Characterizationof pure and Nano(Ag) doped(NiO) thin films obtained by Chemical Spray Pyrolysis

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Abstract :

NanoSilver doped (2%,4% and 6%) (NiO) thin films were fabricated on glassslide substrates at (400^0C) by spraying method using a solution containing Nickel (III) oxide, Silver chloride and water. The effect of silver nanoparticles (AgNP's) on the structural,morphology and opticalproperties of (NiO) thin films were studied, the structural properties werestudied by X-ray diffraction (XRD). The results show that all the samples have a cubic structure. After (Ag) doping, the intensity of the diffraction peaks became smaller than the undoped(NiO) thin film. The topography properties were studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM) while optical properties were studied byUv-vis spectrophotometer. The optical transmittance has been decreased.On the contrary, the optical band gaps of (Ag) doped (NiO)thin films increase as the(Ag) content increased. Single oscillator energy, dispersion parameters and Urbach energy have been investigated which effected by the increasing of (Ag) content.

Keywords: (NiO)Ag; thin film; structural; morphological; opticalproperties; dispersio parameters; urbacenergy.

Introduction :

Nickel oxide is a transparent conductive oxide and p-type semiconducting material , it has a wide bandgap greater than (3eV) [1,2].Because ofmany applications of Nickel Oxide such aschemical sensors , catalysts, anti-ferromagnetic material , dye sensitized solar cells (DSSCs), electrochromic devices [3,4], itengage the researchers attention towards it.Severalmethods to preparing nickel oxide thin films depended on the applications, chemical and physical, such as chemical bath deposition , sol-gel , sputtering and pulsed laser deposition [5,6]. The major interest in spray pyrolysis is due to its low cost, while it is increasingly being used for some commercial processes, such as the deposition of a transparent layer on

glass [7,8]. This paper reports the influence of nano(Ag)as an important parameter on the preparation of nickel oxide (NiO) thin films by spray pyrolysis technique.

Experimental:

The(NiO) thin films were prepared using an aqueous solution of Nickel (III) oxide with (0.1)molarity in de-ionized water. The solution is mixed by a magnetic stirrer for one hour and then the solution was sprayed on the glass substrates at $(400)^{o}C$ with air as the carrier gas. In Other hand Silver chloride solution with (0.1) molarity was dropped into the Nickel (III) oxide solution to accomplish different doping concentration (i.e. 2%, 4%, 6%). And then the resultant solutions were deposited on glass substrates at$(400^{o}C)$by the same procedure. Thicknesses of the films were estimated gravimetricallyand found to be (400 ± 4) nm.

Results and discussion :

1. XRD Analysis :

Different coatings were prepared by changing the ratio of silver nanoparticles (AgNP's) in (NiO) thin films. Fig.(1), Shows the XRD patterns for the samples prepared under the experimental conditions. For pure (NiO) the peaks at scattering angles (2θ) of (37.35^{o}, 43.37^{o}, 62.08^{0} and 79.6^{0}) corresponding to the reflection from (111), (200), (220) and (222) crystal planes, respectively . The peaks assigned to diffractions from various planes correspond to Octahedral structure of (NiO). When (Ag) doped (NiO) by Concentration (2%,4%) and (6%) as shown in Fig. (1). One peak (101) of (Ag) growth in structure at (2θ=40.1°) when the concentration (2%) and there are two peaks for (103) and (102) at angles (45.7°) and (53.6°) respectively when concentration varied from (2% to 4%). Other peaks of (Ag) grown (200)and (102) at angles (44.7°)and (52.8°) respectively in concentration (6%).which could be attributed to metallic (Ag) fcc phase, and indicate the formation of (Ag) as the second phase clusters [9].

By increasing(Ag)concentration,peak position is shifted toward lowervalues, as shown inTable (1).The X-ray of (NiO) reduces with increasing(Ag) concentration. It may be due the increasing volume of unit cell as well as decreasing molecular weight of the samples. The strongest peak of thin films was used to determine the average crystallite size using Scherrer's equation [10,11]:

$$\boldsymbol{D = \frac{0.9\lambda}{\beta Cos\theta}} \qquad \textbf{(1)}$$

Where : (D)is the average crystallite size (nm),(λ) is the (X-ray) wavelength (1.5408) Å,(β) is the full-width at half-maximum (FWHM) intensity (in radians), and (θ) is the half of the diffraction peak angle.The average crystallite size was found todecrease from (32 to10) nm as the concentration of (Ag) increases from (0% to 6%). It may be due to the small grain growth of nano (Ag) doped (NiO) as comprised with pure (NiO).

