Effect of Li Doping on Structure and Optical Energy Gap of 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 pure and Li doped NiO films with different ratios (0.03,0.06,0.09 mol %) . Thin films of NiO were deposited on glass substrates at temperature 298ºK and thickness 200 nm by sol–gel spin coating technique. X-Ray diffraction(XRD) showed that the films are polycrystalline and have cubic structure with a preferred orientation along (111). The Li doping by 0.03,0.06 & 0.09 mol % didn't change the preferable orientation. The average grain sizes of the crystallites (mean crystallites diameter) estimated from XRD data was found to lie in the range of 20.11 – 24.2 nm. Data of atomic force microscope (AFM) indicate that the surface of films is highly smooth.

The optical transmittance value of undoped NiO film reaches to 72% in the Visible and NIR regions, which is important for its applications as window layers in solar cells. The optical transmittance of the films deposited with various concentration of Li shows slightly lower transmittance. The values of optical energy gap for undoped NiO & Li doping by 0.03,0.06,and 0.09 mol % were equal to 3.9, 3.60, 3.54 and 3.47 eV respectively. Other important optical properties such as refractive index, extinction coefficient, , dielectric constant and optical conductivity have been calculated and were found to be increase with increasing doping concentration and thickness.

Keywords: Li:NiO, Thin Film, Sol–Gel Spin Coating Technique

تأثير التطعيم بـ(Li) على تركيب وفجوة الطاقة البصرية لأغشية NiO المحضرة بتقنية المحلول الجيلاتيني

فؤاد شاكر هاشم **خنساء حليم محسن**

الخلاصة

تناول البحث دراسة بعض الخواص التركيبية والبصرية لأغشية NiO النقية والمطعمة بالليثيومLi بالنسب (0.03 ،0.06 ،0.09 mol)% . رسبت أغشية NiO على الزجاج عند درجة حرارة الغرفة بتقنية sol-gel spin coater بسرعة دوران 3000 دورة بالدقيقة لمدة 15 ثانية ولسمك 200 نانومتر

تم التأكد من تركيب الأغشية المحضرة عن طريق فحصها بحيود الاشعة السينية ، وتبين أن هذه الأغشية متعددة التبلور من نوع مكعب ،وبالاتجاه السائد (111).وتم حساب الحجم الحبيبي للنماذج المقاسة عند سمك 200nm من بيانات XRD ووجد انه يزداد بزيادة نسب التطعيم(20.11nm -24.2nm). بيانات مجهر القوة الذرّية (AFM) أشار الى نعومة سطوح الاغشية المحضرة. نفاذية الاغشية تصل الى 72% في المنطقة المرئية والقريبة من تحت الحمراء، وكذلك امتصاصية عالية في منطقة فوق البنفسجي (UV) والتي تجعلها ملائمة كنافذة للخلية الشمسية. فجوة الطاقة البصرية لاغشية NiO النقية والمطعمة بالليثيومLi بالنسب (0.03 ،0.06 ،0.09 mol)% تساوي 3.9, 3.6, 3.54& 3.47eV . تم حساب خصائص بصرية مهمة اخرى والمتمثلة بمعامل الانكسار, معامل الخمود، وثابت العزل والتوصيلية البصرية ووجد انها تزداد بزيادة التطعيم وكذلك بزيادة السمك.

الكلمات المفتاحية: غشاء NiO النقية والمطعمة بالليثيومLi ، تقنية sol-gel spin

1. Introduction

Metal oxide semiconductors have attracted a wide interest owing to their unique properties and massive potential applications in different fabrications. Nickel (II)oxide is the chemical compound with the formula NiO. It is a transition metal oxide having a wide band gap in the range from 3.6 to 4.0 eV [1]. 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 [2]. Stoichiometric NiO at room temperature is an insulator with a resistivity of 10^{13} Ω cm.

Lithium (Li) is a group 1 (IA) element containing just a single valence electron ($1s^2 2s^1$). Group 1 elements are called "alkali metals". Lithium is a solid only about half as dense as water and lithium metal is the least dense metal. A freshly cut chunk of lithium is silvery, but tarnishes in a minute or so in air to give a grey surface. Its chemistry is dominated by its tendency to lose an electron to form Li. In this research, we have prepared thin films from undoped NiO and Li- doped NiO using sol-gel spin coating technique. The effects of Li 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 $NiCl_2 6H_2O$ with purity 98% by using sol–gel method. Two different bath compositions were used. The first one is a prepare of pure nickel oxide solution which is achieved by dissolving 0.59g of $NiCl_2 6H_2O$ with 0.05M in 10ml of ethanol. It was mixed slowly for one hour by using magnetic stirrer device ,then added 2g acetate at a rate 10%, to obtain pure homogeneous solution, and then mixed it slowly for 12 hr at (20-22 ºC), until we get the green solution. The second bath was the same first bath with adding 0.1M of $LiClH_2O$ solution for different concentrations as shown in the Table (1).

