha \text{ cm}^{-1}$) is the absorption coefficient.

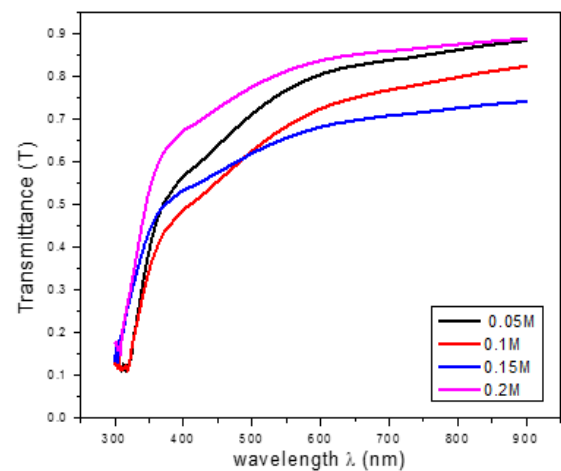


Figure 6: Transmittance (T) versus wavelength (λ) of $Ni_{0.92}Co_{0.08}O$ thin films at different molarities.

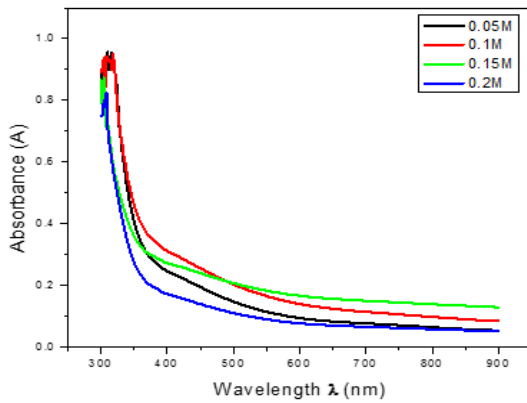


Figure 7: Absorbance (A) versus wavelength (λ) of $Ni_{0.92}Co_{0.08}O$ thin films at different molarities.

It is noticed that all the prepared thin films high absorption coefficient in visible range of solar spectrum, and this could be seen in figure (8) which shows the relation between the absorption coefficient (α) with photon energy ($h\nu$) of $Ni_{0.92}Co_{0.08}O$ thin films at different molarities. The absorption coefficient increases with increase in photon energy ($h\nu$). The values of absorption coefficient were greater than 10^4 cm^{-1} which implies the increase of the probability of the occurrence of direct transitions. It can be noticed that the absorption coefficient decreases with increasing molarity.

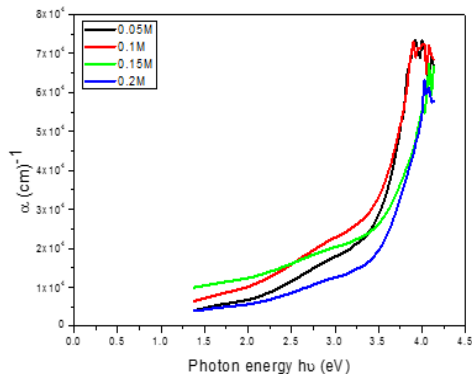


Figure 8: The relation between absorption coefficient and photon energy of $Ni_{0.92}Co_{0.08}O$ thin films at different molarities.

The optical energy gap values (E_g) can be calculated by using two methods: **a.** Tauc relation: The optical energy band gap (E_g) can be calculated using equation [15]:

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

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. In this work, direct band gap was determined by plotting a graph between $(\alpha h\nu)^2$ and $(h\nu)$ in eV, a straight line is obtained which gives the value of the direct band gap. 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). It is noticed that the band gap value decreases when the molarity increases.

