Composition and Optical Dispersion Characterization of Nanoparticles ZnO-NiO Thin Films: Effect of Annealing Temperature

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ABSTRACT

Thin films of $ZnO_{0.7}NiO_{0.3}$ have deposited on glass substrates at room temperature by using thermal evaporation technique under vacuum 10^{-5} mbar. The optical properties and dispersion parameters of the films have been studied. Changes in direct optical energy band gap of films were confirmed before and after annealing. The optical energy gap E_g decreased from 3.11 to 2.86 eV with increasing of annealing temperature to 200 ºC. Some of the optical absorption parameters, such as optical dispersion energies E_o and E_d, Urbach tails E_U , dielectric constant ε, the average values of oscillator strength S_o, and wavelength of single oscillator λ_o have been reported. An increase in the annealing temperature causes an increase in the average oscillator strength from 62.02 to 87.71 eV.

Keywords: TCOs; Dispersion parameters; Thermal evaporation; Zinc Oxide; Nickel Oxide

1. INTRODUCTION

As a II-VI compound semiconductor, zinc oxide (ZnO) is a wide-gap semiconductor with a direct band gap ≈ 3.37 eV [1]. It has a large exciton binding energy (60 meV), which makes it promising for highly efficient optoelectronic devices even at room temperature, such as antireflection coatings, laser mirrors and monochromatic filters, as well as optoelectronics, integrated optics, solar power engineering, microelectronics and optical sensor technology depending on the reflectance and transmittance properties of the films during their preparation [2, 35].

To obtain high quality ZnO thin film, a variety of techniques have been used to prepare ZnO thin films including pulsed laser deposition [3, 4], molecular-beam epitaxy [5], DC magnetron sputtering [6, 7], vacuum evaporation [8], chemical-vapor deposition [9], successive ionic layer adsorption and reaction SILAR [10], chemical spray pyrolysis techniques [11, 12] and sol–gel techniques [13].

Snow is one of the versatile and technologically important semiconductor materials because of its typical properties such as transparency in the visible range, high electrochemical stability, absence of toxicity, abundance in nature etc. [14]. NiO on the other hand is a transition metal oxide that has several potential applications, such as solar thermal absorber, electrodes for battery and photoelectron-catalysts [15]. NiO thin films are promising

materials with excellent electrochromic properties. Another important application of Nickel oxide films includes preparation of alkaline batteries (as cathode material), antiferomagnetic layers and P-type transparent conducting films [16]. The appealing electronic properties of NiO such as large band-gap energy of ($\approx$ 4.00) EV, and high thermal stability, make it a favorable material for electronic device applications [17].

For instance, work has been done on the composition and optical characterization of ZnO-NiO multilayer thin films using chemical bath deposition method [18], microstructure, electrical and optical properties of ZnO-NiO-SiO$_2$ nanocomposite synthesized by Sol-Gel Technique [19]. Other work carried out in this area includes synthesis and characterization of ZnO-NiO composite nano particles by solution method [20]. While in this paper the influence of annealing temperature on the optical dispersion parameters of ZnO NiO thin films prepared by thermal evaporation technique were characterized.

2. EXPERIMENTAL DETAILS

ZnO doped NiO thin films were prepared by thermal evaporation technique onto glass substrates under vacuum 10^{-5} mbar using (Edwared E434) coating system. The (ZnO$_{0.7}$NiO$_{0.3}$) compound was synthesized from pure materials is not less than (99.99%) and then weighting each element according to the density (ρZnO = 6.7 g/cm^3) and (ρNiO = 3.24 g/cm^3) by using sensitive electrical balance type (Mettler H35AR), then mixing these two elements. The required weight of ZnO$_{0.7}$NiO$_{0.3}$ powder was put in a boat mounted under the funnel between two electrodes in the vacuum chamber. The substrates were fixed in a spherical holder and placed in position at a height of about 16 cm above the boat. When the system is pumped down to a vacuum of 10^{-5} mbar, an electric current was passed through the boat gradually to prevent breaking the boat, when the boat temperature reached the required temperature the deposition process starts with a constant deposition rate. After these steps the current supply was switched off and the samples were left in the high vacuum for one day, and then the air was admitted to the chamber, and the films were taken out of the coating unit and kept in the vacuum desiccators until the measurements were made. The thickness of films was 220 nm.

