

# Journal of Chemical, Biological and Physical Sciences



An International Peer Review E-3 Journal of Sciences

Available online at [www.jcbps.org](http://www.jcbps.org)

Section C: Physical Sciences

CODEN (USA): JCBPAT

Research Article

## Effect of Mn Doping on Optical Properties of NiO Thin films Prepared by Chemical Spray Pyrolysis Method

Ziad T. Khodair, Asaad A. Kamil\*, Yamamah K. Abdalaah

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

Received: 3 October 2015; Revised: 8 October 2015; Accepted: 14 October 2015

**Abstract:** Undoped NiO and NiO doped thin films with volume percentage doping of (2,4,6 and 8 %) have been prepared by chemical spray pyrolysis method (CSP) on glass substrates at a temperature of (400 °C). The effect of Mn doping on optical properties has been investigated. 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 allowing direct electronic transition was calculated using Tauc equation and it is found to be (3.59 eV) for undoped NiO thin films. However, the increase in doping percentage causes decreases in the value of the energy gap and it reaches to (3.53 eV) for the doping percentage of (8%). And the energy gap for the forbidden direct electronic transition was calculated. The Urbach energy increases as the doping percentage increase and it is found to be (324 meV) for undoped NiO thin films and it reaches to (560 meV) for doping percentage of (8%). The optical constants, including (absorption coefficient ( $\alpha$ ), extinction coefficient ( $K_0$ ), refractive index ( $n_0$ ), real and imaginary parts of dielectric constant) were also calculated as a function of photon energy.

**Keywords:** NiO thin films; Mn Doping; Chemical Spray Pyrolysis; Optical properties.

### INTRODUCTION

Nickel oxide thin film (NiO) is a semitransparent p-type semiconductor material with wide band gap (3.6–4.0 eV), it shows attractive material due to its excellent chemical stability as well as optical, electrical and magnetic properties<sup>1</sup>. NiO thin films used in many applications such as in catalysts, Electrochromic display devices, fuel cells, positive electrode in batteries, solar thermal absorber, catalyst for oxygen evolution and photo electrolysis<sup>2,3</sup>. NiO thin films have been deposited by different techniques including sol gel, spray pyrolysis, plasma enhanced chemical vapor deposition, pulsed laser deposition and magnetron sputtering<sup>4</sup>. The simplest and most successful method of

preparation is through pyrolysis of 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<sup>5</sup>. In the present paper we report the effect of (Mn) doping on the optical properties of NiO films prepared by chemical spray pyrolysis technique.

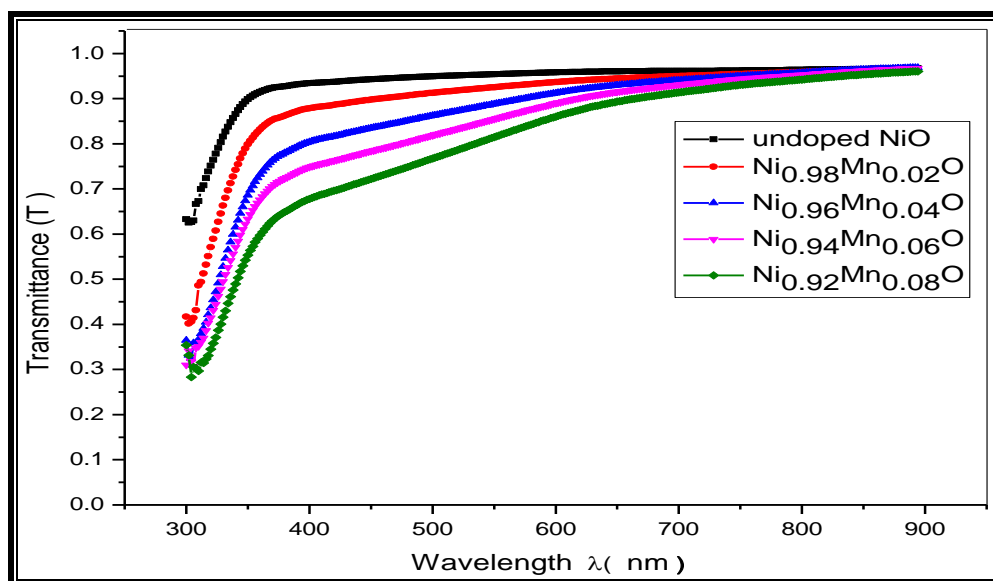
**Experimental Procedure:** Chemical spray pyrolysis technique was used to deposit undoped and Mn-doped NiO films on glass substrates at temperature of (400°C), using Nickel acetate tetrahydrate  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and Manganese acetate anhydrous  $\text{Mn}(\text{CH}_3\text{COO})_2$  with 0.1 molarity in distilled water. The glass substrate slides (2.55 X 2.55 cm<sup>2</sup>) dimensions, were cleaned in acetone solutions in an ultrasonic bath for (5) minutes and rinsed in distilled water and Then dried by a special fabric to get rid of any impact or impurities may be present on the glass substrates, this process is to ensure a clean surface which is necessary for the formation of nucleation centre required for film deposition. Final solutions were prepared by mixing the two initial solutions in appropriate volumetric proportions to get various concentrations of Mn (0,2,4,6 and 8) wt.%. The resultant solution was sprayed on glass substrate. Other deposition condition for undoped NiO and Mn-doped NiO thin films are presented in table (1) were kept constant for each concentration. Optical properties in the wavelength range of (300-900) nm were investigated by using UV-VIS-NIR spectroscopy (Shimadzu, UV-1800).

