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Optical and Structural Properties of Nio Thin Films

KEYWORDS: NiO thin films ,spray pyrolysis

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ABSTRACT *A simple and inexpensive spray pyrolysis technique (SPT) was employed to deposit nickel oxide NiO thin films from hydrated nickel chloride salt solution on to glass substrate. The effect of thickness and molarities of sprayed solution on structural, optical and electrical properties was studies using X-ray diffraction (XRD) , optical absorption and hall effect .it is found that increase in film thickness crystalline of the film, consequently the band gap energy increase from 3.1 to 3.4 eV , electrical properties of NiO films show that the films thickness 100 nm have conductivity of n-type, while the films have 300 nm thickness have conductivity of p-type.*

Introduction

Nickel oxide NiO is a versatile wide band gap semiconductor material. At present, transparent conducting oxide films, such as indium oxide , tin oxide and zinc oxide are routinely used as transparent electrodes and window coatings for onto-electronic devices [1]. These films are p-type semiconductor with versatile applications such as gas sensors[2]. Thin films are prepared by various physical e.g., sputtering , pulsed laser deposition , [3],electron-beam evaporation and chemical methods [6],(atomic layer epitaxy , sol gel , spray pyrolysis , [4],spin coating [5].Other important applications of nickel oxide include preparation of alkaline batteries (as a cathode material) , and ferromagnetic layers [7].Due to the wide band gap (3.6-4) eV , it has a wide range of applications in optoelectronics as well as in thermal applications [8]. Films of NiO have been deposited onto glass substrates kept at 350 °C by employing a spray pyrolysis (SP). An aqueous solutions are commonly used in SP system to deposit thin films due to ease of handling , safety , low coast and availability of wide range water – soluble metal salts . The solute must have solubility to increase the yield of the process. Metal chlorides have highest water solubility relative to other metal salt and used for the industrial production of several oxide and ferrites [9].With the previously mentioned effect, the present paper focused on use of aqueous solution of nickel chloride to deposit NiO thin films on glass substrate by spray pyrolysis technique , and their optical properties studies .because of its better optical, electrical properties, NiO is suitable for gas sensing applications by employing chemi-resistive principle .

Experimental procedure

NiO thin films were coated using spray pyrolysis. the coating solution was made by dissolving nickel chloride hexahydrate ($NiCl_2.6H_2O$),into 100 ml of deionized water to make 1 M solution , the solution was stirred at 25 °C for 30 min to get yellowish-green solution . NiO thin films were deposited from (0.1) M aqueous solution of nickel chloride [10] by conventional spray pyrolysis technique. The layers have been deposited onto glass substrates which are chemically and ultrasonically cleaned before deposition. The overall reaction process can be expressed as heat decomposition of nickel chloride to clusters of nickel oxides in the presence of water and air oxygen. The deposited films may have disordered $Ni(OH)_2$ structure or nanocrystalline NiO structure according to the following reactions[11]:

$$NiCl_2+2H_2O \rightarrow 2HCl + Ni(OH)_2$$

$$NiCl_2+2H_2O \rightarrow 2HCl + NiO + H_2O \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

In order to optimize the deposition temperature, the flow rate , solution concentration , deposition time , the nozzle to substrate distance are kept constant at: 350 °C,1 mbar/sec , (0.1) M, 5 sec and 28 cm respectively. The film thickness of the prepared samples was measured using multiple beam fizeau fringes at reflection using white light (spectrometer SR-25 range 220-1100) nm. The optical transmittance and reflectance of the films were recorded in the wavelength range from 200 nm to 850 nm using (optima 5p-3000 plus UV – visible spectrometer) double beam spectrophotometer. X-ray diffraction analyses were obtained using the model (Shimadzu Lab XRD 6000) X-ray powder diffractometer with Ni filtered CuK_α (1.5406 Å) radiation. While the surface physical morphology and roughness was obtained by means of AFM (Digital Instruments, Nanoscope III USA) analysis. The microstructures of the films were analyzed using a scanning electron microscope [SEM model Japan]. After the deposition of aluminum, the direct electrical conducting NiO films are measured by using the mask ,to study variation of film resistance with temperature we use electrical circuit. (Hantek 365 multimeter) are used to measure the variation in film resistance with temperature. it has been measure from thermocouple wire , and had been recorded film resistance for each ten degree , beginning at room temperature until 150 °C. (hall effect measurement system HMS-3000 VER 3.5)are used to measure the hall effect.