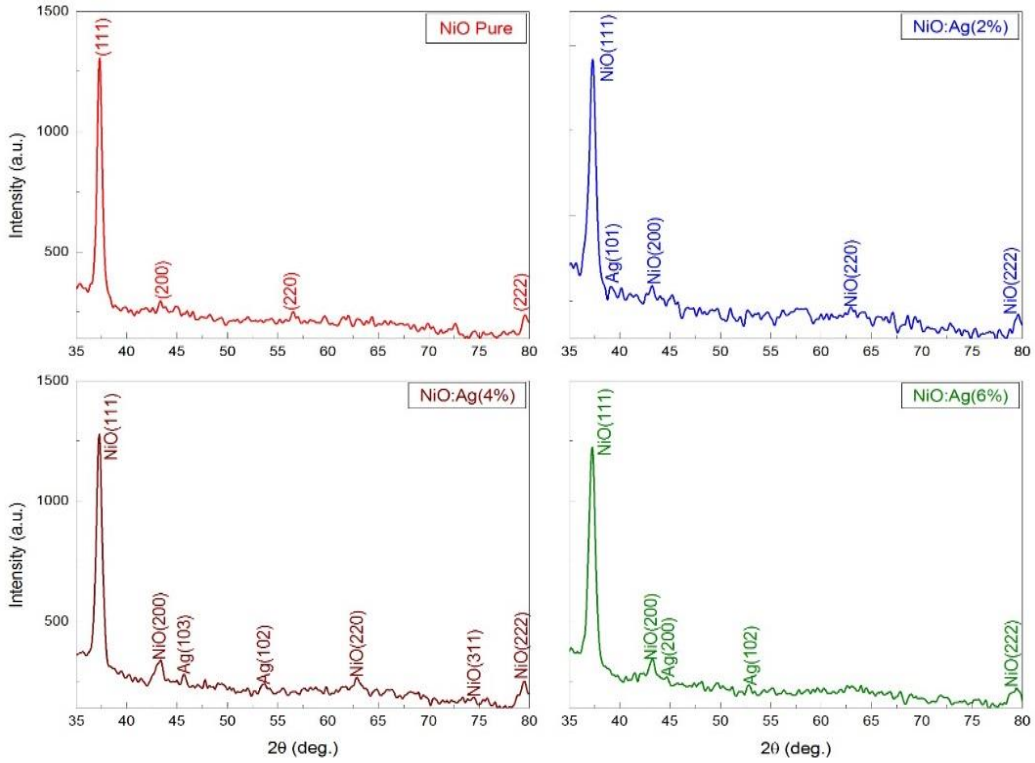


Fig. (1) : XRD Patterns of pure(NiO)and (NiO:Ag) thin films with different (Ag) concentration

Table- (1): Crystallite size and mitter indices of pure and (Ag) doped(NiO) thin films at differentconcentratin

Sample	2θ(degree)	(hkl)	Crystallite Size (nm)
NiO Pure	37.31	(111)	14.2
	43.54	(200)	9.3
	62.96	(220)	10
	79.46	(222)	22.9
NiO:Ag 2%	37.29	(111)	11.5
	39.23	Ag(101)	34.6
	43.1	(200)	13.0
	62.92	(220)	11.3
	79.42	(222)	23.5
NiO:Ag 4%	37.27	(111)	12.8
	43.17	(200)	9.3
	45.68	Ag(103)	18.4
	53.63	Ag(102)	19.6
	62.86	(220)	11.9
	75.4	(311)	16.9
	79.36	(222)	20.6
NiO:Ag 6%	37.25	(111)	11.8
	43.2	(200)	12.6
	44.6	Ag(200)	16.3
	52.8	Ag(102)	32.9
	79.18	(222)	9.7

2. AFM Analysis :

The averagegrain size and surface topography can be obtained by (AFM) analysis. Surface topography of pure and (Ag) doped (NiO)thin films were shown in Fig.(2). The averagegrain sizes were clearly of the order of nanometers and shape of particles was quasi-spherical. The average grain size in range of (70-110) nm as shown in Table (2). Using silver doping, the average grain size increase with increasing concentration and the roughness of surface of thin films increase as concentration increase due to increase centers of nucleation on the surface.