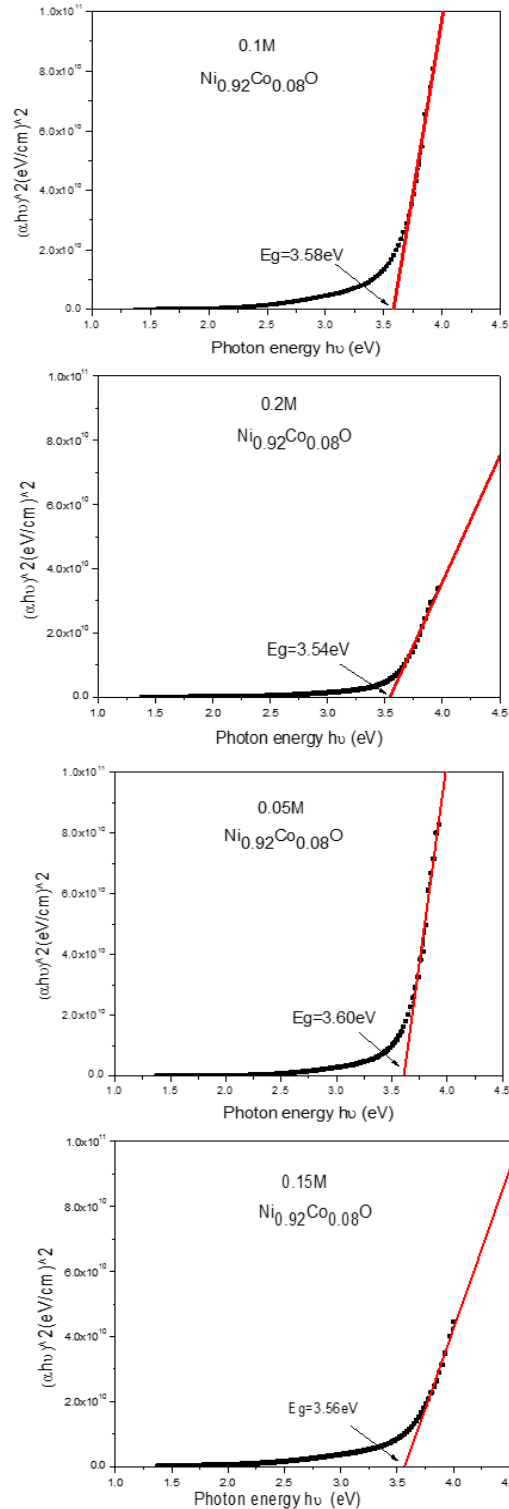


Figure 9: The relation between $(\alpha h\nu)^2$ and $(h\nu)$ of $Ni_{0.92}Co_{0.08}O$ thin films at different molarities.

The decrease in the band gap energy is due to decrease in free electron concentration in the films. **b.** First derivative of absorbance with respect to energy of photon: The energy gap can be calculated by taking the first derivative of the absorbance as a function of photon energy where the energy gap can be found as the energy corresponds to the highest peak of the (dA/dE) versus $E=h\nu$ curve as shown in figure (10). It can be noticed that the band gap decreases as the molarity increases, which is in agreement with energy gap calculated from Tauc relation, as shown in table (3). 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 [15]:

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

Where $h\nu$ is the photon energy, α_o is constant, and E_t is the Urbach energy which refers to the width of the exponential absorption edge. Figure (11) shows the variation of $(\ln\alpha)$ versus photon energy for the films. E_t values were calculated as the reciprocal of the straight line slopes shown in the figure. The obtained E_t values are given in table (4). Urbach energy increases with increase in molarity. E_t values change inversely with optical band gaps of films.

The refractive index has been calculated using the relation [16]:

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

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 $Ni_{0.92}Co_{0.08}O$ thin films at (0.05, 0.1M, 0.15M and 0.2M) is shown in figure (12). Results show that the refractive index values of prepared films have values in the range of (1.65- 2.64). The extinction coefficient (K_o) was calculated using relation [8]:

$$K_o = \frac{\alpha\lambda}{4\pi} \quad (9)$$

Where K_o is the extinction coefficient and λ is the wavelength of incident photon.