Results and discussion

Structural analysis of the NiO films prepared with 0.1 molarity at 350 °C was carried out by using CuK_α (1.5406 Å) and the different patterns of films were recorded by varying diffraction angle(2θ) in the range 30°-70° .Fig (1) , show XRD pattern for the NiO films ,it observed thin films values are in good agreement with standard value and the diffraction peaks are indexed to the Rhombohedral phase of NiO with a=2.9552Å, b=7.2275Å, c=2.4457Å, [joint committee on powder diffraction standards (JCPDS)No:44-1159,1997].it shows well defined peaks having orientations in the (101),(012),(110).compared with those of the bulk counterpart , the peaks are relatively broadened , which

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further indicates that the deposited material has a very small crystallite size .the crystallite size (D) is calculated using equations as follows :

$D=0.9\lambda/\beta \cos\theta$ ..... (2)

Where, β is the full width of half maximum (FWHM) diffraction peak measured in radians, λ is the X-ray wavelength(Å). The calculation of crystalline size from XRD is a quantitative approach which is widely accepted and used in scientific community [8].Grain size for powder NiO is 16.7 nm, while grain size for 200 nm is 23.1 nm and for the thickness 300 nm is 26 nm.

The two – dimensional high magnification surface morphologies of NiO films(thickness was 200 nm) were carried out using SEM images are shown in fig(2).from the micrographs, it is seen that the film consist of nanocrystalline grains with uniform coverage of the substrate surface with randomly orientation morphology , because of very thin film thickness. it is observed that as the concentration of high spray solution and thickness increases grain size also increases. Fig(3) show typical atomic force microscopy AFM scan of NiO films ,ellipsoidal particle are observed in films formed on the glass substrate with average projected diameters of major and minor axes as (2x2)µm .the figures show the ability of AFM to visualize and characterize surfaces of studying NiO thin films deposited by spray pyrolysis on glass with thicknesses (100-300 nm)with 0.1 M. The 100 nm films showed a deviation more than 300 nm film thicknesses, and priority preference for of growing in vertical axis. Optical measurements of spectral transmittance and reflectance of the as- deposited simples showed that the films prepared with 0.1 M of precursor solution concentration has a maximum transmittance of nearly equal to 80 % all over the spectral range (370-850) nm as shown in fig (4).the transmittance increase with decrease of films thickness, with subsequent decrease in absorption fig(5). The absorption coefficient α was obtained using the relation: $\alpha=2.303A/t$, where A is the absorption and t is the film thickness. The absorption coefficient is found to be of the order of (10^4) cm^{-1},fig(6).

The indirect band gap energy is obtained by extrapolating the linear portion of $(\alpha h\upsilon)^2$ versus $h\upsilon$ to energy axis at $\alpha=0$ as shown in fig (8),the energy gap can be calculated from equations $(\alpha h\upsilon)^2=B^2(h\upsilon-E_g)$ and $(\alpha h\upsilon)^{1/2}=B^{1/2}(h\upsilon-E_g)$ fig.(9).

the indirect band gap energy for the NiO films varies from (2.2-1.3)eV as the thickness varies from (100-300)nm. the band gap value decrease (3.4-3.1)eV as the films thickness decreases. Table (1) shows energy band gap for direct and indirect allowed at different thickness .

