

## Annealing Effects on Band Tail Width, Urbach Energy and Optical Parameters of Fe<sub>2</sub>O<sub>3</sub>:Ni Thin Films Prepared by Chemical Spray Pyrolysis Technique

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### ABSTRACT

*In this research, nickel doped Iron oxide (Fe<sub>2</sub>O<sub>3</sub>:Ni) thin films were deposited onto glass substrates by using chemical spray pyrolysis (CSP) technique. The deposited films thickness was found to be about 350±30 nm. The films were annealed at two different temperatures (450 °C and 500°C). The X-ray Diffraction spectra (XRD) results indicate that the structure of the three prepared thin films was polycrystalline in nature and has a hexagonal phase with preferred orientation along (104) plane. Temperature annealing effects on the optical properties of the deposited films was studied. It was found that, the optical parameters, such as the refractive index (n), the real (ε<sub>1</sub>) and imaginary (ε<sub>2</sub>) parts of dielectric constant which related to n, Urbach energy and the energy gap; all depend on the annealing temperature. The results show that there was a reduction in the optical absorbance as well as the dielectric constants. The dispersion parameters decreased with the increasing annealing temperature while the determined Urbach energy was increased. The optical energy gap decreased from 2.74 to 2.67 eV with the increasing annealing temperature, on the account that there is an inverse relation between Urbach energy and energy gap.*

**Keywords:** Fe<sub>2</sub>O<sub>3</sub>:Ni, Structural Properties, Optical Properties, Dispersion Parameters, Urbach Energy, Chemical Spray Pyrolysis.

### 1. INTRODUCTION

Hematite (α-Fe<sub>2</sub>O<sub>3</sub>) is a material with a band gap of about 2-2.2eV allowing the absorption of ~40% solar energy via its visible area. Due to this factor, Fe<sub>2</sub>O<sub>3</sub> is considered as a promising material for solar energy application. Fe<sub>2</sub>O<sub>3</sub> is low cost due to its abundance in nature and it also behave as corrosion-resistant in acidic and alkaline media [1]. This metal oxide has found its way for many other applications according to its dielectric properties and its breakthrough having at once high thermopower [2-7].

However, some major efforts have been done in the fabrication of a Fe<sub>2</sub>O<sub>3</sub> photoanode as well as electrocatalyst, such as low electrical conductivity of the material itself and the necessity of having less than 5 nm particle synthesis as to prevent electron-hole recombination related to the extremely short diffusion distance of holes, among others [8]. By impurity doping, its resistivity can be lowered and considerations of the diffusion length of minority carriers have indicated that p-type Fe<sub>2</sub>O<sub>3</sub> could be a better photoanode [9]. Many researchers have been using different techniques for depositing Fe<sub>2</sub>O<sub>3</sub> such as; colloidal chemistry method [10], sol-gel [11],

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usual ceramic technique [12], spray pyrolytic method [13-14], spin coating solution deposition [15], sputtering [16], pulsed laser deposition [17], and molecular beam epitaxy [18]. Different physical parameters have been studied for this metal oxide material such as the optical and structural parameters.

From the literature, and to our best knowledge, there is no study about the effects of annealing temperature on the optical parameters such as the dispersion parameters and Urbach energy of Fe<sub>2</sub>O<sub>3</sub>:Ni thin films prepared by utilizing the chemical spray pyrolysis (CSP) technique. In this work, we investigate the effects of annealing temperatures (400, and 500°C) on the optical parameters of the deposited Fe<sub>2</sub>O<sub>3</sub>:Ni thin films by using the chemical spray pyrolysis (CSP) technique.

## 2. RESERCH METHODOLOGY

Ni-doped Fe<sub>2</sub>O<sub>3</sub> thin films was prepared using CSP technique. A homemade glass atomizer was used to spray the solution. The films were deposited onto cleaned glass slides substrates heated to 400°C. The initial solution was including a 0.1M of FeCl<sub>3</sub> (Somatco Supplies Chemicals, India) and 0.1M of NiCl<sub>2</sub> (Spectrum Chemicals, India) diluted with redistilled water to obtain an aqueous solution. Few drops of HCl were added in order to obtain a clear solution during the deposition. The volumetric concentration of Ni content was 3%. The optimum conditions was achived at the following condition: spraying rate was about 4 ml/min, spraying time was 7 seconds lasted by (1.5 minutes) to avoid any excessive cooling, the air carrier gas (at a pressure of 10<sup>5</sup> Pascals), and the distance between the nozzle and the substrate was about 28±1 cm.