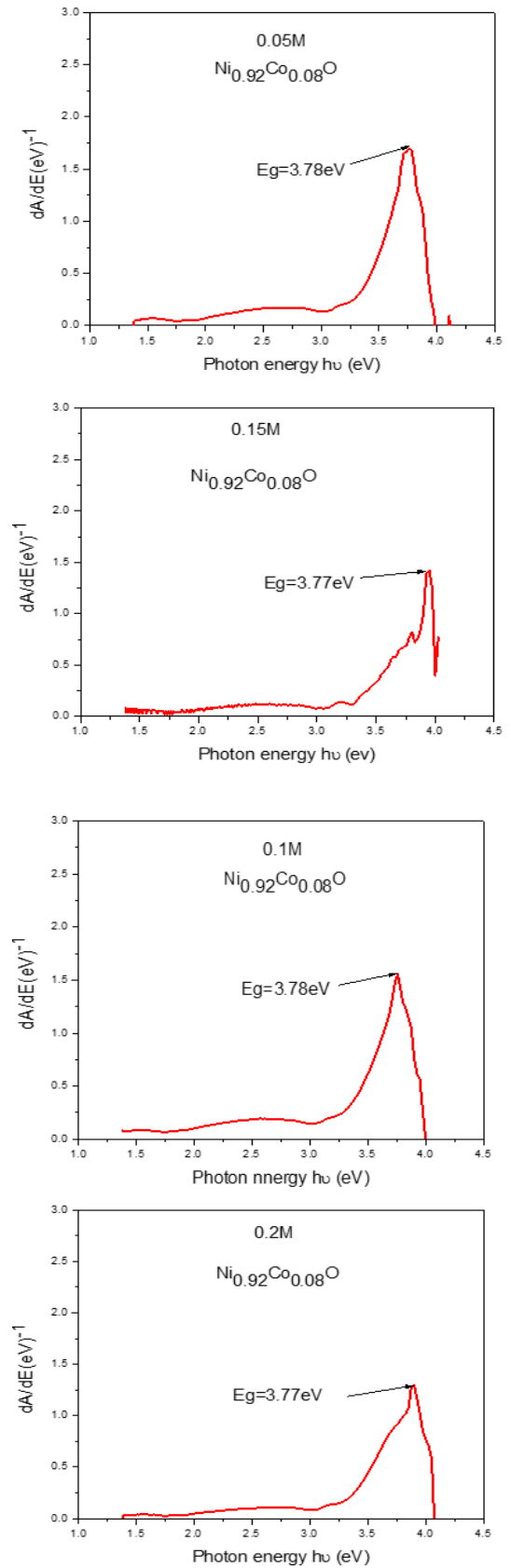


Figure 10: The relation between (dA/dE) and $(h\nu)$ for $Ni_{0.92}Co_{0.08}O$ thin films at different molarities.

Table 3. Energy gap from Tauc relation and first derivative of Ni_{0.92}Co_{0.08}O thin films at different molarities.

Molarity (M)	E _g (eV) [Tauc]	E _g (eV) [Derivative]
0.05	3.60	3.78
0.1	3.58	3.78
0.15	3.56	3.77
0.2	3.54	3.77

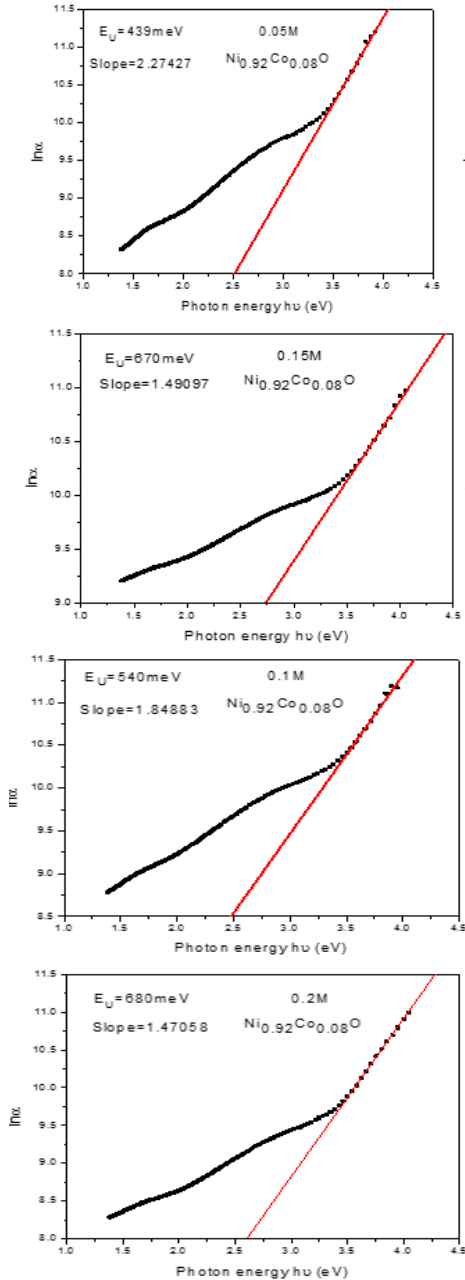


Figure 11: The Urbach plots of Ni_{0.92}Co_{0.08}O thin films at different molarities.

Table 4. Urbach Energies (E_U) for Ni_{0.92}Co_{0.08}O thin films at different molarities.