**Table 1:** Deposition condition for undoped NiO and Mn-doped NiO thin films

Nozzle substrate distance	30 cm
Spray time	8 sec
Spray interval	2 min
Pressure of the carrier gas	1.5 bar

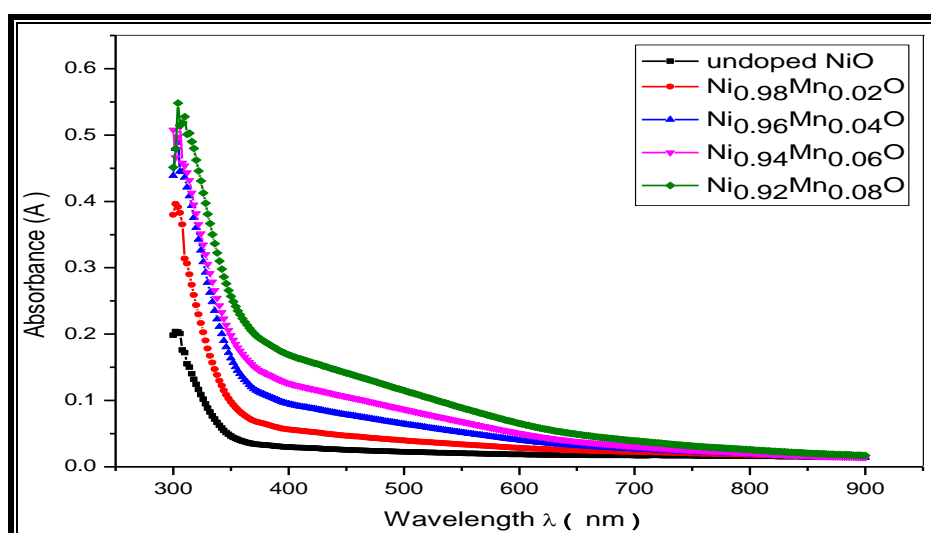
## RESULTS AND DISCUSSION

The optical measurement results include relations of the transmittance and absorbance with wavelength for undoped NiO and Mn-doped NiO thin films deposited at different percentage doping (2,4,6 and 8%), and investigate their influence on these properties and also calculated some optical constants. Figure (1) shows the relation between transmittance and wavelength for Mn-doped Nickel Oxide thin films. It can be noticed that the transmittance increases rapidly as the wavelength increases in the range of (300-370) nm, and then increases slowly at higher wavelength. The spectrum shows high transmittance in the visible and infrared regions, and low in the ultraviolet region. It can also be noticed that the transmittance for the all films is minimum at the fundamental absorption edge (Short wavelengths), but when doping the transmittance decreases with increasing the proportion of doping so that they are less worthless when the ratio doping 8%, due to the entry atoms of manganese (Mn) within the crystal structure of the oxide nickel and that this leads to be new localized levels down conduction band and this ready to receive electrons and generate tails in the optical energy gap is working toward minimizing the optical energy gap levels and is a defects crystalline.



**Fig. 1:** Transmittance versus wavelength for undoped and Mn-doped Nickel Oxide thin films

Figure (2) shows the relation between absorbance ( $A$ ) and wavelength ( $\lambda$ ) for the thin films deposition. The absorbance decreases rapidly at short wavelengths corresponding to the energy gap of the film. 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 increases when the proportion of doping increases, this confirms entry manganese atoms (Mn) within the crystal structure of the film record and that through the formation of localized levels within the energy gap which in turn results in the absorption of photons with low energy.

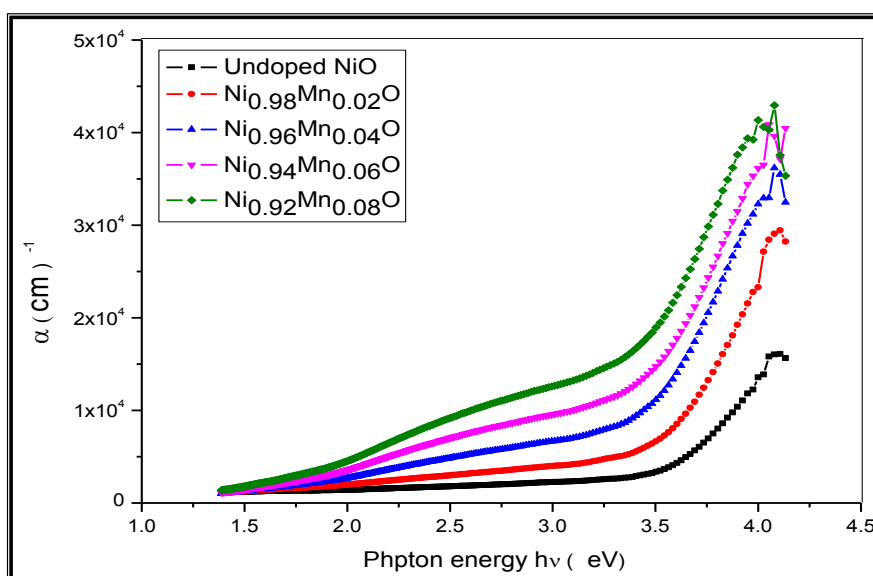


**Fig. 2:** Absorbance versus wavelength for undoped and Mn-doped Nickel Oxide thin films

The absorption coefficient can be estimated from the absorbance using the formula<sup>6</sup>:

$$\alpha = (2.303 * A) / t \quad (1)$$

where (A) is the absorbance, (t) is the thickness and ( $\alpha$ ) is the absorption coefficient. It have been noticed that all the prepared thin films have high absorption coefficient in visible range of spectrum, and this could be seen in Figure (3). The absorption coefficient increases with increase in photon energy ( $h\nu$ ). The absorption coefficient of the deposited thin films at different Mn doping levels has values of ( $\alpha > 10^4 \text{ cm}^{-1}$ ) which implies the increase of the probability of the occurrence of direct transitions.