This increases in the band gap can be related to the structural modification of the films with higher molarities. it can be supposed that more oxygen atoms from the sprayed deposition can replace either substitution or interstitial site in the NiO lattice creating the structural deformation. The introduction of more oxygen atoms creates some additional energy level in the NiO band gap close to the valence band edge, with a subsequent reduction of the energy associated with indirect transition of the films coated with higher molarity. The values of band energy agree with reported values of band gap [8, 12]. The refractive index has been calculated by using the relation:

$n = (1+(R)^{1/2})/(1-(R)^{1/2})$ ..... (3)

Where R is the optical reflection in fig (7)we observed that the reflectance have high value which increasing with increasing wavelength for 0.1 M, but the reflectance have high value which decreasing for all films at low thickness fig(7). The decreases may be attributed to lower packing density and the change in crystalline structure [17].From the figure ,it is clear that the refractive index is increases (2-7.5) with increasing photon energy in the range (1.5-3.5) eV. The electrical direct conductivity $\sigma_{d.c}$ is calculated from the variation of resistance ρ_o for films with temperature by using the following equation :

$\rho_o = R_c.b.t/L$ ..... (4)

where:

R_c : is resistance of the film (Ω)

L : is distance between aluminum electrode (cm)

b : is width of pole (cm)

t : is thickness of film (cm)

the electrical direct conductivity $\sigma_{d.c}$ equals inverse of resistivity as the following equation :

$\sigma_{d.c} = 1/\rho_o$ ..... (5)

Hall effect is measured on NiO films to know the type of charge carriers and hall coefficient R_H were measured by the hall measurement system [HMS-3000,Ecopia] . Using electrical circuit concentration of charge carriers and mobility could be calculated. After there will be deposition a mask of aluminum on the film .

The electrical direct conductivity $\sigma_{d.c}$ is calculated from equation (5).fig(11) shows the relation between (ln $\sigma_{d.c}$) and (1000/T) for for NiO films .the XRD investigation of NiO films observed that film is polycrystalline then it will calculated two activation energies for low and high temperatures within thermal range (20-150)°C. Table (2) show activation energy E_a for all different thickness of NiO films, within thermal range.

Hall effect measurement is noticed at film thickness 300 nm have conductivity of p-type ,but at thickness 100 nm have conductivity of n-type. Hall coefficient the mobility and concentration of charge carrier have calculated from the relation $R_H = (V_H/I)x(t/B)$,as in the table (3).

Where t :is the thickness of the film.the carrier density (n_H) is related to the hall coefficient by the following equation:

$n_H = \pm 1/qR_H$, where q : is the charge of electron. $\mu_H = \sigma$ x R_H where μ_H : hall mobility .

The electrical conductivity of NiO films has a strong depended on the microstructure defects existing in NiO crystallites , such as nickel vacancies and interstitial [13].Furthermore ,the microstructure and composition ,as well as the deposition conditions and environment, are the main factor affecting the electrical properties of NiO film. Surface chemical reaction [14,16] may happen in pure oxygen atmosphere at evaluated substrate temperature .Luatel [15] had discussed the variation of carrier concentration with substrate temperature and probable reaction on the surface. in our suggestion, the carrier concentration variation depends on both crystalline microstructures and surface

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chemical reaction during the spray pyrolysis process.

Conclusion

NiO thin films of various thickness were deposited ,by sprayed solution , onto glass substrate using a simple and inexpensive spray pyrolysis technique at 350 °C. The pyrolytic decomposition of a precursor $NiCl_2.6H_2O$ was used to derive the deposition temperature . The XRD studies show that two thickness deposition were NiO (Rhombohedral) with orientation along (101),(012),(110) direction . Increase in film thickness leads to a slight improvement in the crystallinity. The optical band gap energy of NiO film increases from (3.1-3.4) eV with increasing in film thickness.

Table (1) shows direct and indirect energy gap for allowed transition for different thickness of NiO thin films.

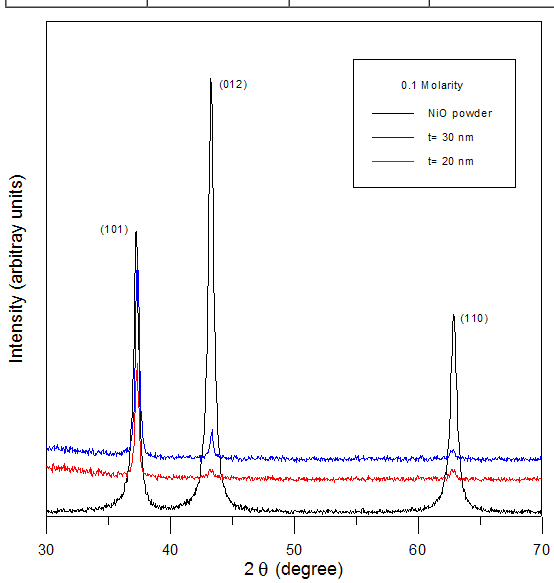
thickness (nm)	Direct allowed E_g (eV)	Indirect allowed E_g (eV)
100	3.1	1.3
200	3.3	2
300	3.4	2.2

Table (2) shows activations energy for different thickness of NiO films, with thermal range (20-150)°C.