The structural properties were determined by X-ray diffraction (XRD) using CuKα radiation of wavelength 1.54 Å, the current was 20 mA, the voltage was 30 kV, and the scanning angle 2θ was varied in the range of (20-50) degree with the speed of 2 cm·min^{-1}. Optical transmittance was recorded with a double beam Shimadzu UV-visible spectrophotometer in the wavelength range 300-1100 nm. In this work the main parameter that controls the properties of the films are the annealing temperatures (100, 150, and 200) ºC. The effect of annealing temperatures on the optical dispersion characterization of nanoparticles ZnO-Ni thin films were examined.

3. RESULTS AND DISCUSSION

The optical properties of ZnO$_{0.7}$NiO$_{0.3}$ thin films by means of optical absorption in the UV to Vis region of (300-1100) nm have been investigated. The absorption coefficient (α) could be calculated by using the following relation [21]:

$$\alpha = \frac{2.303A}{t} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where (A) is the absorption and (t) is the film thickness.

Fig. 1. Shows the dependence of the absorption coefficient (α) on the wavelength. The effect of annealing temperature on the absorption coefficient of the films has been investigated. It can be seen from the figure that the absorption coefficient (α) decreases with the increasing of wavelength. This behavior suggests decreasing in the energy gap with the increasing of annealing temperature. From this figure, the region of higher values of α, that is $\alpha > 10^4$ cm^{-1} correspond to transition between extended state in both valence and conduction bands, while the lower values, that is $\alpha \leq 10^4$ cm^{-1} is the region where absorption present a rough exponential behavior, which could be attributed to the lattice absorption bands correspond to the electronic transitions between the highest filled energy band to the lowest empty band. Similar types of results was reported by Ajuba *et al.* [22].
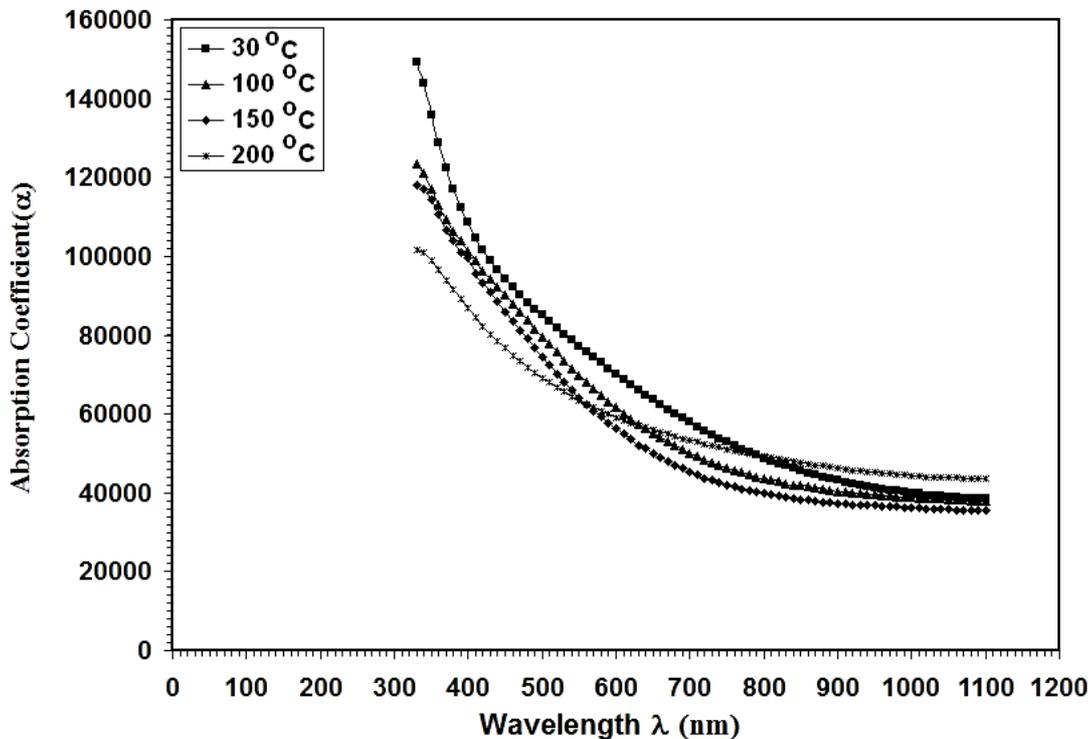
Fig. 1. Absorption coefficient as a function of wavelength for $ZnO_{0.7}NiO_{0.3}$ thin films at different annealing temperatures.