Table (1): The rates and concentrations of doped nickel oxide solution.

Rank	$NiCL_2 6 H_2O$ (ml)	$NiCL_2 6 H_2O$ (M)	$LiCL H_2O$ (ml)	$LiCL H_2O$ (M)	Li/NiO
First	9.85	0.05	0.15	0.1	0.03 %
Second	9.70	0.05	0.30	0.1	0.06 %
Third	9.40	0.05	0.60	0.1	0.09 %

The spin coater device was used to prepare the films under the conditions of speed 3000 rpm and time 15 sec. Then taking 20µl from the solution and dropped it on the substrate by using spin coater device, dried in electrical oven at 100 ºC for 2 min in order to remove the effect of the solvent (ethanol). Finally this process was repeated three times, to get sample with 30 layers. The samples were annealed by 500^0C for 1hr using jinyu-700 device to reduce the crystal defects and increasing the conductivity of the sample. Fig.1 shows flow chart of Li:NiO synthesis and the structural and optical measurements.

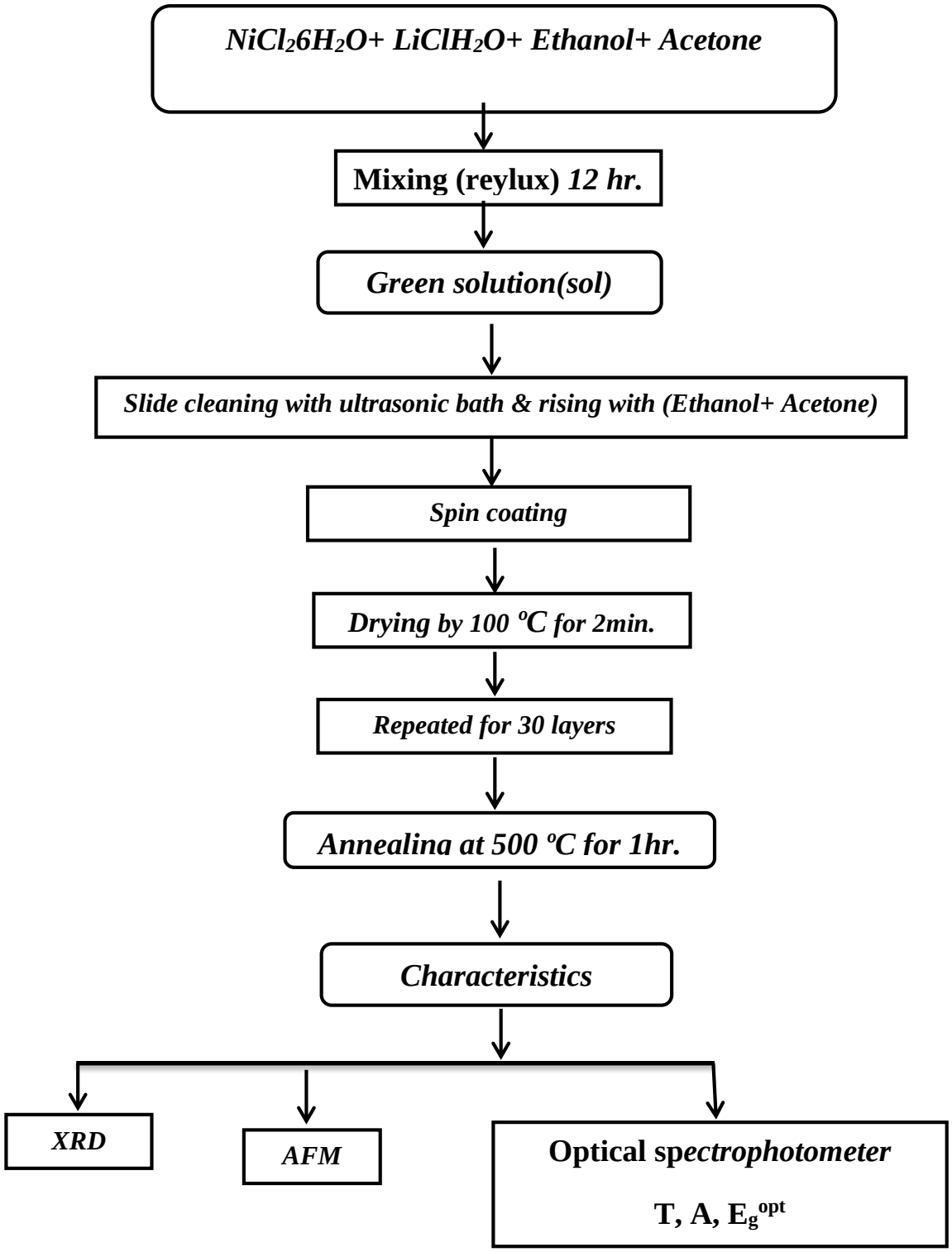

Fig. (1): Flow chart of Li:NiO synthesis and the structural and optical measurements.

The structure examined by using Philips pw 1050 X-ray diffractometer of 1.54 Å from Cu-kα, the XRD patterns of samples were recorded in the range $2\theta=20\text{-}60^0$. Surface morphologies were analyzed by an atomic force microscope (AFM) (AA3000, Angstrom Advanced Inc USA). The spectral absorbance and transmittance was measured over the spectral range of 200-1100 nm by using UV-Visible–NIR spectrophotometer supplied by shimadzu company **.**

2.2 Basic relations

The lattice constant (a) are estimated from the relation[3]:

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

The average grain size dimension (D),can be estimated using Scherrer's formula [4].

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

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

At the absorption edge, the absorption coefficient (α) can be calculated using the expression [5]:

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

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 [6]:

$$\alpha h\nu = A\,(h\nu - E_g^{opt})^n \qquad (4)$$