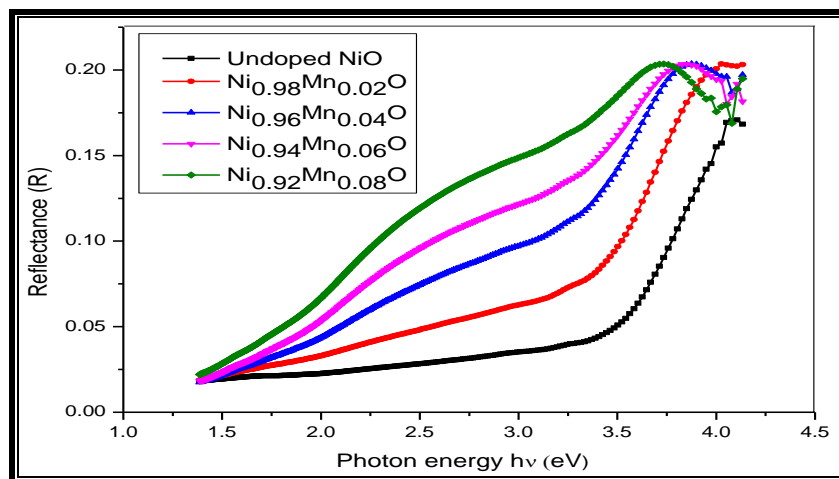


**Fig. 3:** Absorption coefficient versus photon energy for undoped and Mn-doped NiO

The reflectance calculated (R) from spectral absorbance and transmittance under the energy conservation described the relationship  $Act(2)^7$ , figure (4) shows the reflectance of the films undoped nickel oxide (NiO) and doped manganese as a function of photon energy, as we note that the reflectance increases with energy photon and then immediately begin a downward in the extent of potential high-photonic, although the reason for this is because the absorption is very small at energies photonic least of the value of the energy gap optical either when equal power almost to the value of the optical energy gap increases absorption as a result of transfers of electronic between the top of valence band and bottom conduction band causing decrease in reflectance values, and that this decrease increases with the percentage of doping manganese This is a result of the change in the crystal structure of the film as a result of compensation atoms of manganese (Mn) for nickel atoms ( $Ni^{+2}$ ) within the installation crystalline nickel oxide.

$$R = [(n_0 - 1)^2 + K_0^2] / [(n_0 + 1)^2 + K_0^2] \quad (2)$$

Where: R reflectance,  $n_0$  reflective index,  $K_0$  extinction coefficient.