Film thickness was measured by gravemetric method and it was found that the thickness was in the range of 350±30 nm. The prepared films were annealed at different temperatures (450 and 500°C). The optical transmittance and absorbance spectra were recorded in the wavelength range of 380-900 nm by using double beam UV-Visible spectrophotometer (Shimadzu UV probe 1650, Japan).

The average crystallite size (D) of the hematite films was determined by using Scherrer formula [19].

$$D = \frac{K\lambda}{B \cos \theta} \quad (1)$$

where B is the FWHM (in radians) of X-ray Diffraction spectra (XRD) intensity,  $\lambda$  is the X-ray wavelength (Cu K $\alpha$  =0.154 nm),  $\theta$  is the Bragg diffraction angle, and K is the shape factor which is taken as 0.9.

To determine the total defects in the films, the dislocation density ( $\delta$ ) was calculated using the relation [19]:

$$\delta = \frac{1}{D^2} \quad (2)$$

The micro strain ( $\varepsilon$ ) of the deposited film on the substrate was calculated using the relation [19]:

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

The real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) parts of dielectric constant are related to the refractive index (n) and extinction coefficient (K) values. The  $\epsilon_1$  and  $\epsilon_2$  values were calculated using the formulas in (4) and (5) [20]:

$$\epsilon_1 = n^2 - K^2 \quad (4)$$

$$\epsilon_2 = 2nK \quad (5)$$

The amplitude of the electromagnetic wave reduced by a factor of  $e$  after passing through a known thickness called a skin depth (x) which can be calculated by the following relation [21]:

$$x = \frac{\lambda}{2\pi k} \quad (6)$$

In the exponential edge region, the Urbach rule is expressed as [22]:

$$A = \alpha_0 \exp (hu/E_U) \quad (7)$$

where  $\alpha_0$  is a constant,  $E_U$  is the Urbach energy that characterizes the slope of the exponential edge, and  $hu$  is the photon energy.

In order to estimate the refractive index dispersion of the films, the single-oscillator model developed by DiDomenico and Wemple [23] was used. In terms of the dispersion energy ( $E_d$ ) and single-oscillator energy ( $E_o$ ), the single-oscillator model for the refractive index dispersion is expressed as follows [23]:

$$n^2 - 1 = \frac{E_o E_d}{E_o^2 - E^2} \quad (8)$$

where  $E_d$  and  $E_o$  are single oscillator parameters.  $E_o$  is the single oscillator energy while  $E_d$  is the so-called dispersion energy which measures the average strength of interband optical transitions, and  $E$  is the photon energy ( $hu$ ).

The oscillator energy ( $E_o$ ) is an average of the optical band gap ( $E_g$ ) [24] and can be obtained by an empirical formula to the optical band gap value:

$$E_o = 2E_g \quad [25]. \quad (9)$$

The static refractive index,  $n(0)$  was evaluated from the equation ( $n(0) = 1 + E_d/E_o$ ) and the value of the static dielectric constant ( $\epsilon_\infty = n^2(0)$ ) was calculated. The dispersion data of refractive index can be estimated according to the following relation [26]:

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1 - (\lambda_o/\lambda)^2} \quad (10)$$