From the transmittance data and according to Tauc [23] relation, $(\alpha h\upsilon)^2$ versus incident photon energy ($h\upsilon$), plots were obtained. The graphs are represented in Figure 2, which shows the direct optical energy gap of $ZnO_{0.7}NiO_{0.3}$ thin films at room temperature and after annealed to different annealing temperature (100, 150, 200) °C. From this figure, we can see that the value of energy gap E_g decreases with increasing of annealing temperature. This is possibly due to the crystal growth and reorganization of the films. Such result was obtained by Lokhande *et al.*, they showed that the energy gap was affected by the thickness of the film and its crystallite size [24].
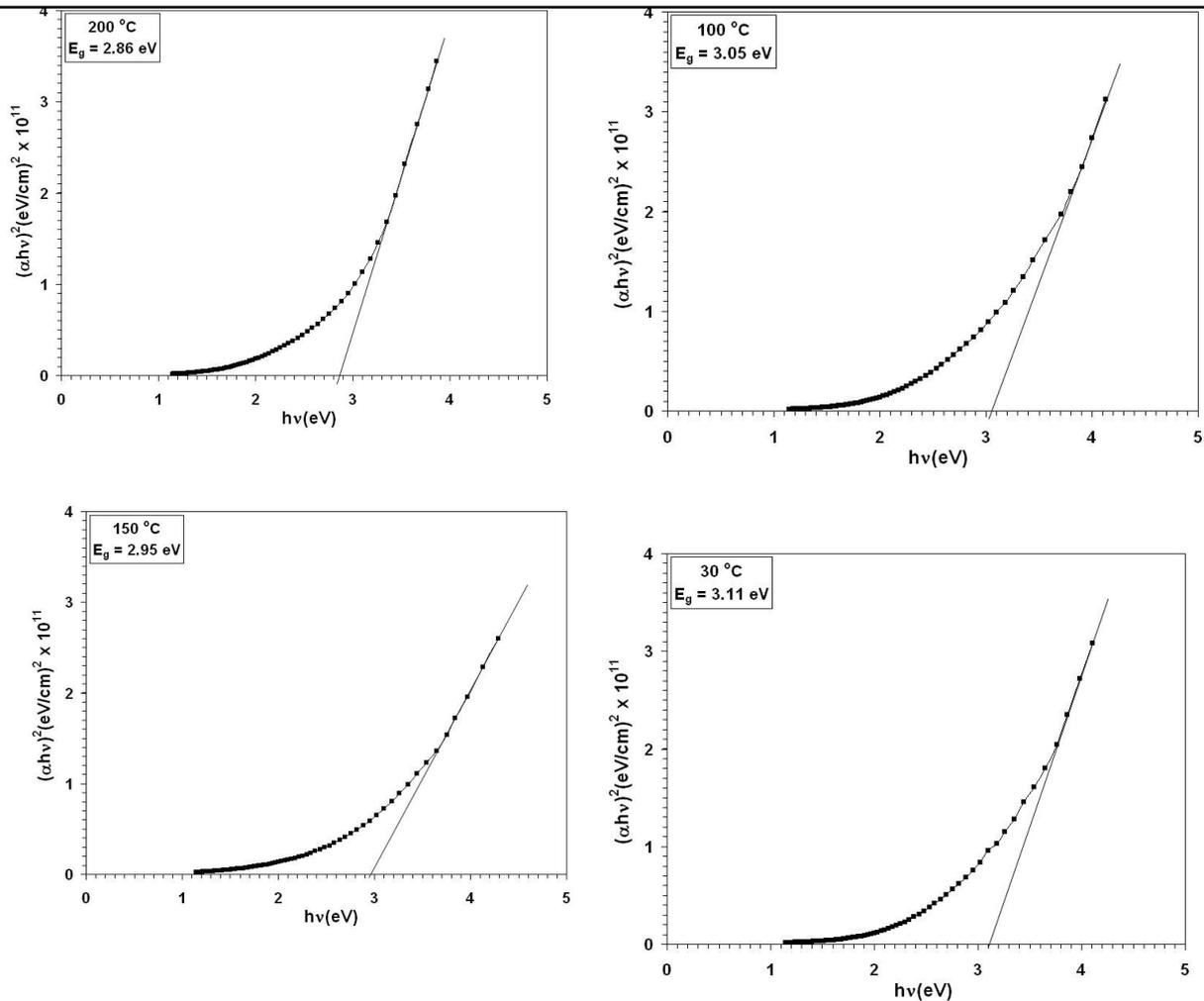
Fig. 2. Variation of $(\alpha h\upsilon)^2$ with photon energy for $ZnO_{0.7}NiO_{0.3}$ thin films.