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 (Ts)=298K, and thicknesses consistently around 200 nm are shown in Fig.2. The films of pure NiO and Li doped NiO 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 Hao and Patil [7,8]. (111)-Oriented NiO and Li: NiO films can be used as buffer layers that are deposited on oxide films with other orientations, such as c-axis oriented perovskite type ferromagnetic films and super conducting films [9]. The average grain sizes of the crystallites (mean crystallites diameter) for major reflex (111) increase gradually with the increase of Li concentrations. It is found to be 20.11nm, 21.29 nm, 23.35nm, and 24.2nm for doping concentrations (0, 0.03, 0.06, and 0.09 mol)% of Li respectively. With the increase of Li concentration,the intensity of (111) peak was increased, this may be due to increase in the crystallite size as mentioned above.

Nickel Oxide films texture depends on both the oxygen content in the film and the deposition temperature [10,11]. The crystallographic orientations of NiO films are affected by the arrangement of O^{2-} at non-elevated substrate temperature (298K in our case). In this situation the Ni^{2+} and O^{2-} ,collide separately onto the growing film surface during deposition, and as long as the radius of O^{2-} (0.140nm) is larger than that of Ni^{2+} (0,069 nm)[12],to minimize the surface energy of the growing NiO film, O^{2-} must be arranged in the most densely packed plane; (111),which means the $Ni^{2+}$and O^{2-} have no enough energy to recombine, and thus films will be formed with non-stoichiometric ratio form Ni^{2+} and O^{2-} ,which is electrostatically polar .

In spite of, having no reflection peaks in the spectrum of XRD which indicate the presence of conglomerates of Li, The diffraction peaks of samples NiO doped with concentration 0.03,0.06, and 0.09 mol % of Li are slightly shifted towards higher 2θ values (diffraction peaks of (111) emerged at 2θ degree of 37.00 and 37.10, 37.15 , 38.05 for pure NiO and 0.03 ,0.06 , and 0.09 mol % of Li-doped NiO respectively**)** in comparison with peaks for pure 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 Li (0.076 nm) compared with that values of Ni(0.069 nm) [12].

The lattice parameters of undoped NiO and Li doping by 0.03,0.06 & 0.09 mol %, were calculated using equation (1). The lattice parameters were 4.2, and 4.101, 4.181, and 4.091 A° respectively. The JCPDS value of NiO was 4.178 A°.