Thickness (nm)	E_a (eV)at low temperature	Eg (eV)	E_a (eV)at high temperature
100	0.1394	3.1	0.244
200	0.313	3.3	0.165
300	0.239	3.4	0.014

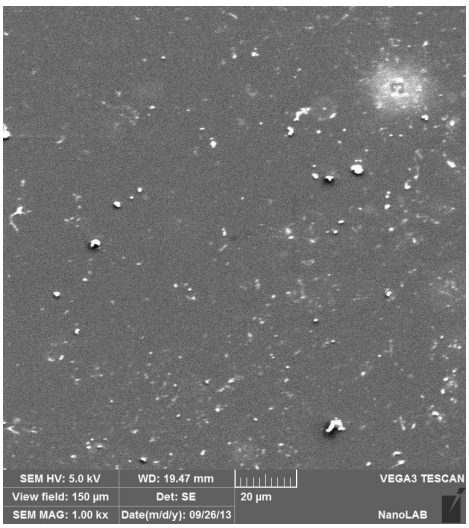
table (3) show the hall coefficient and concentration and of charge carriers of NiO films.

Thickness (nm)	R_H (cm^3/C)	N_D (1/cm)	μ_H (cm^2/V.sec) low
100	$-4.862x10^4$	$-2.44x10^9$	$5.187x10^1$
300	$6.44x10^6$	$2.9x10^7$	$2.31x10^3$



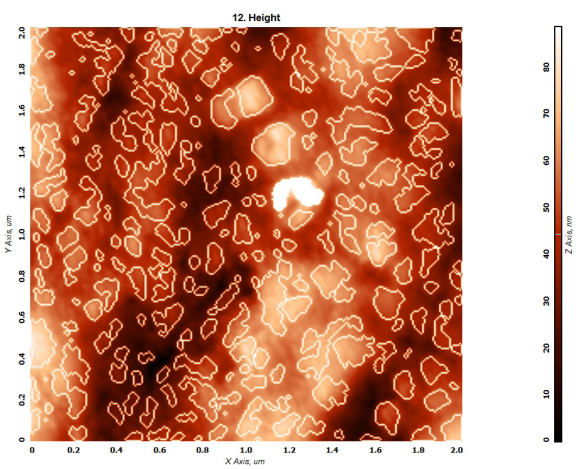
Fig(1) : XRD pattern of NiO thin films coated with 0.1 M ,thickness 200 and 300 nm

Fig(2): SEM micrographs of NiO thin films coated with 0.1 M with different thickness at 350 °C ,((a)200 nm

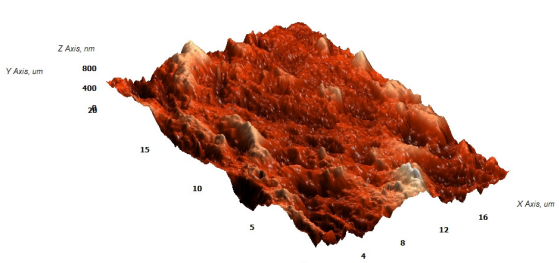


(b)300 nm

Fig(2): SEM micrographs of NiO thin films coated with 0.1 M with different thickness at 350 °C



(A)