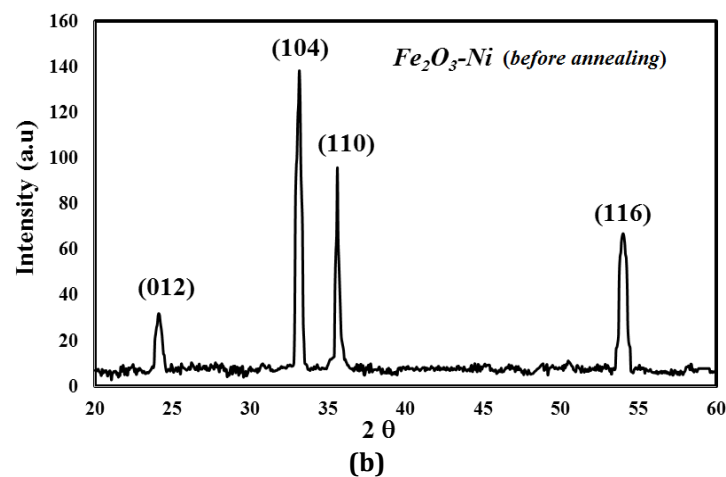
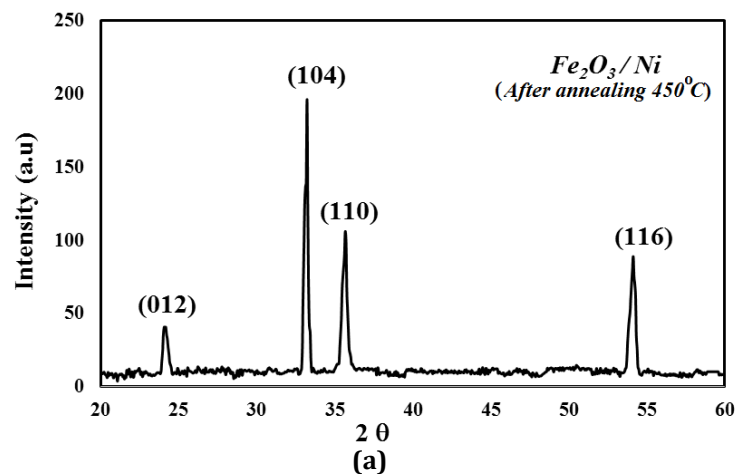
Thus, the determination of the moments ( $M_{-1}$  and  $M_{-3}$ ) of the  $\epsilon_i$  spectrum is very important for the optical applications.  $M_{-1}$  and  $M_{-3}$  can be obtained from the following relations [27]:

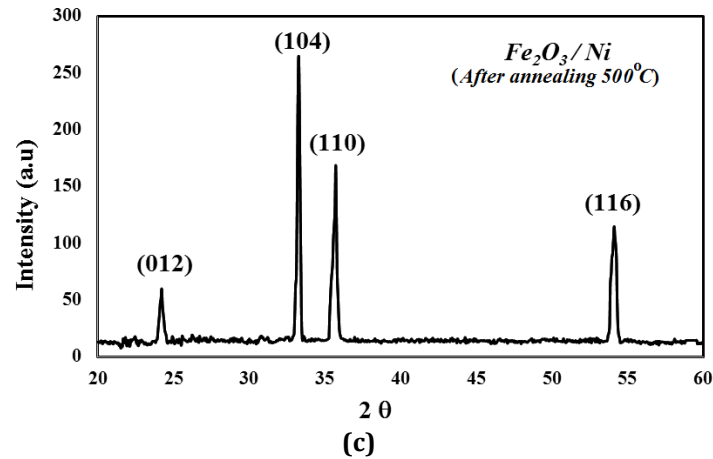
$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad (11)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (12)$$

### 3. RESULTS AND DISCUSSIONS

Figure 1 shows three XRD diffraction patterns of the deposited  $\text{Fe}_2\text{O}_3\text{:Ni}$  thin films on glass substrates. Figure 1(a) shows the XRD diffraction patterns after annealing with  $450^\circ\text{C}$ , Figure 1(b) is the pattern for before annealing and Figure 1(c) is the pattern obtained after annealing with  $500^\circ\text{C}$ . with  $2\theta$  peak referred to (012), (104), (110) and (116) direction respectively. By comparing the  $2\theta$  peak direction to the International Center for Diffraction Data (ICDD), it is clear that the preferred orientation for the three films is in the (104) direction indicating that the films has a hexagonal phase. These results were in good agreement with the results reported by Ubale and Belkhedkar [19]. The figures show that for the three deposited films; the strong peak value corresponds to (104) direction located at  $2\theta=33.175$ ,  $33.225$  and  $33.275$  with full width at half maximum intensity (FWHM) of 0.45, 0.30 and 0.25 respectively, while the (012, 110 and 116) peaks values are lower intensity than the (104) peak. The figures also show that as the annealing temperature increases while the FWHM decreases, the diffraction peaks become sharper and their intensity is enhanced; this indicates that the film structure improved as the annealing temperature increased.





**Figure 1.** XRD patterns of Fe<sub>2</sub>O<sub>3</sub>:Ni thin films (a) after annealing at 450°C, before annealing and after annealing at 500°C.