Table- (2):AverageGrain size roughness of pure and (Ag) dope (NiO) thin films at different concentrations

Sample	Average Grain Size (nm)	Roughness (nm)
NiO pure	70.71	1.01
NiO:Ag 2%	83.32	1.52
NiO:Ag 4%	96.28	1.39
NiO:Ag 6%	110.19	2.63

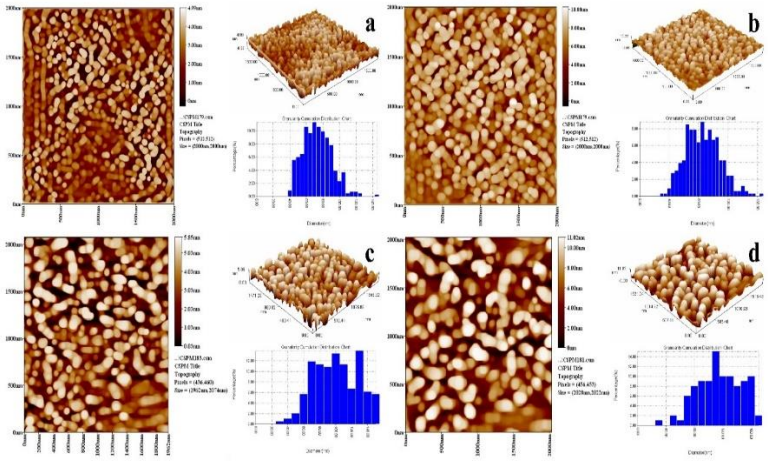


Fig. (2): AFM images of pure (NiO) and (NiO:Ag) thin films with different (Ag) concentrationa) pureNiO b) NiO:Ag 2% c) NiO:Ag 4%, d)NiO:Ag 6%

3. SEM Analysis :

The morphology of the thin films was studied using (SEM). It was clearly showninFig.(3), that the increase appearance of porous was noticed after using the (Ag)nanoparticles and showing an increase by increasing (Ag) content, these analysis ofSEM coincendent with the results of XRD and AFM analyses as previously discussed.

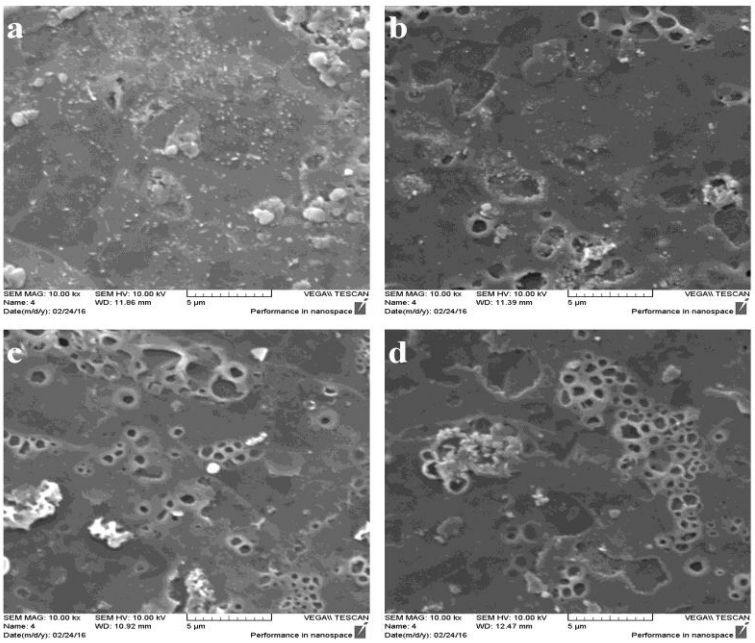


Fig. (3): SEM micrographs of a)pure NiO b) NiO:Ag 2% c) NiO:Ag 4% d) NiO:Ag 6%

4. Optical Properties :

Fig.(4), shows that the transmittance spectra of nano (NiO:Ag) thin films with different nano (Ag)concentration.The transmittance decreases with increasing doping concentration. This continuous decreasein transmittance is due to lattice defects. The nano(Ag^{+}) may occupy interstitial site on the(NiO)lattice and decrease transmittance of light thereby increasing the absorbance.Fig.(5), shows the reflectance spectra as a function of wavelength were found to increase with increasing the (Ag) contents in (NiO) thin films .