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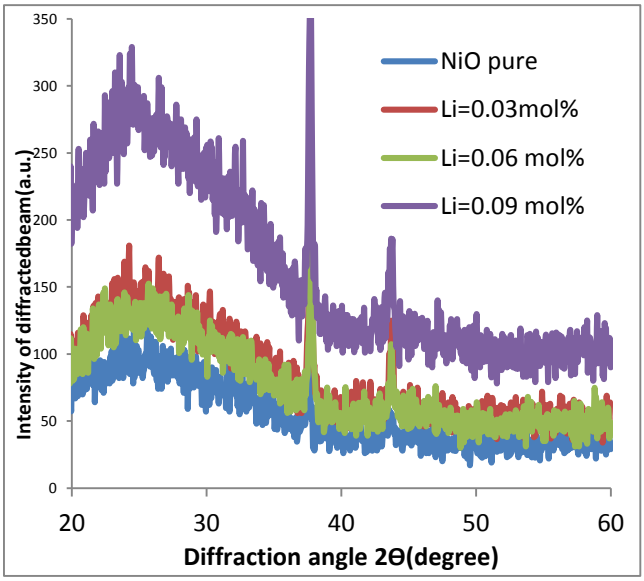
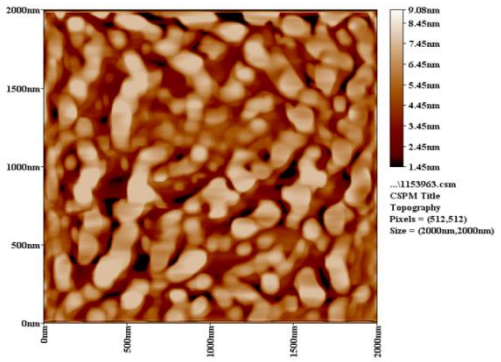


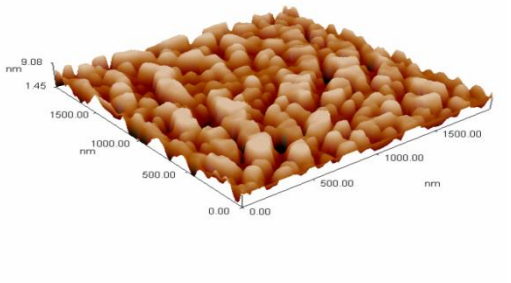
Fig.2:XRD patterns of NiO and Li-NiO doped thin films at different concentration.

3.2 surface morphological studies

The surface morphology of undoped NiO and Li doping by 0.03,0.06 & 0.09 mol %,was studied at thickness of 200nm, It was observed with AFM micrographs as shown in Fig. 3. It can be notice that a root mean square (RMS) roughness ranged of 0.477-1.67 nm, and a maximum peak to peak height, Sz (ten point height) ranged of 2.7 - 6.16 nm. Data above indicate that the surface of films is highly smooth as can be seen from the results listed in Table 1.

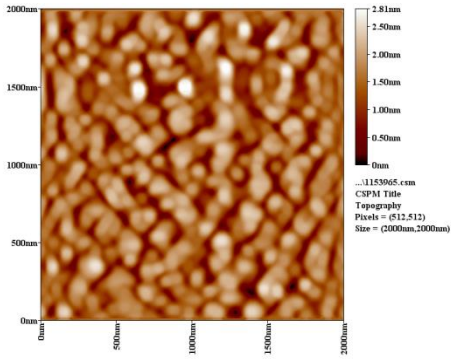


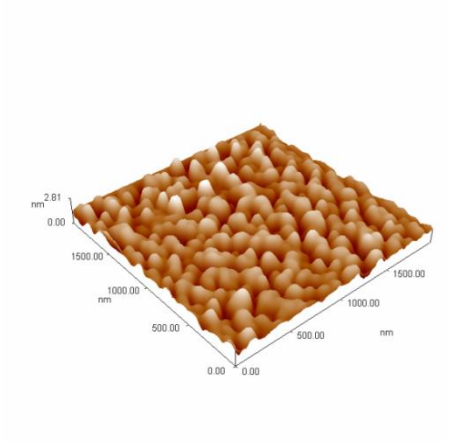
-1-



-2-

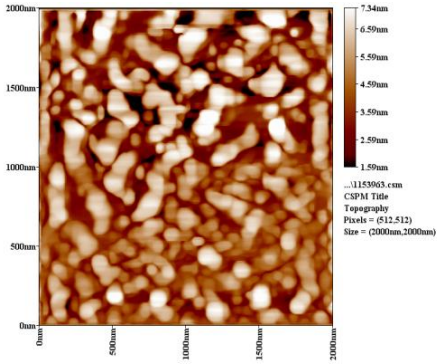
(NiO pure)