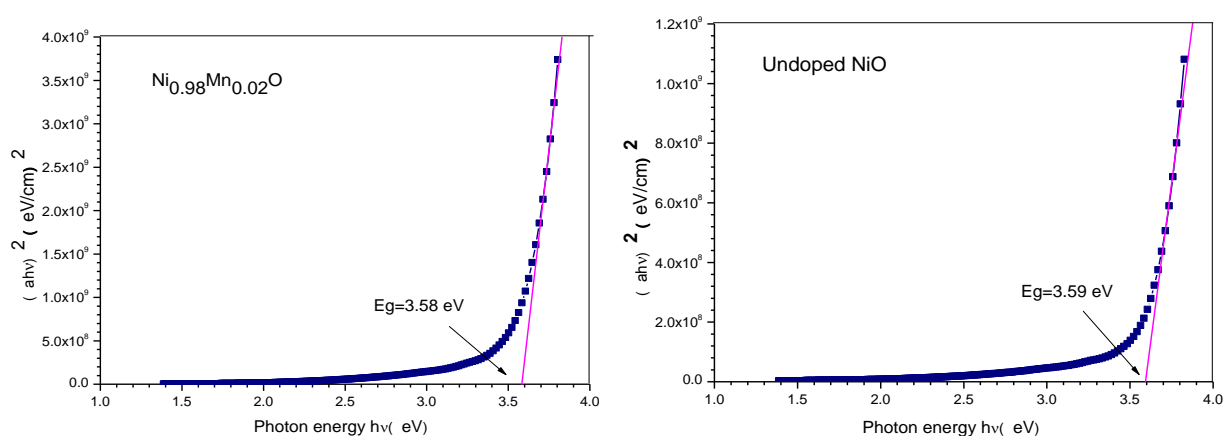


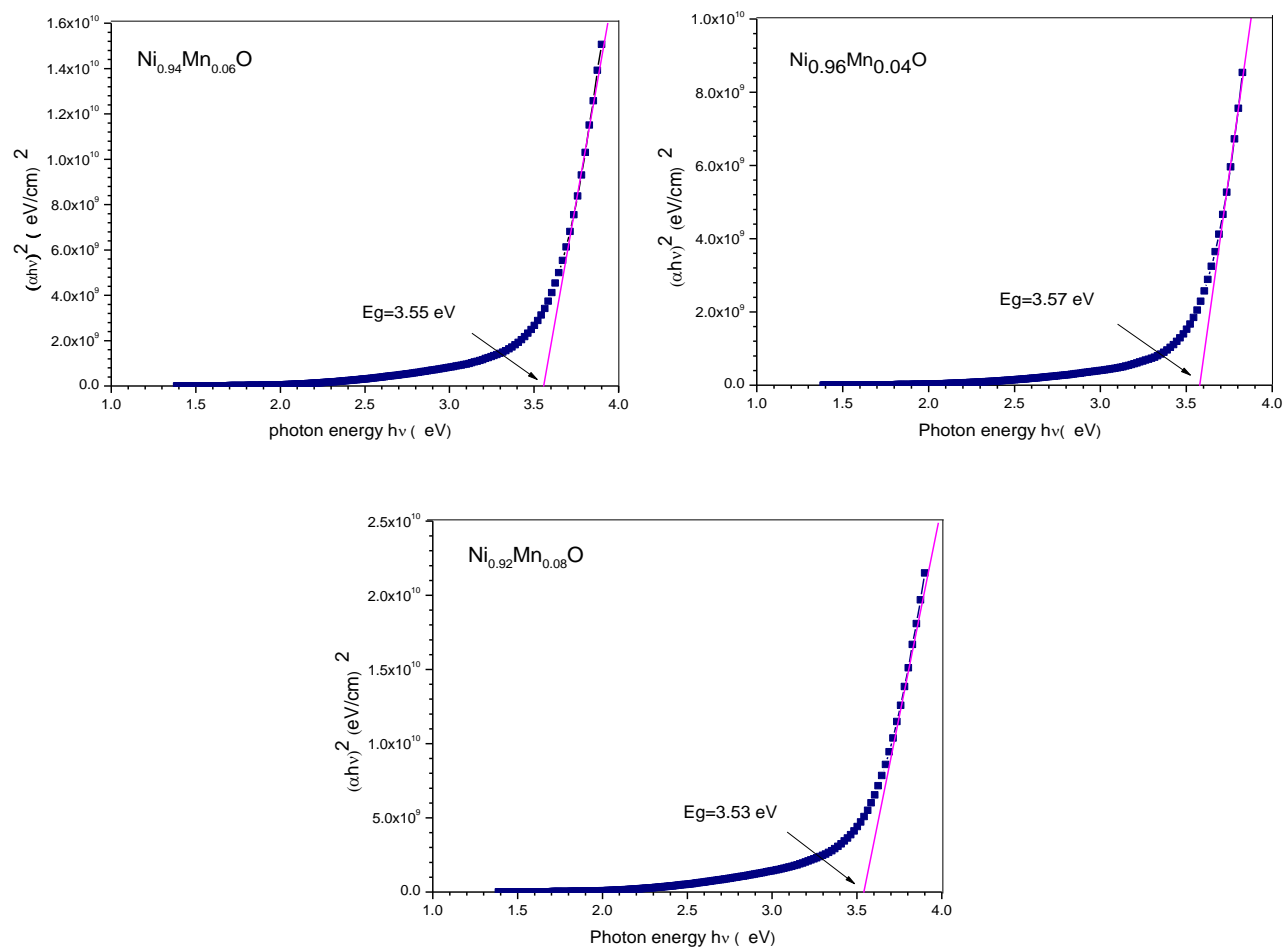
**Fig. 4:** Reflectance versus photon energy for undoped and Mn-doped Nickel Oxide thin films

The optical energy band gap ( $E_g$ ) is given by the relation<sup>8</sup>:

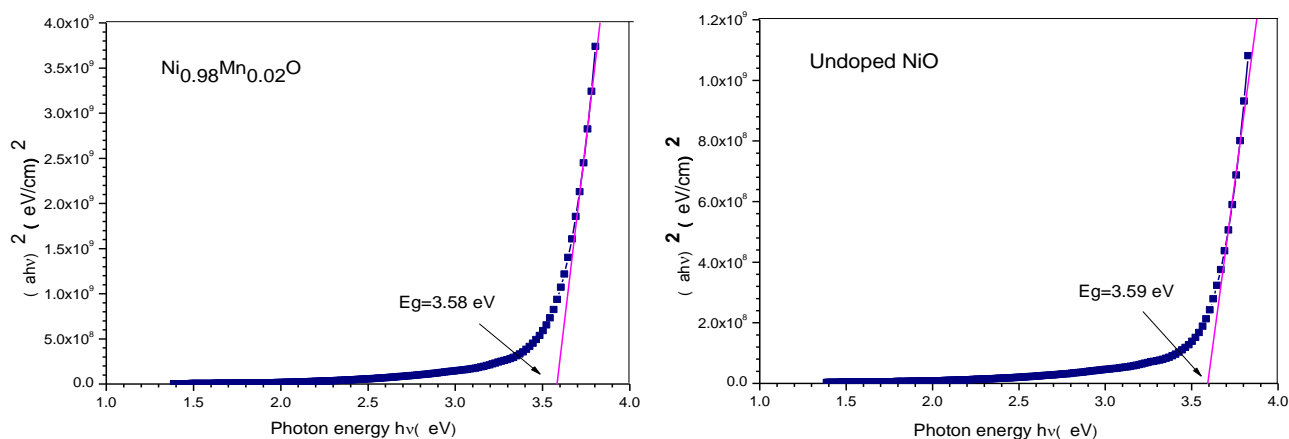
$$\alpha h\nu = A(h\nu - E_g)^r \quad (3)$$