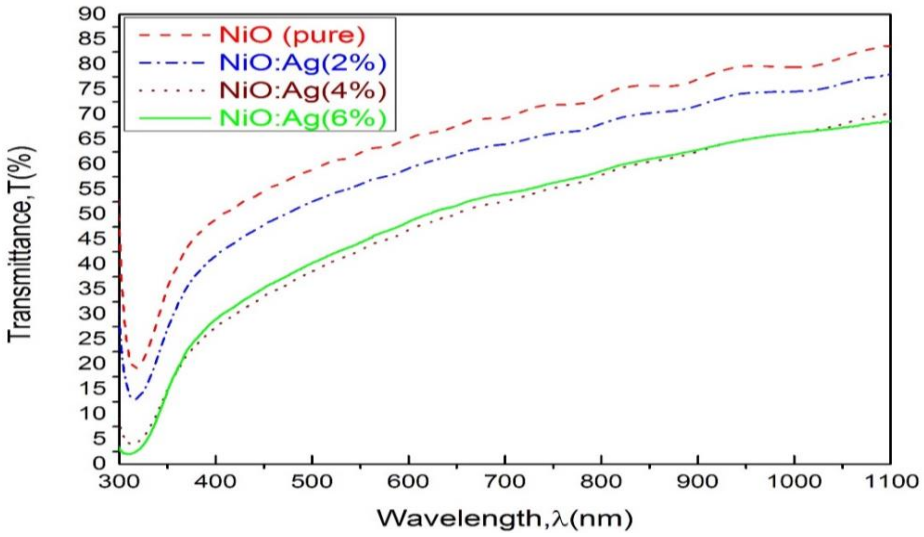


Fig. (4): Transmittance (T) as a function of wavelength (λ) for pure (NiO)and Different (Ag) Concentration

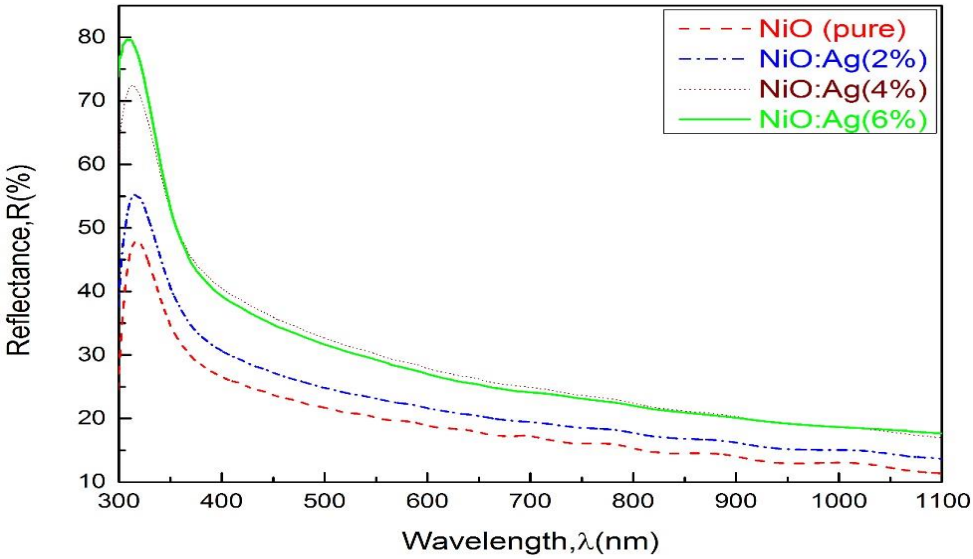


Fig. (5): Reflectance (R) as a function of wavelength (λ) for pure (NiO) and Different (Ag) Concentration

The optical energy band gap(Eg) can be estimated by assuming a direct transition between the valence bandand conduction band using Tauc relation[12,13]:

$$\alpha h\upsilon = A(h\upsilon - Eg)^{1/2} \quad (2)$$

$$\alpha = -\frac{1}{d}\ln(T) \quad (3)$$

Where: (α), (d), (hυ), (A), and (T) are the absorption coefficient,film thickness, photon energy,proportional constantand transmittance; respectively.The dependenceof $(\alpha h\upsilon)^2$ versus photon energy (hυ) for (NiO:Ag) thin films with different dopant concentration Fig. (6). The energy gap (Eg) is estimated byextrapolating the linear part of curve $(\alpha h\nu)^2$as a function of to intercept energy(X-axis).It was found that the(Eg)values varies from (3.41eV to 3.54eV) with increasing (Ag) doping concentration. Increasing grain size leads to increased grain boundaries and increasing the barrierheight between the grains and finally energy gap increased.