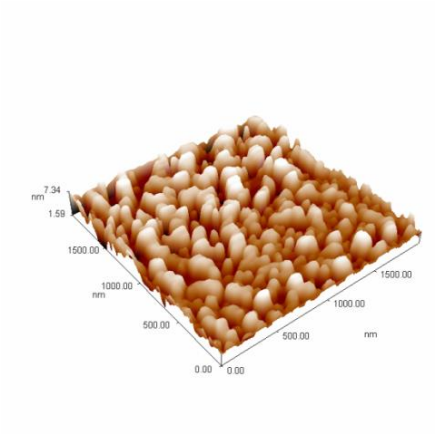




-1- -2-

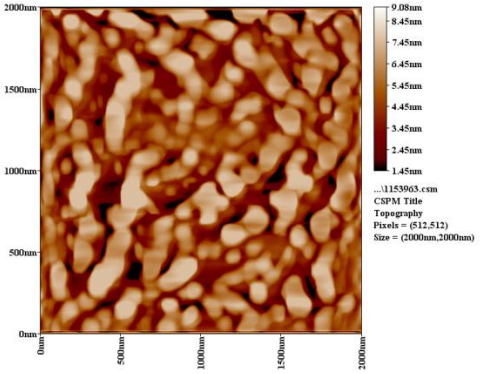
(Li=0.03mol%)

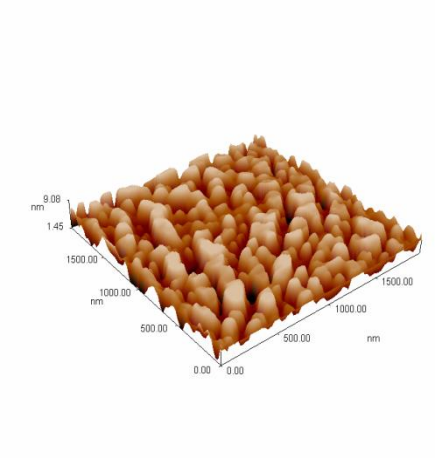




-1- -2-

(Li=0.06mol%)





-1- -2-

(Li=0.09mol%)

Fig.3: AFM images for undoped NiO and various Li –doped NiO films

. (-1- for 2D, & -2- for 3D)

Table 1: AFM data for undoped NiO and various Li –doped NiO films measured at thickness of 200 nm films .

Concentration Of Li (%)	Roughness average Sa(nm)	Root mean square Sq(nm)	Ten point height Sz(nm)
0	1.06	1.26	5.36
0.03	0.382	0.477	2.7
0.06	1.24	1.46	5. 46
0.09	1.41	1.67	6.16

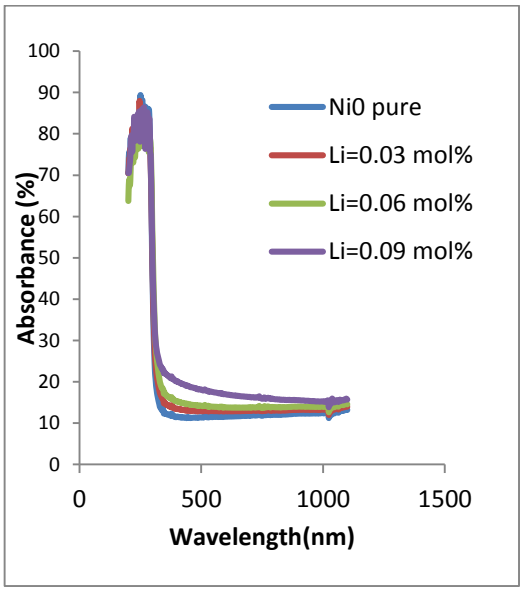


Fig. 4:Optical absorbance VS. wavelength for undoped NiO and various Li-doped NiO films.

3.3 Some optical studies

3.3.1 Absorbance

Fig.4 shows the dependence of absorbance on the wavelength (λ) in the spectral range 200-1100 nm for NiO and Li-doped NiO thin films measured at thicknesses of 200 nm. From this Figure 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 Li concentration. This is attributed to the presence of intraband 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 (ultraviolet region),and low absorption on the higher wavelength side (visible range). 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.