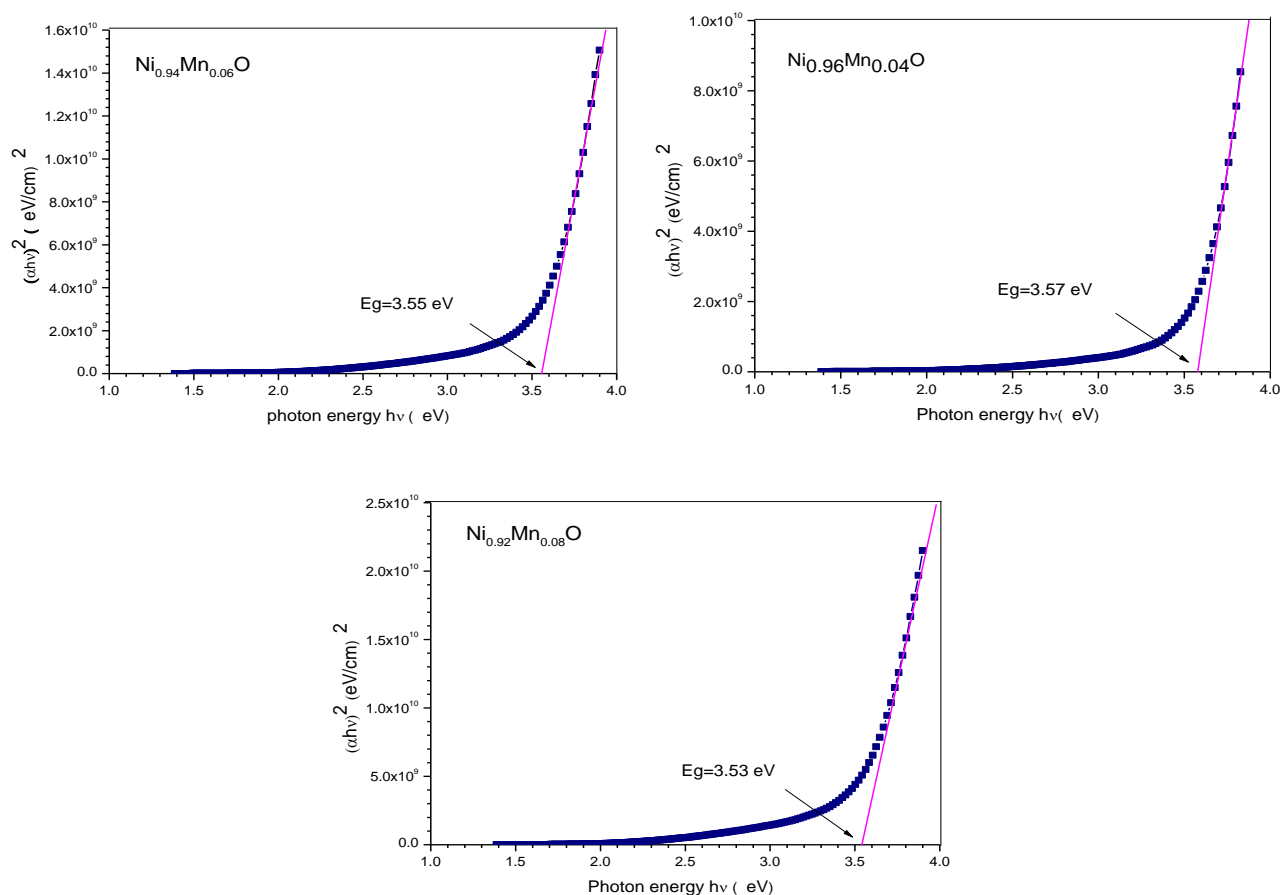
where ( $\alpha$ ) is the absorption coefficient, ( $h\nu$ ) is the photon energy, ( $E_g$ ) is the optical band gap, ( $A$ ) is a constant which does not depend on photon energy and ( $r$ ) has four numeric values (1/2) for allowed direct, (2) for allowed indirect, (3) for forbidden direct and (3/2) for forbidden indirect optical transitions. In this work, allowed direct energy 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 a bandgap. 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 (5). We observe that the band gap value decreases with increase in Mn-doping concentration due to the formation localized levels close to the conduction band contributed to increasing the number of electrons that reach the conduction band, that doping led to the displacement of the edge of the fundamental absorption towards the energies low, which are attributed to the exchange interactions ( $sp-d$ ) any electrons level interaction ( $d$ ) topical ions manganese and electrons oxide nickel band, this shows compensation manganese ions ions for the original article in the crystal structure of. forbidden direct energy gap was determined by plotting a graph between  $(\alpha h\nu)^{2/3}$  and ( $h\nu$ ) in eV as shown in the figure (6).





**Fig. 5:** The relation between  $(\alpha h\nu)^2$  and  $(h\nu)$  for undoped and Mn-doped NiO thin films





**Fig. 6:** The relation between  $(\alpha h\nu)^{2/3}$  and  $(h\nu)$  for undoped and Mn-doped NiO thin films

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<sup>8</sup>.

$$\alpha = \alpha_0 \exp (h\nu/E_u) \quad (4)$$

where  $(h\nu)$  is the photon energy,  $(\alpha_0)$  is constant, and  $E_u$  is the Urbach energy which refers to the width of the exponential absorption edge. Figure (7) shows the variation of  $(\ln \alpha)$  versus photon energy for the films. The  $E_u$  values were calculated as the reciprocal of the straight line slopes shown in the figure (7).