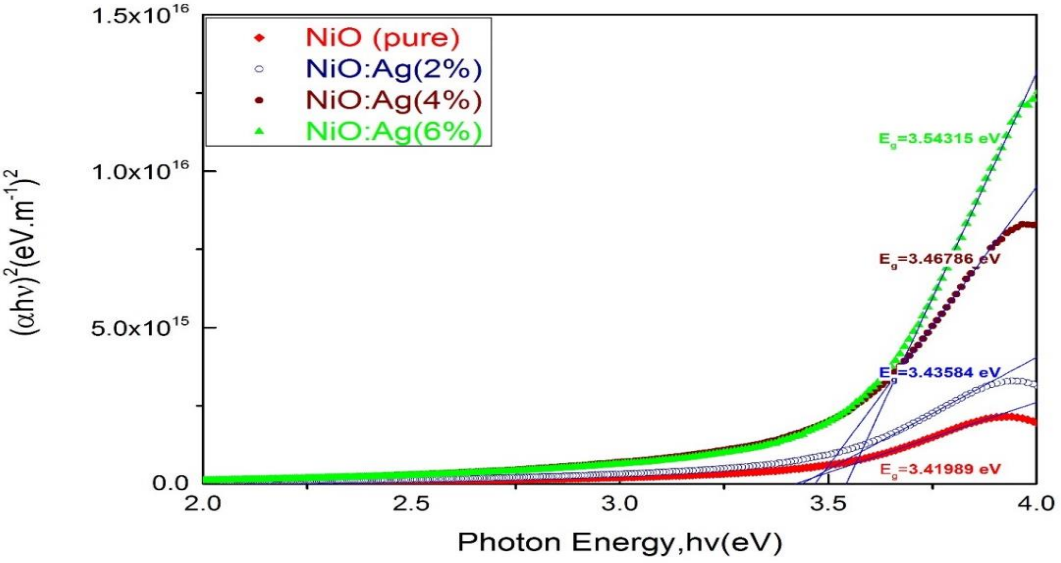


Fig.(6): $(\alpha h\upsilon)^2$ versus energy (hυ) curves of pure (NiO)and Different (Ag) Concentration

The absorbance spectraas a function of wavelength of pure and (Ag) doped (NiO) thin films at different concentrations were shown in (fig.7), it clearly show that the absorbance increased with increasing of (Ag) contents in (NiO) lattice due to the increase in grain size as shown previously in (AFM)analysis.Refractive index (n) is an important parameter of metal oxide semiconductors, it was calculated by the following relationship[10,14]:

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad (4)$$

Where: (R) , (k) and (λ) are the reflectance , extinction coefficient and wavelength; respectively.Fig. (8), shows that the refractive index as afunction of wavelength of pure and (Ag) doped (NiO) thin films at different concentrations; It is found that the refractive index increase with increasing the (Ag) contents in (NiO) thin films due to the decrease in transmittance as shown previously.

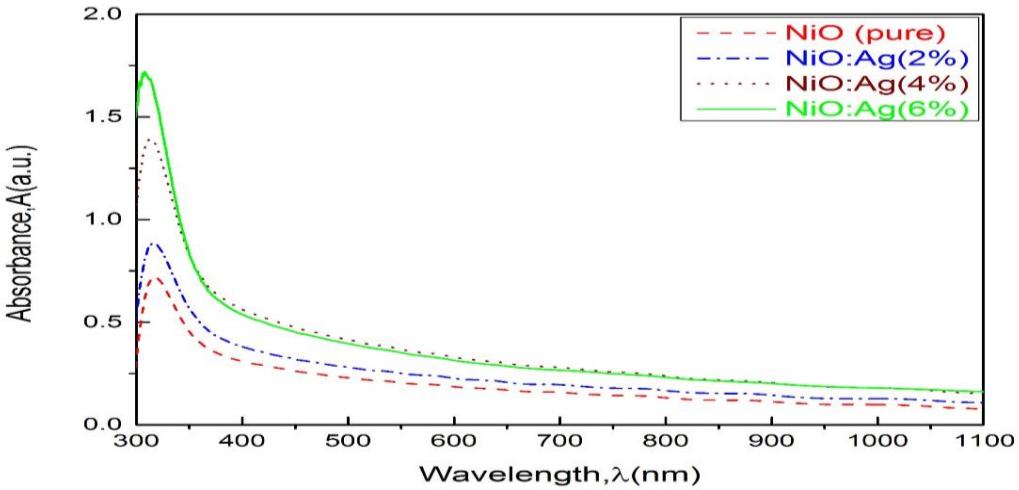


Fig.(7): Absorbance(A)as a function of wavelength(λ) for pure (NiO) and Different (Ag) Concentration