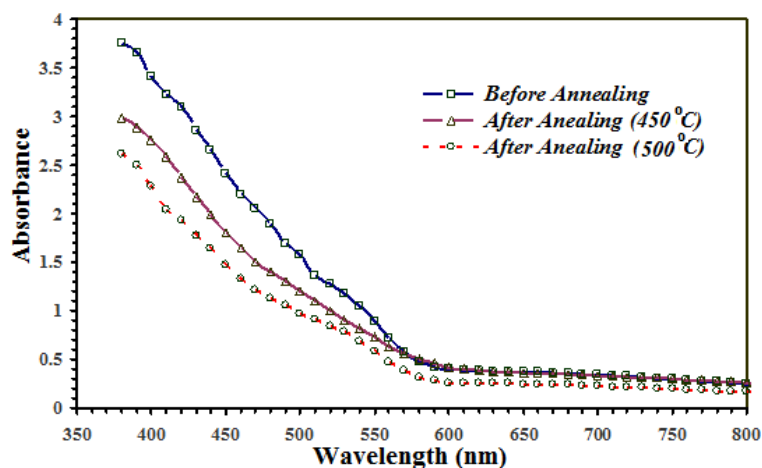
By using Scherrer formula (Equation1), the value from the prominent peak (104) increased as the annealing temperature increases indicating that the crystalline quality of the film is improved. It is found that for the smaller crystallite size, the dislocation density is higher and it decreases as crystallite size increases. It is very natural that, when the crystallite size increases and the grain boundaries density decreases; this means that the crystallinity of the thin films is improved.

The micro strain provides the information about the defects present around the lattice. The variation of crystallite size, dislocation density and micro strain values for Fe<sub>2</sub>O<sub>3</sub>:Ni films deposited before and after annealing at 450 and 500°C are listed in Table 1.

**Table 1** X-ray diffraction data summary for the preferential orientation (104) direction for Fe<sub>2</sub>O<sub>3</sub>:Ni thin films before and after annealing at 450 and 500°C

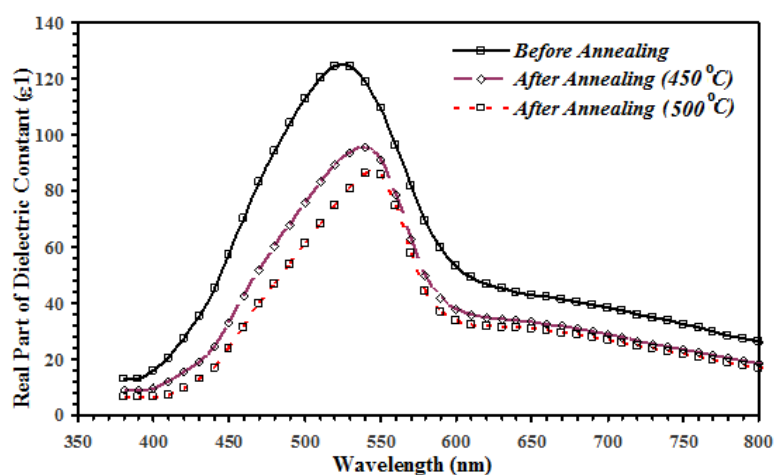
Fe <sub>2</sub> O <sub>3</sub> /Ni	2θ (°)	Peak intensity	FWHM (°)	Crystallite Size (nm)	Dislocation density (δ) (10 <sup>-4</sup> nm <sup>-1</sup> )	Micro Strain (ε) × 10 <sup>-2</sup>
Before annealing	33.175	138.513	0.450	18.225	30.106	10.780
Annealing (450°C)	33.225	198.273	0.300	27.340	13.378	7.186
Annealing (500°C)	33.275	264.712	0.250	32.811	0.928	5.988

The absorption spectra of the three deposited Fe<sub>2</sub>O<sub>3</sub>:Ni thin films before and after annealing with 450 and 500°C are shown in Figure 2. From the figure, it can be seen that the absorbance decreases with wavelength and has relatively low values in the visible (after 550 nm) and IR regions of the spectrum. The result indicates that there is a very small amount optical absorption in the visible region compared to the UV region, hence the film has a potential application in the fabrication of solar cell and UV photodetector. The results show that the absorbance increases as the annealing temperature decreases.

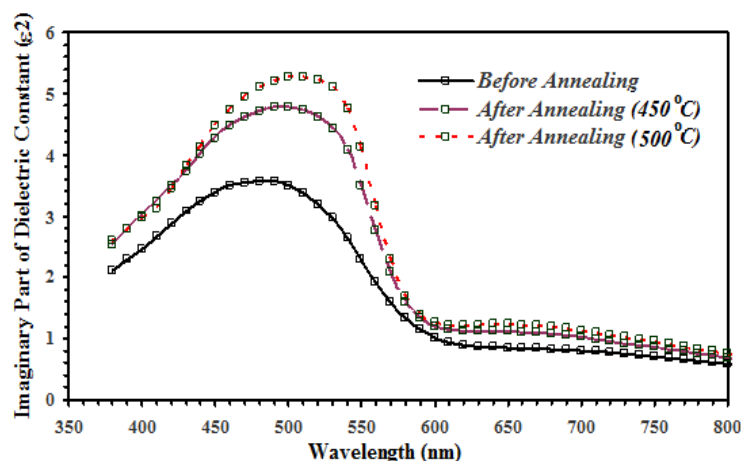


**Figure 2.** Absorbance spectra of Fe<sub>2</sub>O<sub>3</sub>:Ni thin films before and after annealing at 450 and 500°C.