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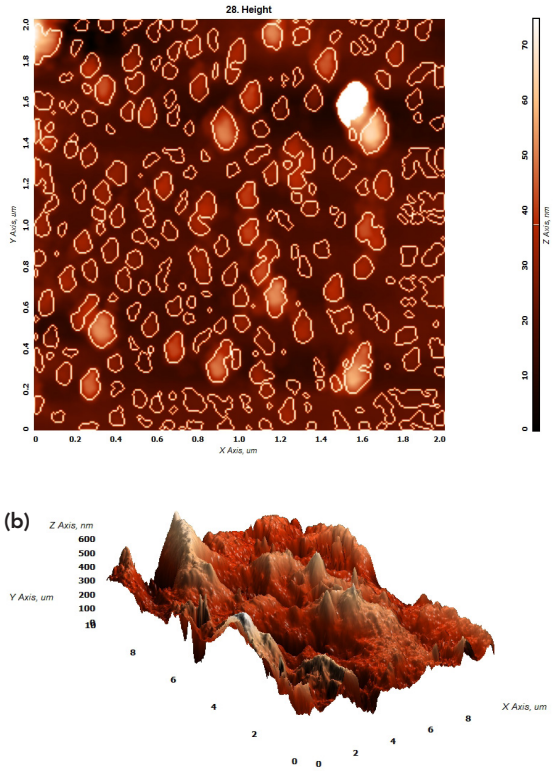
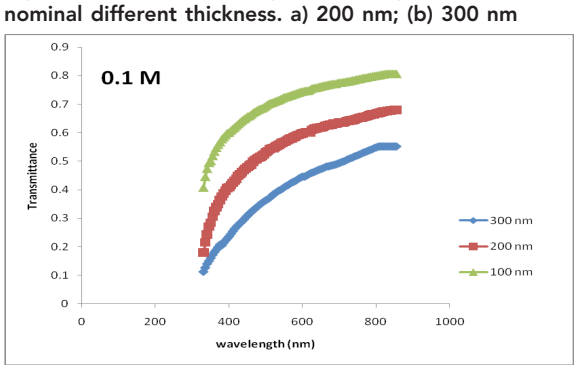
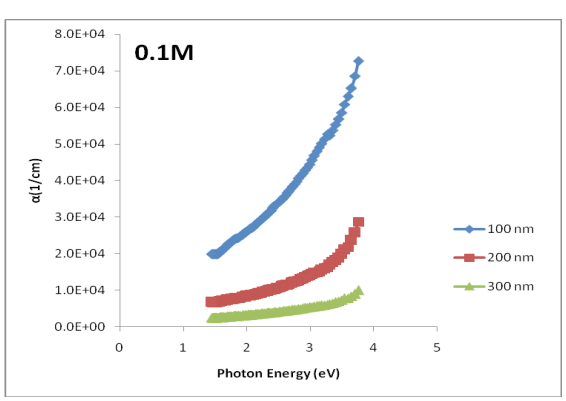
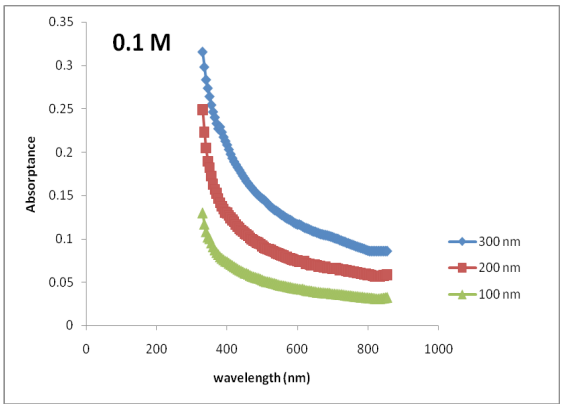


Fig(3) : 3D,2D AFM images of NiO/glass thin films of nominal different thickness. a) 200 nm; (b) 300 nm