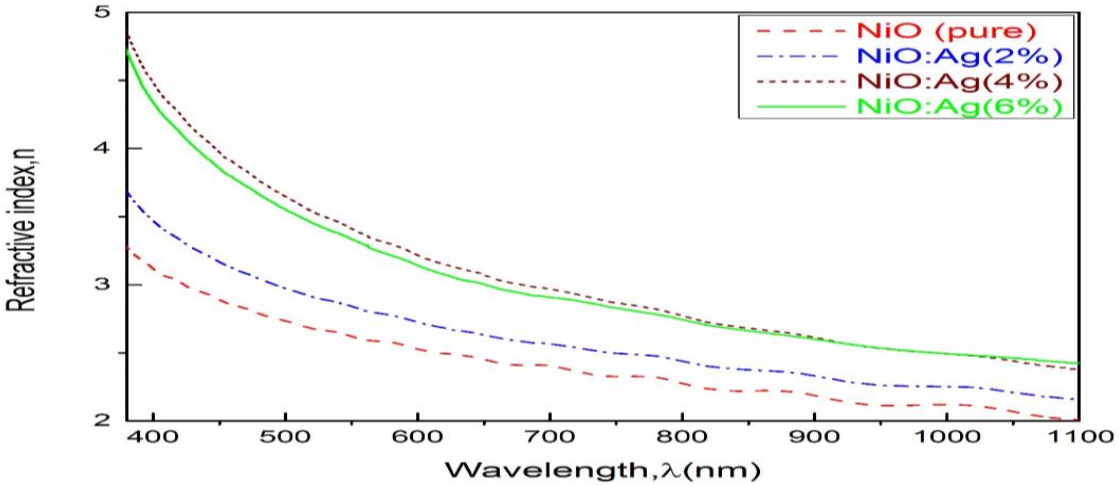


Fig.(8): Refractive index (n) as a function of wavelength (λ)forpure (NiO) and Different (Ag) Concentration

5. Dispersionparameters and Urbach energy:

Dispersion parameters considered as an important characteristics of semiconductor materilas, Wemple and DiDomenicorelationship [15], can be used to calculate the single oscillator energy(Eo) and dispersion energy (Ed) which are important in the search of optical materials ,be cause it is a significant factor in optical devices [16].The model describes the dielectric response for transitions below the optical gap.The dispersion parameters of the films were determined from the relation given by [17]:

$$n^2 = 1 + \frac{E_o E_d}{E_0^2 - (h\upsilon)^2} \qquad (6)$$

Where : (E_o) and (E_d) are single oscillator energy and dispersion energy; respectively, which areintensity measurement of the interband optical transitions. This model describes the dielectric response for transitions below the optical gap $(n^2-1)^{-1}$versus (hυ) plots for the pure and (Ag) doped (NiO)thin films were plotted see Fig. (9). (E_o) and (E_d) values were determined from the slope , (E_o E_d) and intercept (E_o/E_d) , on the vertical axis . The parameter (E_o) is an average energy gap and can be related by an empirical formula to the optical gap value, the values of (E_o~2Eg). (E_o) and (E_d) are listed in Table (3).

The refractive index (n_∞) at infinite wavelength, (λ_o) can be determined by the following relation [18] :

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \qquad (7)$$

The plot of $(n^2-1)^{-1}$versus $(\lambda^{-2})$was plotted to obtain ($\varepsilon_\infty = n_\infty^2$), where the intercept represents $(1/S_o\lambda_o^2)$ and the slope represents $(1/S_o)$.The values of pure and (Ag) doped (NiO) thinfilms as shown in Fig. (10). The moments of the opticalspectral (M_{-1}) and (M_{-3}) can be obtained from the relationships below [19]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \qquad (8)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad (9)$$

The obtained (M_{-1}) and (M_{-3}) , moments decreases with the increasing (Ag)contents in (NiO)thin films as listed in Table (3).The absorption coefficient near the band edge shows an exponential dependence on photon energy [21] :

$$\alpha = \alpha_o e^{\frac{h\upsilon}{E_U}} \qquad (10)$$

Where (E_U) is the Urbach energy which corresponds to the width of the band tail and can be evaluated as the width of the localized states ,(α_o) is a conastant and (hυ) is the photon energy . Thus a plot of Ln (α)versu (hυ) shoud be liner and Urbach energy can be obtained from the slope that shown in Fig. (11),the Urabach energy values are listed in Table(3).