Molarity (M)	E _U (meV)
0.05	439
0.1	540
0.15	670
0.2	680

The relation between extinction coefficient and wavelength for Ni_{0.92}Co_{0.08}O thin films at (0.05, 0.1M, 0.15M and 0.2M) is shown in figure (12). The extinction coefficient (K₀) decreases rapidly at short wavelengths (300-400) nm and after that the value of (K₀) remains constant. The rise and fall in the value of (K₀) is directly related to the absorption of light. The lower value of (K₀) 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 Ni_{0.92}Co_{0.08}O thin films at (0.05, 0.1M, 0.15M and 0.2M) are in the range of (0.028 - 0.18).

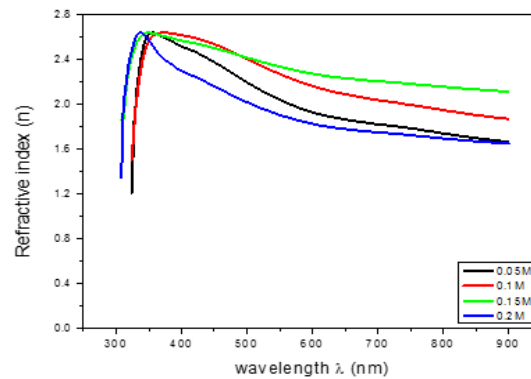


Figure 12: The relation between the refractive index and wavelength of Ni_{0.92}Co_{0.08}O thin films at different molarities.

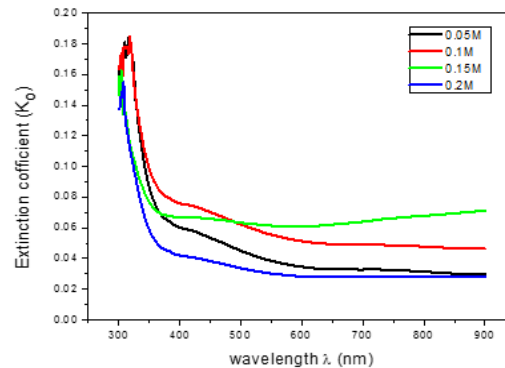


Figure 13: The relation between the extinction coefficient and wavelength of Ni_{0.92}Co_{0.08}O thin films at different molarities.

The dielectric constant can be represented by the flowing equation [17]:

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 \quad (10)$$

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

$$\varepsilon_1 = n^2 - k_0^2 \quad (11)$$

$$\varepsilon_2 = 2nk_0 \quad (12)$$

The relation between real and imaginary parts of dielectric constant and photon energy for $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films at (0.05, 0.1M, 0.15M and 0.2M) is show in figure (13). It can be seen that both the real and imaginary parts of the dielectric constant increases as photon energy increases (1.25-3.5) eV and after that the value of the real and imaginary parts decreases. It is observed that both the real and imaginary parts of the dielectric constant decreases with increase in molarity.

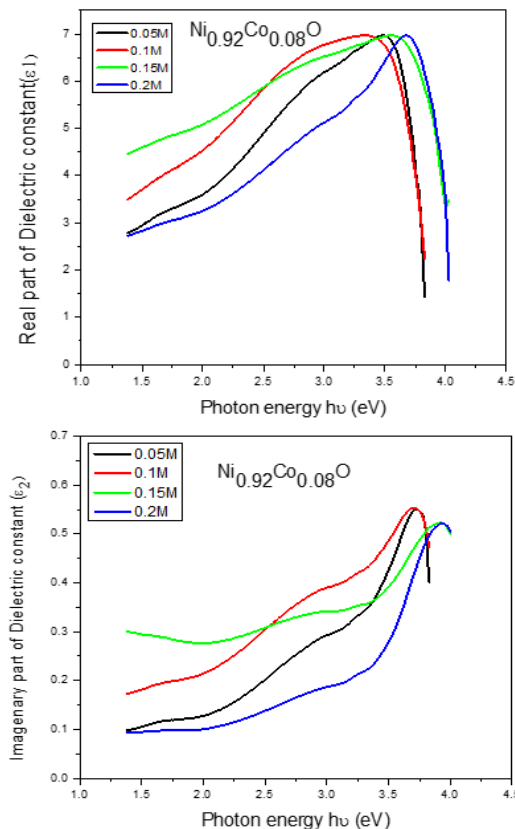


Figure 14: The relation between the real (ε_1) and imaginary parts (ε_2) of dielectric constant and photon energy of $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films at different molarities.