The incorporation of impurity into the semiconductor often reveals the formation of band tailing in the band gap. The tail of the absorption edge is exponential, indicating the presence of localized states in the energy band gap. The amount of tailing can be predicted to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach [25], which is related directly to a similar exponential tail for the density of states [26].

The absorption edge gives a measure of the energy band gap and the exponential dependence of the absorption coefficient, in the exponential edge region Urbach rule is expressed as [27, 28]:

$$\alpha = \alpha_o \exp(h\upsilon / E_U) \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where α_o is a constant, E_U is the Urbach energy, which characterizes the slope of the exponential edge. Figure 3, shows Urbach plots of the films. The value of E_U was obtained from the inverse of the slope of $\ln\alpha$ vs. $h\upsilon$ and is given in Table 1. The dopants change the width of the localized states in the optical band.

E_U values change inversely with the optical band gap. The Urbach energy values of the films were calculated to be increased from 641 to 775 me as increasing annealing temperature to 200 ℃.

The increase in E_U is attributed to the increase of disorder of the material occurred by doping. This increase leads to a redistribution of the states, from band to tail, thus allows for a greater number of possible bands to tail and tail to tail transitions [29]. As a result, both a decrease in the optical gap and a broadening of the Urbach tail have taken place.
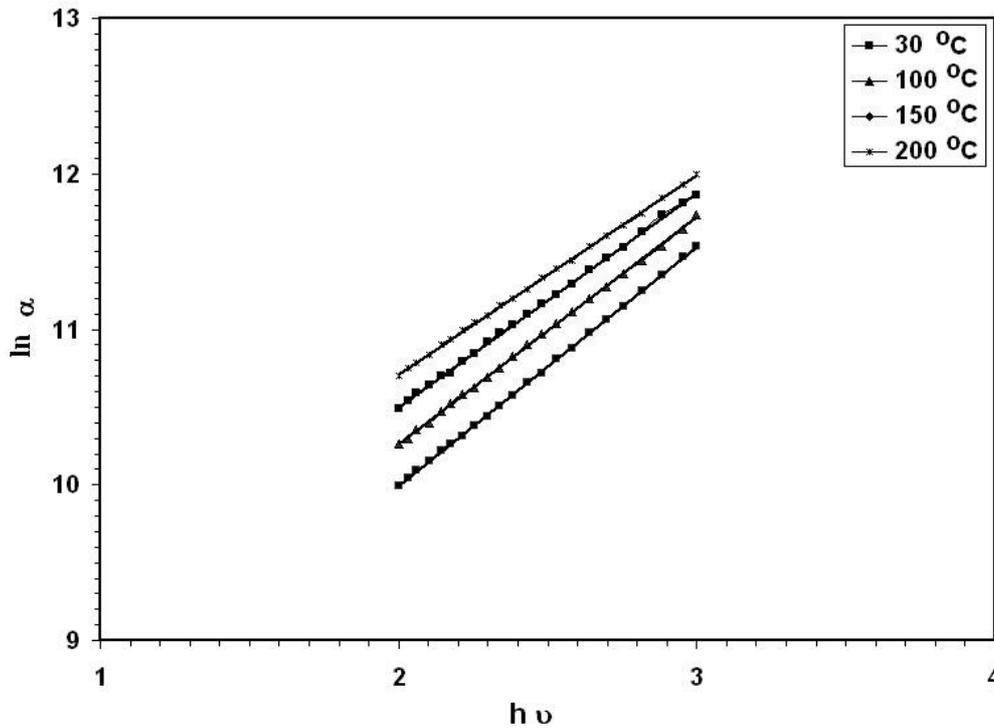

Fig. 3. lnα versus photon energy for $ZnO_{0.7}NiO_{0.3}$ thin films.

The dispersion energy plays an important role in the research for optical materials because it is a significant factor in optical communication and in designing devices for spectral dispersion. The dispersion of refractive index in $ZnO_{0.7}NiO_{0.3}$ films was analyzed using the concept of the single oscillator and can be expressed by Wemple and Di-Domenico relationship [30]:

$$n^2 - 1 = [E_d E_o / E_o^2 - E^2] \quad \ldots\ldots\ldots (3)$$

The physical meaning of the single-oscillator energy E_o is that it simulates all the electronic excitation involved and E_d is the dispersion energy related to the average strength of the optical transitions [31]. The parameter E_d, which is the measure of the intensity of the inter band optical transition, does not depend significantly on the band gap. A plot of $(n^2-1)^{-1}$ versus $(h\upsilon)^2$ of $ZnO_{0.7}NiO_{0.3}$ deposited films for different annealing temperatures as shown in Figure 4.