3.3.2Transmittance

Fig.5 shows the dependence of the optical transmittance on the wavelength (λ) in the spectra range 200-1100 nm for undoped NiO and Li-doped NiO thin films measured at thickness of 200 nm. The transmittance value of undoped NiO film reaches to72% in the visible and NIR regions, which is important for its applications as window layers in solar cells. The optical transmittance of the samples deposited with various concentrations of Li, shows slightly lower transmittance, with respect to the increasing of Li concentration. This behavior may be attributed to microstructural features of prepared films, as the photon scattering increases by crystal defects [12,13]

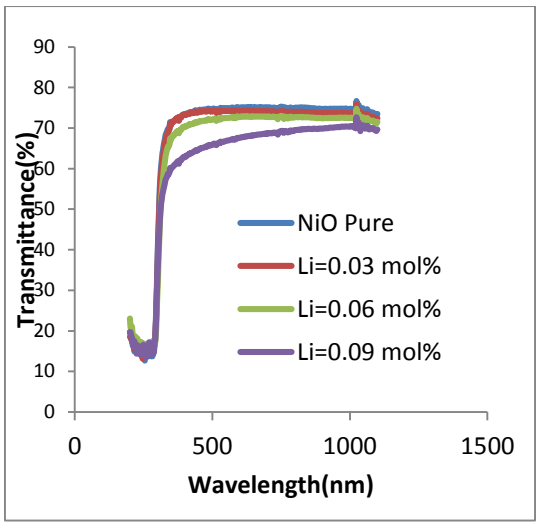


Fig.5: Optical transmittance spectra VS. wavelength for undoped NiO and various Li-doped NiO films.

3.3.3 Optical absorption coefficient

Fig.6 shows the dependence of optical absorption coefficient on the wavelength (λ) in the spectral range of 200-1100 nm for undoped NiO and Li –doped NiO thin films measured at thickness of 200 nm. The optical absorption coefficient values increase with the increase of Li-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 values of $\alpha > 10^4$ cm^{-1},which caused the increase of the probability of the occurrence of direct transition.

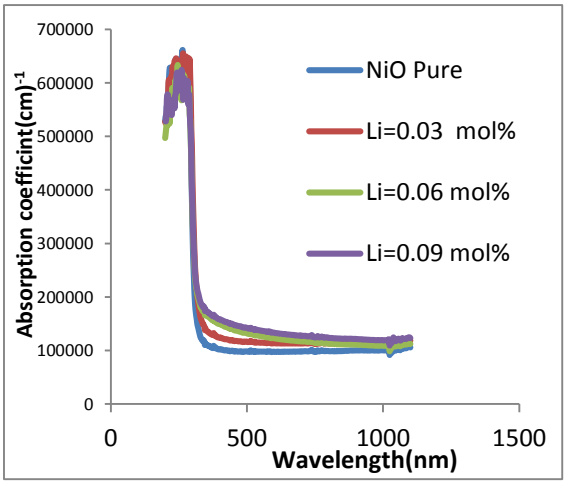


Fig. 6: The absorption coefficient for undoped NiO and various Li-doped NiO films .

3.3.4 Optical energy gap (E_g^{opt})

The optical energy gap could be obtained from the intercept of $(\alpha h\nu)^2$ VS. photon energy hν for direct allowed transitions. The experimental values of $(\alpha h\nu)^2$ plotted against(hν) of pure NiO and Li:NiO contains (0.03,0.06,and 0.09 mol) % of Li concentration deposited at Ts=298 K for 15 sec and thickness consistently around 200 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 films NiO and Li:NiO 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 (0.03,0.06, 0.09 mol) % of Li doped NiO films were equal to 3.9, and 3.6, 3.54 3.47 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 Li in the deposited films.

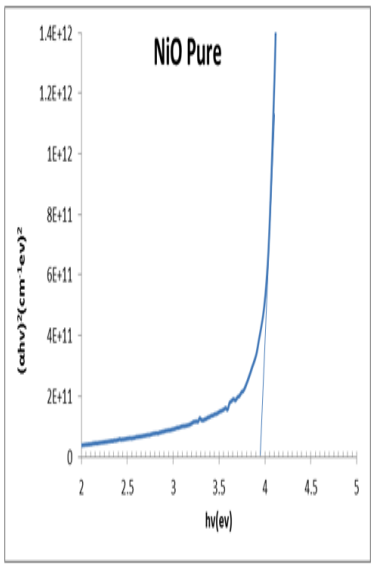


Fig. (7,a): Plot of $(\alpha h\nu)^2$ VS. photon energy (hν) for NiO films.