4 Conclusions

In this study, $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films with different molarities (0.05 M, 0.1 M, 0.15 M and 0.2 M) were successfully deposited on glass substrate at (400 °C) by chemical spray pyrolysis technique using Nickel and Cobalt nitrates as the Ni and Co source. XRD patterns of the $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films indicate that all films are

polycrystalline with cubic crystal structure. The main characteristic peaks are assigned to the (111), (200) and (220) planes. AFM results showed homogenous and smooth $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films. The molarity 0.2M has highest grain size, average roughness and RMS roughness. The transmittance for $\text{Ni}_{0.92}\text{Co}_{0.08}\text{O}$ thin films increases rapidly as the wavelength increases in the range of (300- 350 nm), and then increases slowly at higher wavelengths. The band gap decreases when the molarity increases and the band gap values range between 3.60eV and 3.54 eV. The Urbach energy increases as the molarity increases and the Urbach energy values range between 439 meV and 680 meV.

References

- [1] Nibras F. AlShammery, "Optical characteristics of NiO thin film on glass formed by Chemical spray pyrolysis", *Journal of Kufa- Physics* vol. **2(1)**, (2010).
- [2] P. S. Patil, L. D. Kadam, "Preparation and characterization of spray nickel Oxide (NiO) thin films", *Applied surface science*, vol. **199**, p. 211, (2002).
- [3] K. Lascelles, L. G. Morgan, D. Nicholls, D. Beyersmann, "Nickel Compounds", in Ullmann's Encyclopedia of Industrial Chemistry Wiley-VCH, Wein-heim, (2005).
- [4] M. Caglar, S. Ilcan, Y. Caglar, "Influence of Substrate Temp-erature on Structural and Elect-rical Properties of ZnO Films", *Trakya Univ. J. Sci*, vol. **7(2)**, p. 153, (2006).
- [5] Arwaa Fadil Saleh, " Structural and morphological studies of NiO thin films prepared by Rapid thermal oxidation method", *International Journal of Application or Innovation in Engin-eering and Management*, vol. **2(1)**, p.16, (2013).
- [6] C. Barret, T. B. Massalki, "Structure of Metals", Oxford Pergamon, (1980).
- [7] Greenwood, Norman N. Earnshaw, Alan, "Chemistry of the Elements", Oxford, Pergamon Press, pp. 1336–37, (1984).
- [8] A. R. Balu, V. S. Nagarethinam, N. Arunkumar, M. Suganya, "Nanocrystalline NiO thin films prepared by a low cost simplified spray technique using perfume atomizer ", *Journal of Electron Devices*, vol. **13**, pp. 920-930, (2012).
- [9] Nabeel A. Bakr, Sabah A. Salman, Ahmed M. Shano, "Effect of Solution Molarity on Structural and Optical Properties of Nickel Oxide Thin Films Prepared by Chemical Spray Pyrolysis Technique", *International Journal of Current Research*, vol. **6(11)**, pp. 9644–9652, (2014).

- [10] V. D. Mote, Y. Purushotham, B. N. Dole, "Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles", *Journal of Theoretical and Applied Physics*, vol. **6(6)**, (2012).
- [11] M. Caglar, S. Ilcan, Y. Caglar, "Influence of Substrate Temperature on Structural and Electrical Properties of ZnO Films" *Trakya Univ. J. Sci.*, vol. **7(2)**, p. 153, (2006).
- [12] Arwaa Fadil Saleh, "Structural and morphological studies of NiO thin films prepared by Rapid thermal oxidation method", *International Journal of Application or Innovation in Engineering & Management (IJAIEM)*, vol. **2(1)**, p.16, (2013).
- [13] Nabeel A. Bakr, Sabah A. Salman, Ahmed M. Shano, "Effect of Co Doping on Structural and Optical Properties of NiO Thin Films Prepared By Chemical Spray Pyrolysis Method", *International Letters of Chemistry, Physics and Astronomy*, vol. **2**, pp. 15-20, (2015).
- [14] B. Sahin, F. Bayansala, M. Yukselc, N. Biyiklib, "Effect of coumarin concentration on the physical properties of CdO nanostructures", *J. Ceramics International*, vol. **40**, pp. 5237-5243, (2014).
- [15] J. I. Pankove, "Optical Process in Semiconductors", Dover Publishing, Inc., New York. (1971).
- [16] C. F. K. Lingshirn, "Semi-conductor Optics", Springer Verlag, Berlin Hridelberg, (1st ed.), (1997).
- [17] Sudad S. Ahmed, Eman K. Hassan, Ghuson H. Mohamed, "Investigation of Optical Properties of NiO_{0.99}Cu_{0.01} Thin Film by Thermal Evaporation Technique", *International Journal of Advanced Research*, vol. **2(2)**, pp.633- 638, (2014).
-