The  $\epsilon_1$  and  $\epsilon_2$  values, dependence of wavelength are respectively shown in Figures 3 and 4. From the two figures, notice that the  $\epsilon_1$  values are higher than that of  $\epsilon_2$  values. The  $\epsilon_1$  and  $\epsilon_2$  values decrease with the increasing of annealing temperatures. The decrease in refractive index could be attributed to the increase of homogeneity of Fe<sub>2</sub>O<sub>3</sub>:Ni films with annealing temperature.

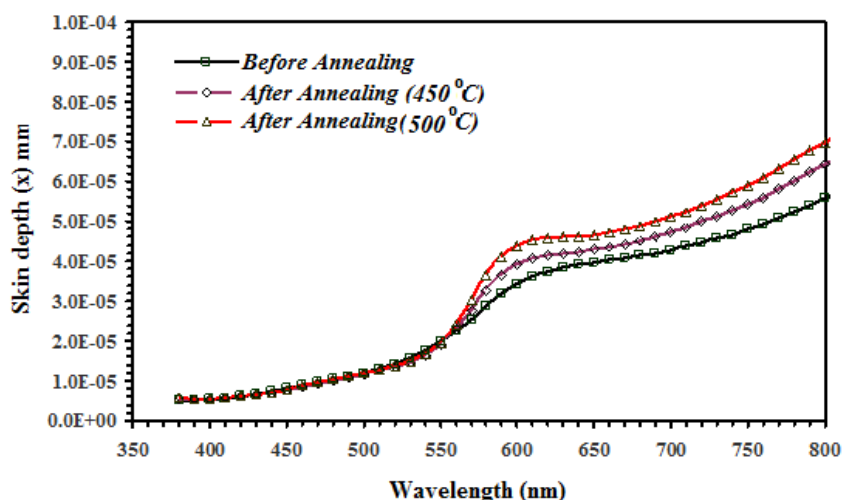


**Figure 3.** Plot of the real part of the dielectric constant for Fe<sub>2</sub>O<sub>3</sub>:Ni thin films before and after annealing at 450 and 500°C.



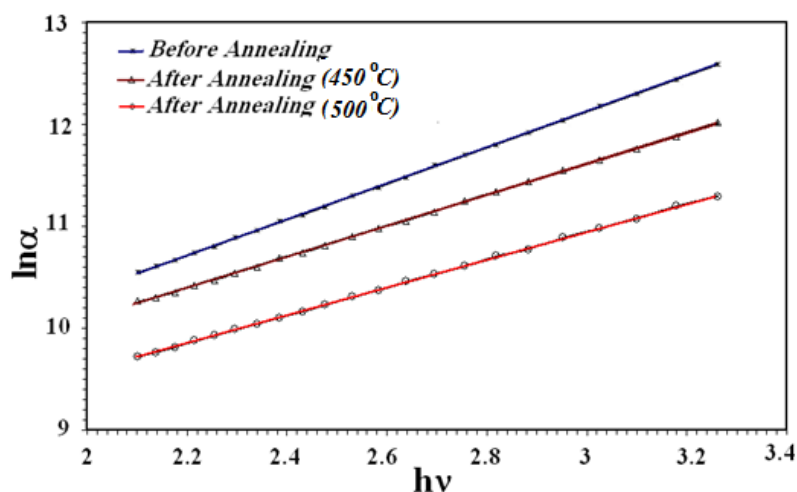
**Figure 4.** Plot of the imaginary part of the dielectric constant for Fe<sub>2</sub>O<sub>3</sub>:Ni thin films before and after annealing at 450 and 500°C.

The skin depth can take the value of one hundred to several thousands angstrom depending on the characteristics of the material. Figure 5 shows the variation of skin depth versus wavelength. It can be seen that; at shorter wavelengths there is no change in their values before and after annealing. This might be due to the absorption of equal probability in this region, but after wavelength,  $\lambda$  (cut off) ( $\sim 520\text{nm}$ ) the skin depth values became larger as the annealing temperature increases.