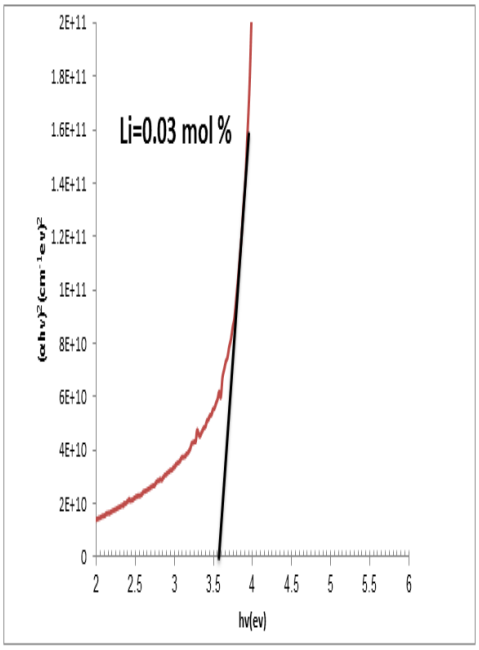


Fig. (7,b): Plot of $(\alpha h\nu)^2$ VS. photon energy (hν) for 0.03 mol % Li- doped NiO film.

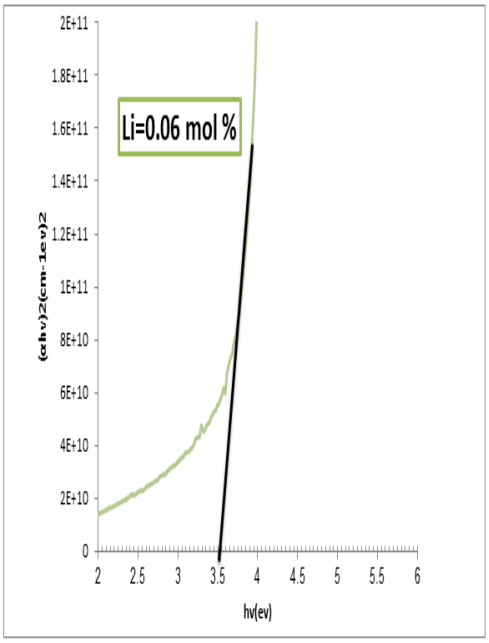


Fig. (7,c): Plot of $(\alpha h\nu)^2$ VS. photon energy (hν) for NiO 0.06mol % Li- doped NiO film.

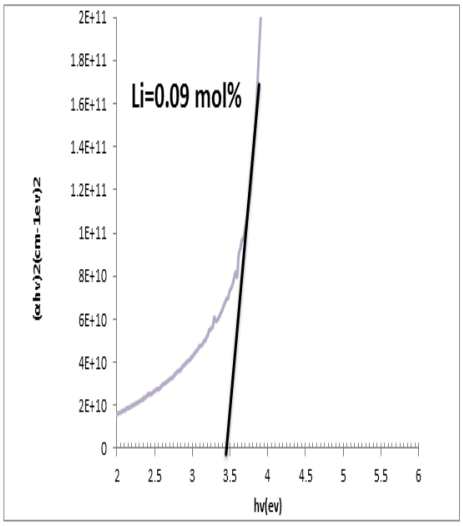


Fig. (7,d): Plot of $(\alpha h\nu)^2$ VS. photon energy (hν) for 0.09 mol % Li- doped NiO films.

Conclusions

The XRD resuls revealed that NiO and Li doping by 0.03,0.06, and 0.09 mol % thin films were found to be polycrystalline and have cubic structure. The XRD data showed the dominating peak is (111). (111)-Oriented NiO and Li: NiO films can be used as buffer layers that are deposited on oxide films with other orientations, such as c-axis oriented perovskite type ferromagnetic films and super conducting films. With the increase Li concentration, the intensity of (111) peak was increased **.** The AFM results revealed that the surface of films is highly smooth. With the Li content increase, the roughness of film surface decreases. The transmittance value of undoped NiO film reaches to 72% 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, 0.03,0.06,and 0.09) % of Li thin films were equal to3.9, 3.6, 3.54, and 3.47 eV.

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