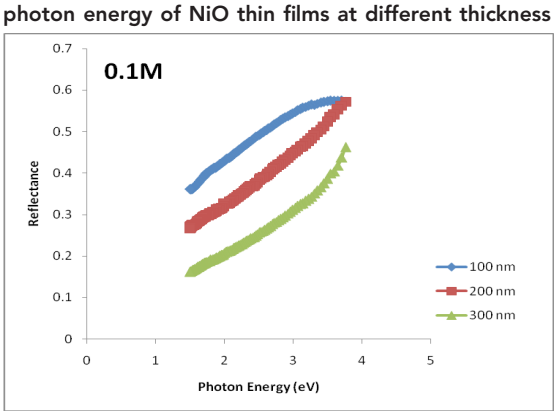




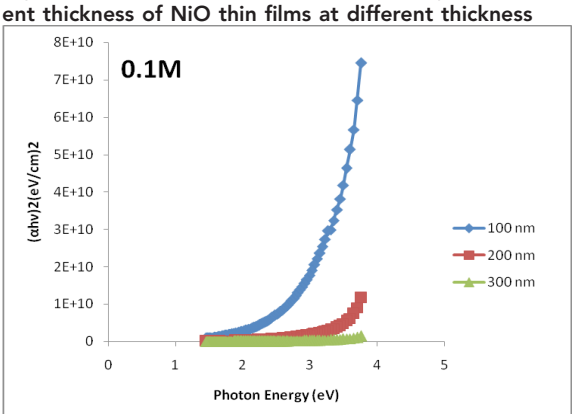
Fig(4) the relation between transmittance and wavelength of NiO thin films at different thickness



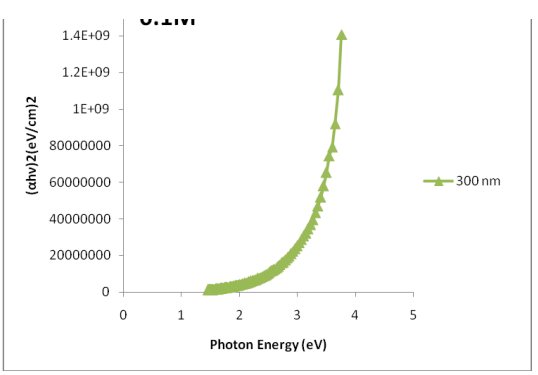
Fig(5) the relation between absorption coefficient and photon energy of NiO thin films at different thickness



Fig(6) absorbance as function of wavelength for different thickness of NiO thin films at different thickness



Fig(7) the reflectance as function of photon energy of NiO thin films at different thickness.