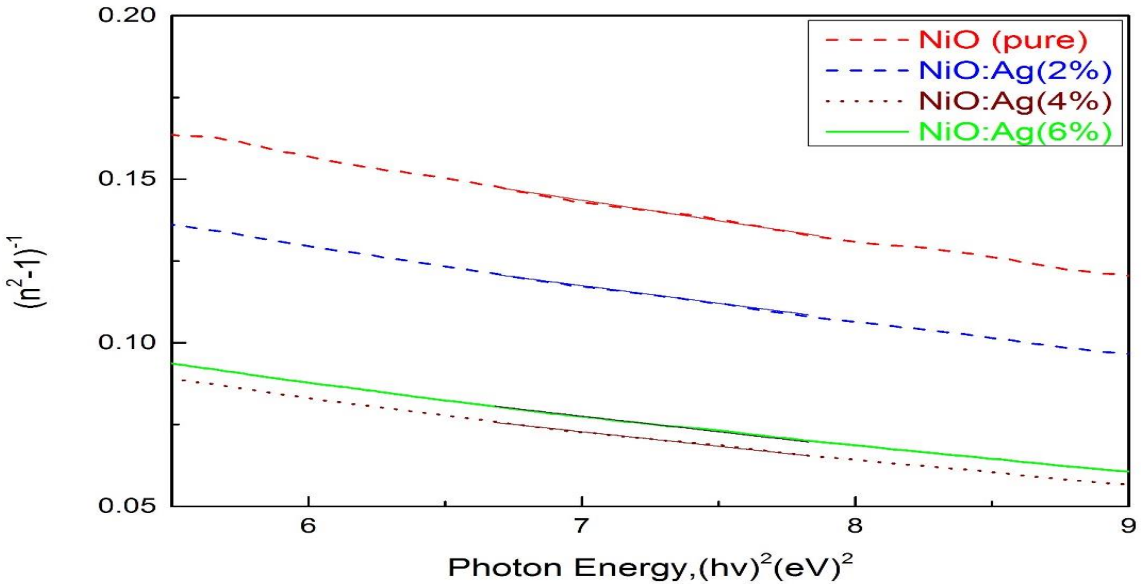


Fig.(9): $(n^2-1)^{-1}$ as a function of photon energy (hυ) for pure(NiO) and Different (Ag) Concentration