**Table 2:** The  $E_u$  and  $E_g$  values for undoped and Mn-doped Nickel Oxide thin films

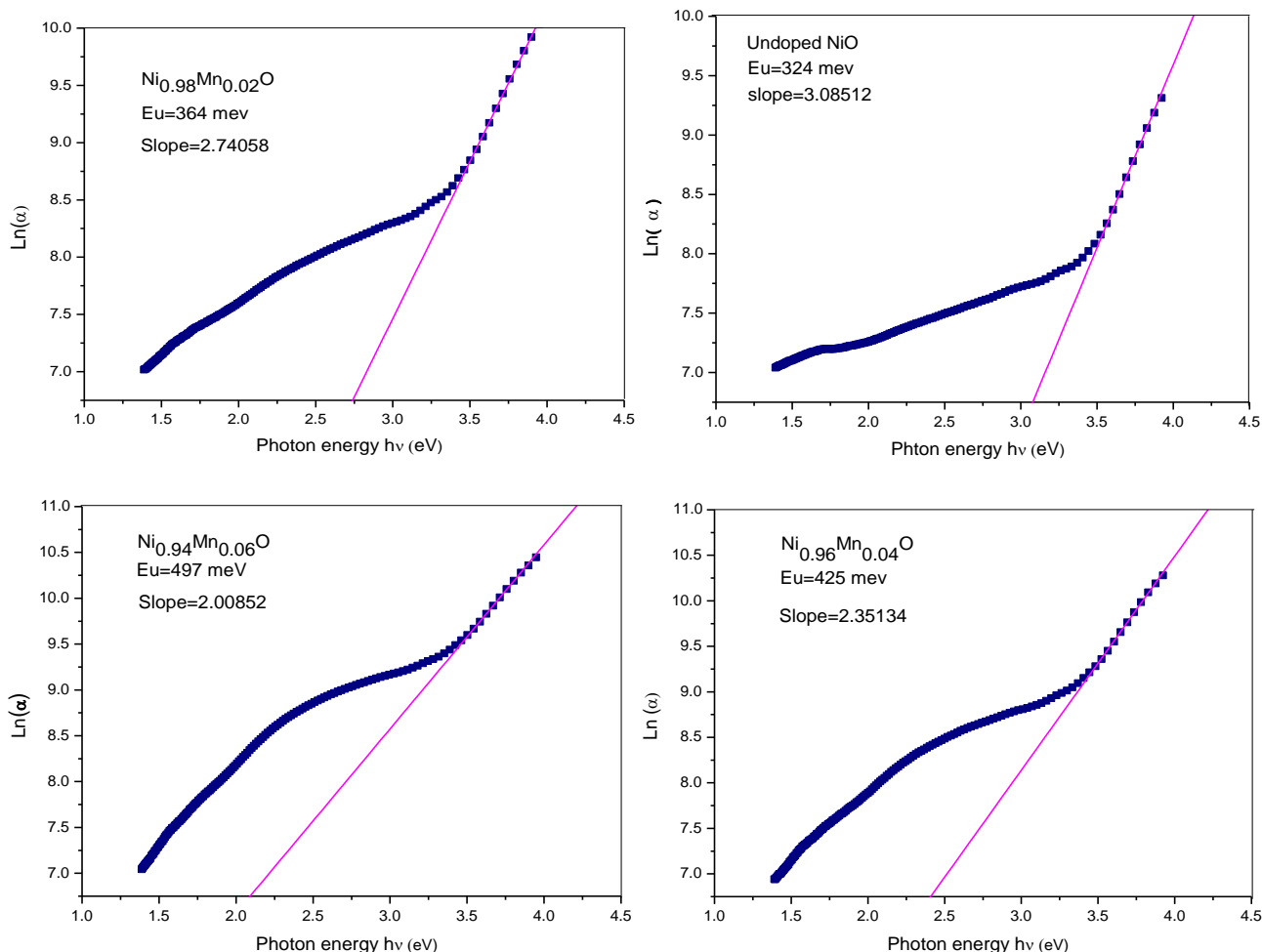
Percentage	$E_u$ (meV)	$E_g$ (eV) (allowed direct)	$E_g$ (eV) (forbidden direct)
Undoped NiO	324	3.59	3.33
Ni <sub>0.98</sub> Mn <sub>0.02</sub> O	364	3.58	3.21
Ni <sub>0.96</sub> Mn <sub>0.04</sub> O	425	3.57	3.12
Ni <sub>0.94</sub> Mn <sub>0.06</sub> O	497	3.55	3.00
Ni <sub>0.92</sub> Mn <sub>0.08</sub> O	560	3.53	2.91

Urbach energy increases with increases in Mn-doping concentration. The Urbach energy values change inversely with optical band gaps of films. The Urbach energy ( $E_u$ ) and energy gap values are given in Table (2):

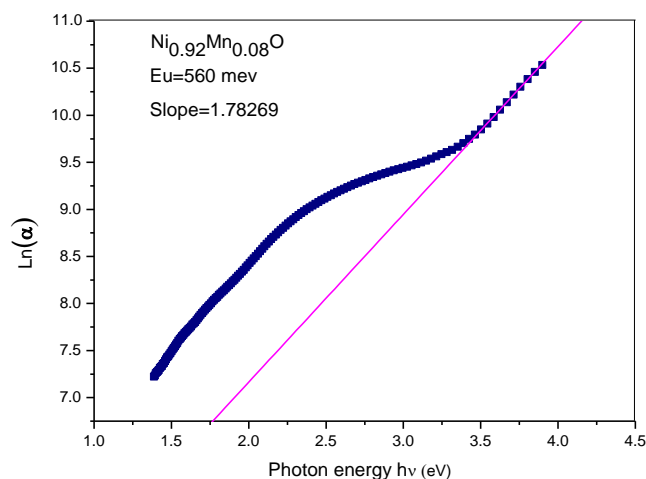
Extinction coefficient ( $K_o$ ) for undoped and Mn-doped Nickel Oxide thin films was determined using the relation<sup>9</sup>:

$$K_o = (\alpha \lambda) / (4 \pi) \quad (5)$$

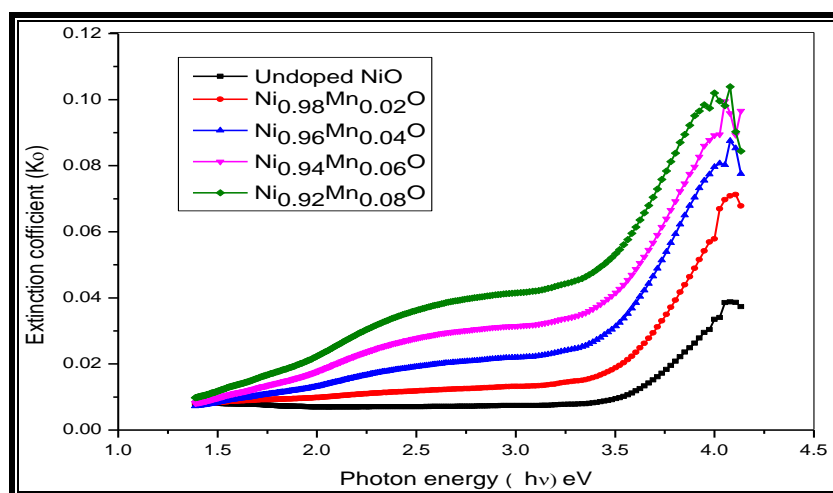
Where  $\lambda$  wavelength, figure (8) show the change extinction coefficient with photon energy. We note that there are similarities between the curve extinction coefficient and absorption coefficient curve as this similarity is due to the adoption of the expense of extinction coefficient values for the values of absorption coefficient as is evident in the equation (5). The extinction coefficient increases significantly when low photonic energies and is increasing rapidly and suddenly in the extent of the corresponding energies to the edge of the fundamental absorption (energies high photonic) and this increase may be the result of the rapid increase of the coefficient of absorption at these energies, which indicate the occurrence of electronic transitions, and increase the proportion of doping lead to increased extinction coefficient values due to the structural changes that have occurred as a result of the film to enter the manganese atoms (Mn) within the crystal structure of nickel oxide (NiO).







**Fig. 7:** Urbach plots of undoped and Mn-doped Nickel Oxide thin films



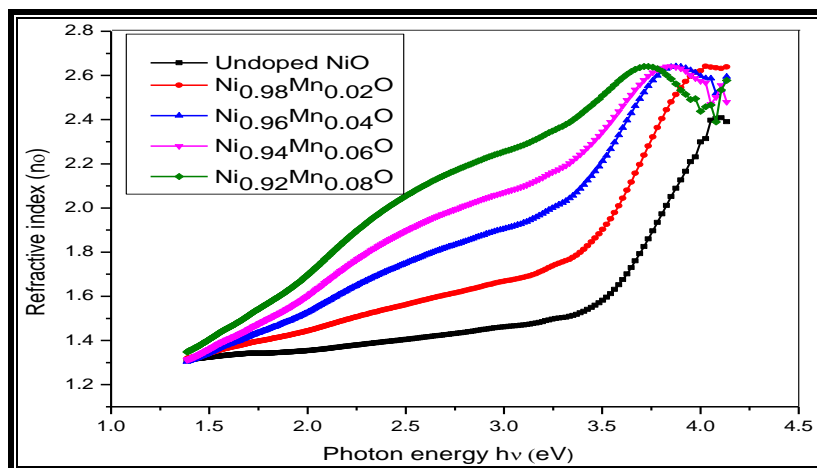
**Fig. 8:** Extinction coefficient ( $K_0$ ) versus photon energy ( $h\nu$ ) for undoped and Mn-doped Nickel Oxide

The refractive index ( $n_0$ ) for all films prepared was determined using the relation<sup>10</sup>:

$$n_0 = \left[ \left( \frac{1+R}{1-R} \right)^2 - (k_0^2 + 1) \right]^{1/2} + \frac{1+R}{1-R} \quad (6)$$

Figure (9) show change refractive index as a function of photon energy, through the form we note that the nature of the curved refractive index similar almost curved reflectance as they relate to the relation (6), and the refractive index of all films gradually increases with photon energy and then at least toward energies high photonic, although the reason for the decrease refers to decrease the reflectance values and increase the absorbance which confirms the occurrence of transfers electronics, either when you increase the percentage of doping, the curves of the refractive index tops pushed toward energies low photonic (lengths high wavelengths) due to increased absorption coefficient of the films and the drooping of the optical energy gap. The real dielectric constant ( $\epsilon_1$ ) calculation according to the equation (7)<sup>11</sup>:

$$\epsilon_1 = n_0^2 - k_0^2 \quad (7)$$



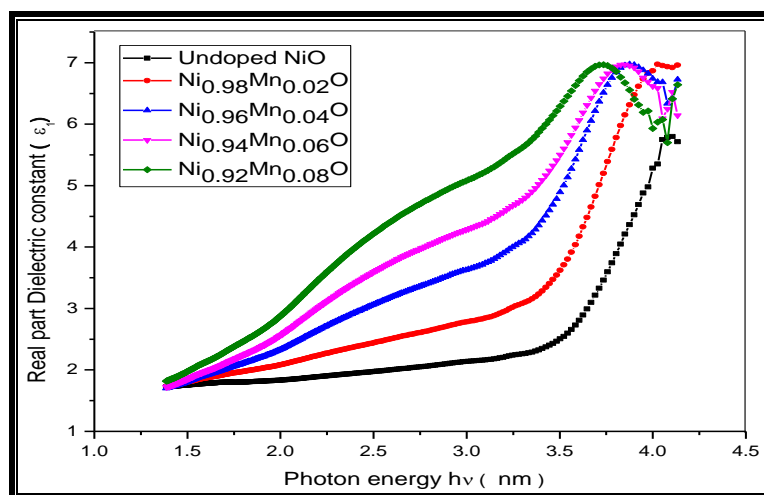
**Fig. 9:** Refractive index ( $n_0$ ) versus photon energy ( $h\nu$ ) for undoped and Mn-doped Nickel Oxide

figure (10) shows the real part of the dielectric constant as function of photon energy of the films prepared, it is through the shape note how similar between the real dielectric constant curves and curves of the refractive index ( $n_0$ ), and this similarity is due to the adoption of the expense of the values of the real part of the dielectric constant on the values of the refractive index of more than values extinction coefficient because the effect of extinction coefficient is small compared to the impact of the refractive index are neglected, and the real dielectric constant gradually increases with photon energy and then at least toward high energies photonic also note displacement curves and the real part of the dielectric constant peaks toward low photonic energies (wavelengths high).