It is clear that, the effect of annealing temperature on the refractive index and semiconductor dispersion profiles were exhibited a linear displacement in the shape of the

dispersion profile with a decreasing refractive index. The refractive index declines towards long wavelengths. This is due to the influence of lattice absorption.

The values of E_d and E_o were obtained from the slope, $(E_oE_d)^{-1}$ and intercept (E_o/E_d), on the vertical axis and are given in Table 1. The values of E_o was found to be decreased with increasing of annealing temperature, while the values of E_d increased. This could be attributed to the increase in the number of scattering center due to the dissolving of iridium atoms in the film matrix.

According to the single-oscillator model, the single oscillator parameters E_o and E_d are related to the imaginary part of the complex dielectric constant ε_2, the moments of the imaginary part of the optical spectrum M_{-1} and M_{-3} moments can be derived from the following relations [32,33]:

$$E_o{}^2 = M_{-1} / M_{-3} \quad \ldots\ldots\ldots (4)$$

$$E_d{}^2 = M^3{}_{-1} / M_{-3} \quad \ldots\ldots\ldots (5)$$

The oscillator energy E_o, which was independent of the scale of ε_2 is consequently an average energy gap, whereas E_d depends on the scale of ε_2 and thus serves as an interband strength parameter.

The obtained M_{-1} and M_{-3} moments changes with dopants. The values obtained for the dispersion parameters E_o, E_d, M_{-1} and M_{-3} are listed in Table 1.
For the definition of the dependence of the refractive index n on the light wavelength (λ), the single-term Sellmeier relation can be used [34]:

$$n^2(\lambda) - 1 = S_o.\lambda_o{}^2 / 1 - (\lambda_o/\lambda)^2 \quad \ldots\ldots\ldots (6)$$

Where λ_o is the average oscillator position and S_o is the average oscillator strength. The parameters S_o and λ_o in Eq. (6) can be obtained experimentally by plotting $(n^2 - 1)^{-1}$ against λ^{-2} as shown in Fig. 5, the slope of the resulting straight line gives $1/S_o$, and the infinite-wavelength intercept gives $1/S_o\lambda_o{}^2$.

The results show a decrease in the band gap which may be attributed to the presence of crystal defects, that increase the density of localized states and cause a widening in the Urbach tail and consequently decrease the energy gap.

Table 1. The optical parameters.

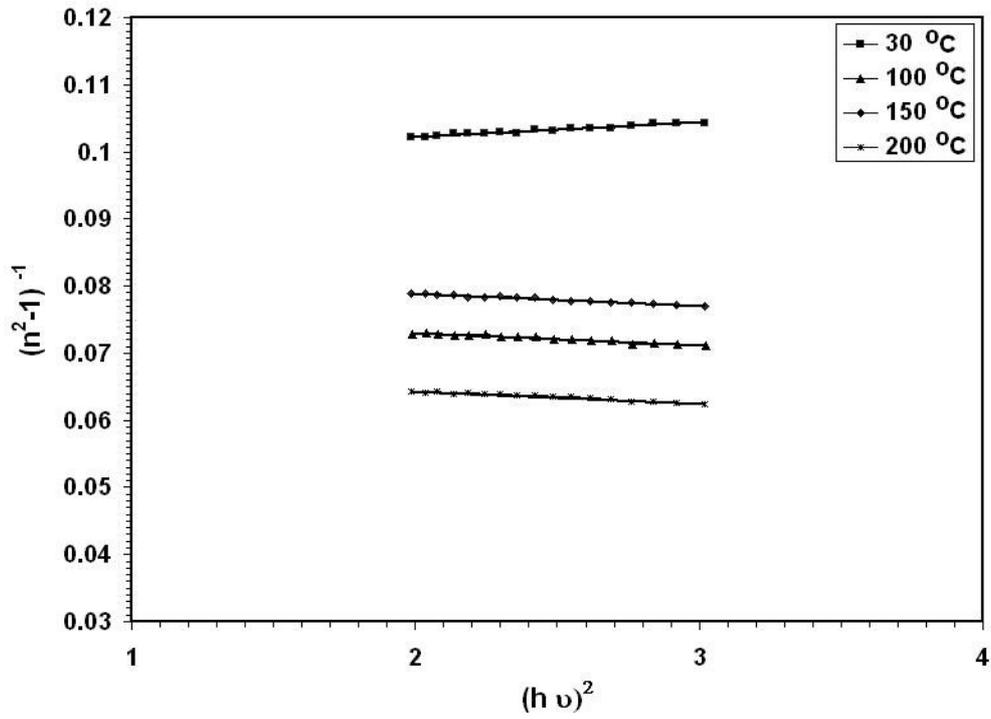| Ta °C	E_o (eV)	E_d (eV)	E_g (eV)	E_u meV	ε_∞	n(o)	M_{-1}	M_{-3} eV^{-2}	$S_o \times 10^{13}$ m^{-2}	λ_o nm
30	6.20	62.02	3.10	641	11.00	3.32	10.00	0.26	9.32	391
100	6.03	75.38	3.02	680	13.50	3.67	12.50	0.34	9.29	423
150	5.98	79.68	2.99	724	14.30	3.79	13.30	0.37	8.57	452
200	5.70	87.71	2.85	775	16.00	4.05	15.38	0.47	6.94	526