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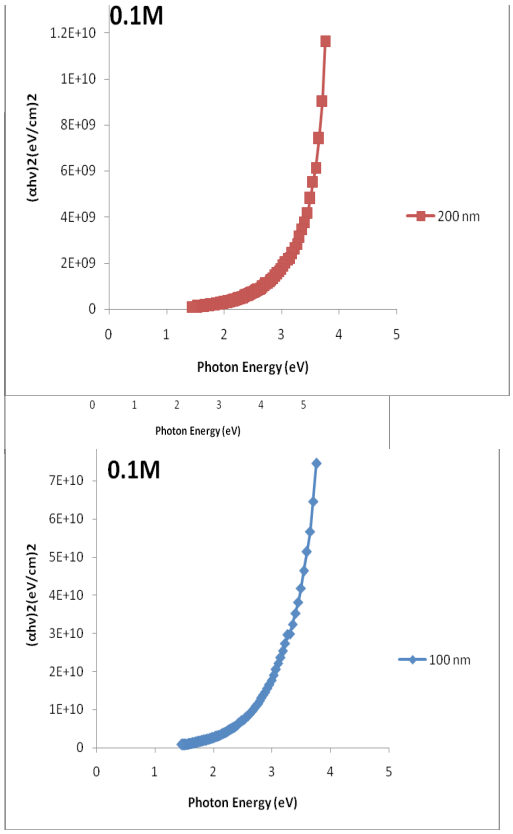
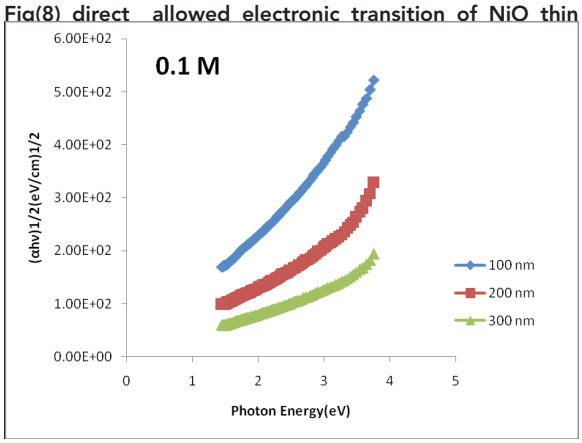
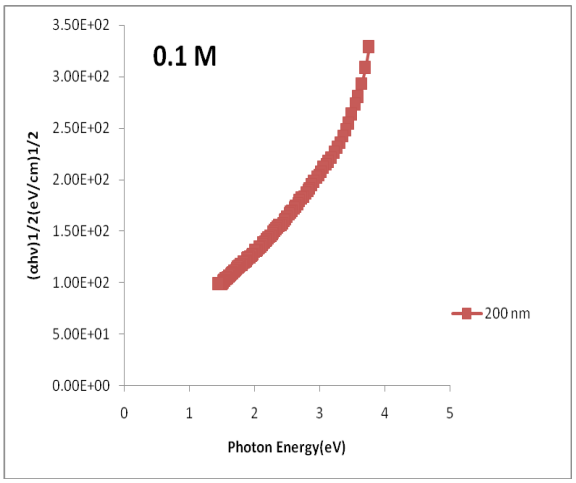
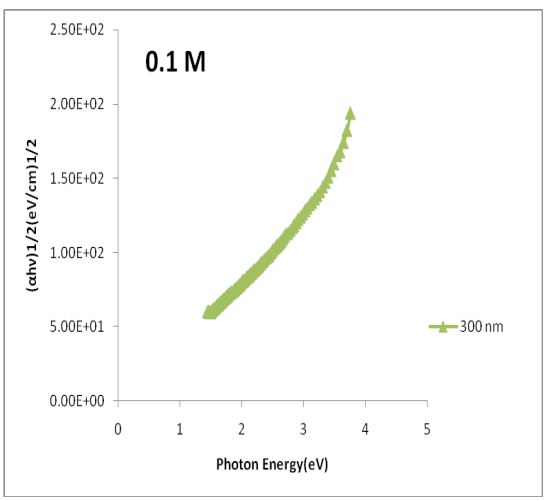


Fig(8) direct allowed electronic transition of NiO thin







Fig(9) indirect allowed electronic transition of NiO thin films at different thickness .

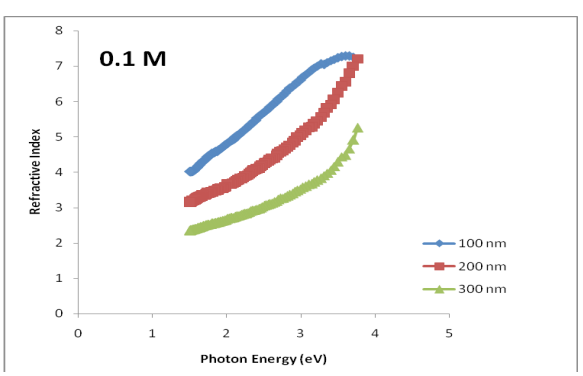


fig.(10) refractive index as function of photon energy of NiO thin films at different thickness.

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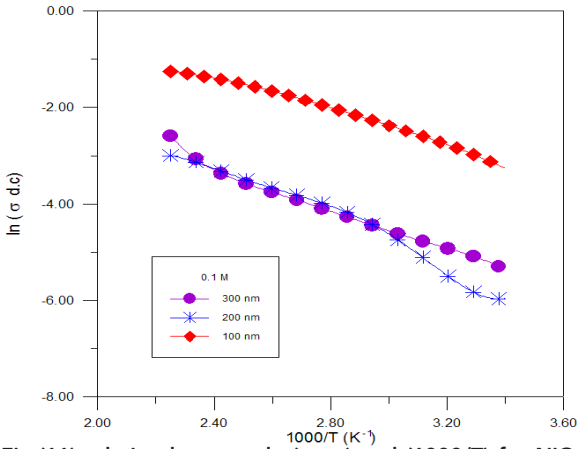

Fig.(11) relation between ln ($\sigma_{d.c}$) and (1000/T) for NiO thin films for deferent thickness.

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