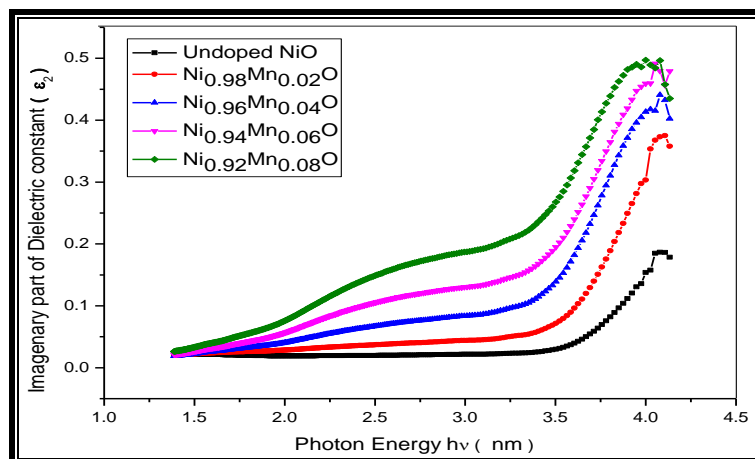
The imaginary dielectric constant ( $\epsilon_2$ ) calculation according to the equation (8) <sup>11</sup>:

$$\epsilon_2 = 2 n_0 k_0 \quad (8)$$

Figure (11) show imaginary part of the dielectric constant as function of photon energy of the films prepared, the imaginary dielectric constant increases with photon energy, although the nature of the curve is similar to the curve extinction coefficient ( $K_0$ ) and here is the effect of the refractive index ( $n$ ) very few so neglects, either when the doping, the imaginary dielectric constant increases with the proportion of doping and pushed tops curves toward energies photonic low (wavelengths high).



**Fig. 10:** Real part of dielectric constant ( $\epsilon_1$ ) versus photon energy ( $h\nu$ ) for undoped and Mn-doped Nickel Oxide



**Fig. 11:** Imaginary part of dielectric constant ( $\epsilon_2$ ) versus photon energy for undoped and Mn-doped Nickel Oxide

## CONCLUSIONS

In this study Nickel-Manganese Oxide ( $\text{Ni}_{(1-x)}\text{Mn}_x\text{O}$ ) thin films, where ( $x = 0, 2, 4, 6$  and  $8\%$ ) were successfully deposited on glass substrate at ( $400^\circ\text{C}$ ) by chemical spray pyrolysis technique using Nickel and Manganese acetate as the Ni and Mn source. The transmittance of Mn-doped Nickel Oxide thin films increases rapidly as the wavelength increases in the range of ( $300\text{--}370\text{ nm}$ ) and then increases slowly at higher wavelengths. The band gap decreases as the Mn-concentration increases and the allowed direct band gap values range between ( $3.59\text{ eV}$ ) and ( $3.53\text{ eV}$ ), and forbidden direct band gap values range between  $3.33\text{ eV}$  and  $2.91\text{ eV}$ . The Urbach energy increases as the Mn-concentration increases and the Urbach energy values range between ( $324\text{ meV}$ ) and ( $560\text{ meV}$ ).

## REFERENCES

1. S. I. Abbas and A. Q. Ubaid, Structural Optical and photoluminescence properties of nanocrystalline NiO thin films, *Journal of advances in physics*, 2014, 6(1), 1016-1023.
2. K. Lascelles, L. G. Morgan, D. Nicholls, D. Beyersmann, Nickel Compounds, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2005.
3. Fasaki, A. Koutoulaki, M. Kompitsas and C. Charitidis, Structural, electrical and mechanical properties of NiO thin films grown by pulsed laser deposition, *Journal of Applied Surface Science*, 2010, 257.
4. S. S. Ahmed, E. K. Hassan and G. H. Mohamed, Investigation of optical properties of  $\text{NiO}_{0.99}\text{Cu}_{0.01}$  thin film by thermal evaporation technique, *International Journal of advanced research*, 2014, 2(2), 633-638.
5. N. Greenwood and A. Earnshaw, Chemistry of the Elements, Oxford, Pergamon Press, 1984.
6. N. A. Bakr, Z. T. Khodair and I. A. Alghalabi, Effect of Co doping on structural and optical properties of ZnO thin films by chemical spray pyrolysis method, *International Journal of Current Research*, 2015, 7(2), 12411-12417.
7. K. H. Abass,  $\text{Fe}_2\text{O}_3$  thin Films prepared by Spray Pyrolysis Technique and Study the Annealing on its Optical Properties, *International Letters of Chemistry, Physics and Astronomy*, 2015, 6, 24-31.

8. N. F. Al. Shammery, Optical characteristics of NiO thin film on glass formed by chemical spray pyrolysis, *Journal of Kufa-Physics*, 2010, 2(1).
9. S. A. Salman, Z. T. Khodair and R. K. Ismail, Study the effect of thickness on the optical properties of  $\text{ZnFe}_2\text{O}_4$  films prepared by chemical spray method, *International Journal of Current Research*, 2014, 6(1), 9669-9675).
10. M. Ohring, The materials science of thin films, Academic press, san diego-New York-Boston-London sydney-Tokyo toronto, 1992.
11. C. Hamaguchi, Basic Semiconductor physics, Book, 2<sup>nd</sup> Edition, Springer, 2001.

**\* Corresponding author: Asaad A. Kamil;**

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