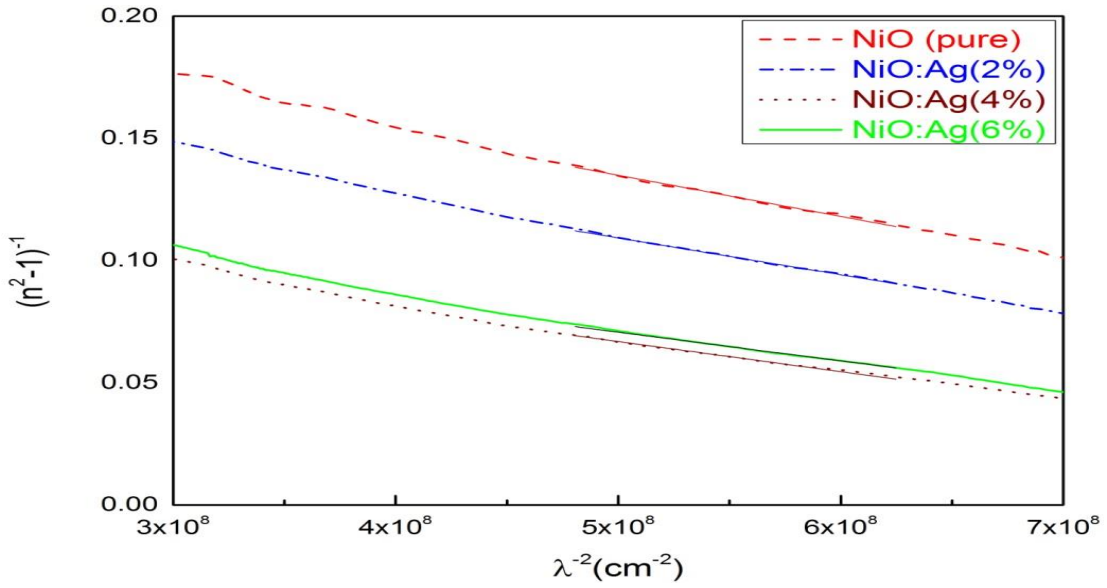
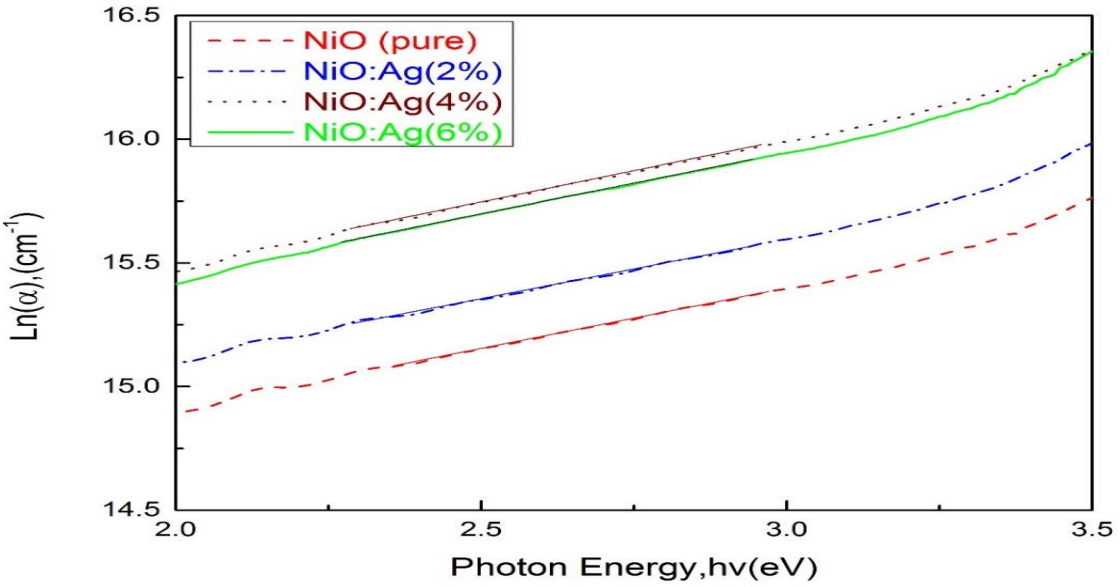


Fig.(10) : $(n^2-1)^{-1}$ as a function of lamda for(λ) pure(NiO) and Different (Ag) Concentration



Fig(11): Ln(α) as a function of photon energy(hυ) for pure (NiO) and Different (Ag) Concentration

Table -3: Dispersion parameters and Urbach energy of pure and (Ag) doped (NiO) thin films at different constrations

sample	E_g(eV)	E_o(eV)	Ed(eV)	ε_∞	n_o	M_{-1}	M_{-3}(eV^{-2})	λ_o (nm)	$S_o x10^{13}$ m^{-1}	E_U(eV)
NiO pure	**3.41**	**6.70**	**19.15**	**5.38**	**2.32**	**4.38**	**0.229**	**277**	**5.89**	**2.06**
NiO:Ag2%	**3.43**	**6.59**	**21.55**	**6.12**	**2.47**	**5.11**	**0.288**	**289**	**6.34**	**2.07**
NiO:Ag4%	**3.46**	**6.46**	**30.47**	**8.63**	**2.94**	**7.63**	**0.479**	**305**	**8.53**	**2.02**
NiO:Ag6%	**3.54**	**6.30**	**28.26**	**8.11**	**2.85**	**7.10**	**0.449**	**306**	**7.94**	**2.01**

6. Conclusion:

The increase of (Ag) concentration on (NiO) thin film led to increasing volume of unit cell as well as decreasing molecular weight of the thin film, topographic analysis shows that the average grain size increased with Ag contents leading to decrease the energy gap, these results are valuable to manufacture gas sensors and optoelectronics.

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