Fig. 4. Variation in $(n^2 - 1)^{-1}$ as a function of $(h\upsilon)^2$ for ZnO/NiO thin films.
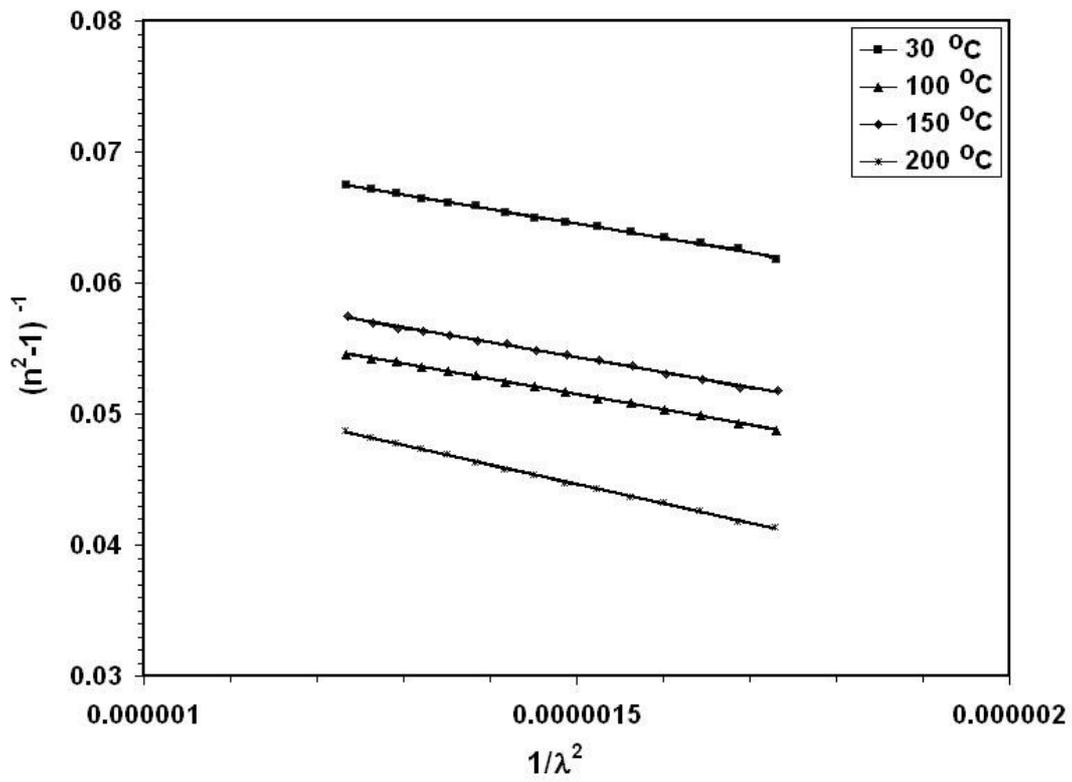

Fig. 5. Variation in $(n^2 - 1)^{-1}$ as a function of $(\lambda)^{-2}$ for ZnO/NiO thin films.

4. CONCLUSION

$ZnO_{0.7}NiO_{0.3}$ thin films were prepared by using thermal evaporation technique. The refractive index of the prepared films depends on the annealing temperature. The optical band gap decreased due to increasing annealing temperature. The single–oscillator parameters were determined. It was shown that the dispersion parameters of the films obeyed the single oscillator model, the change in dispersion was investigated and its value decreased from 6.20 to 5.70 eV for films with increasing annealing temperature to 200 ºC.

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