**Figure 5.** Plot of skin depth for  $\text{Fe}_2\text{O}_3:\text{Ni}$  thin films before and after annealing at 450 and 500°C.

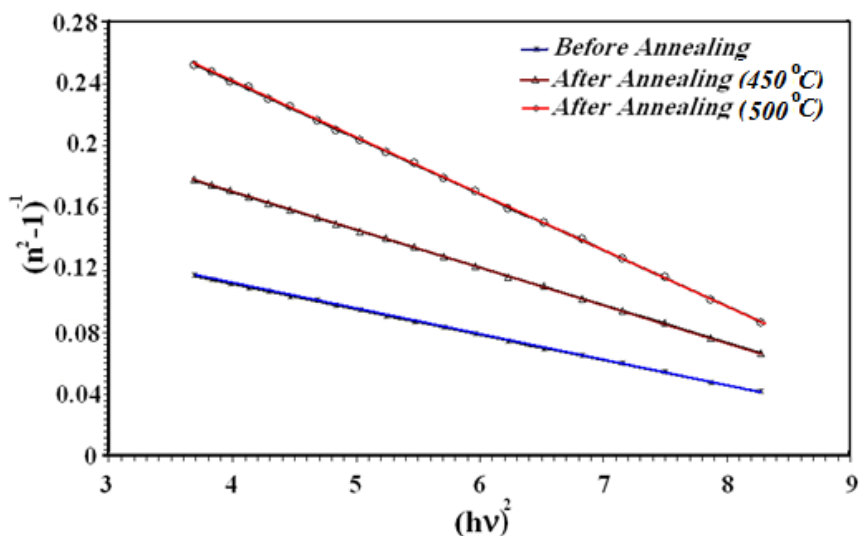
Equation (7) describes the optical transition between occupied states in the valence band tail to the unoccupied states of the conduction band edge. The value of  $E_U$  was obtained from the reciprocal of the slope of  $\ln\alpha$  vs.  $h\nu$  as shown in Figure 6 and listed in Table 2. It can be seen that there is an inverse relation between energy gap and Urbach energy. The decrease in the optical energy gap is attributed to the increase of disorder of the material due to doping[28].



**Figure 6.**  $\ln(\alpha)$  vs ( $h\nu$ ) for  $\text{Fe}_2\text{O}_3:\text{Ni}$  thin films before and after annealing at 450 and 500°C.

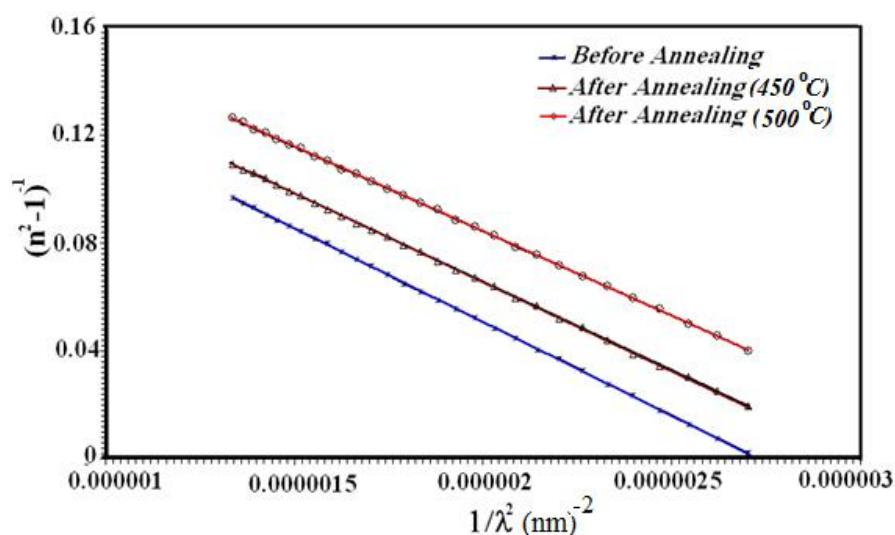
From Equation (8) and by plotting  $(n^2-1)^{-1}$  vs.  $(h\nu)^2$  as illustrated in Figure 7;  $E_o$  and  $E_d$  values were determined from the slope  $(E_oE_d)^{-1}$  and intercept  $(E_o/E_d)$  on the vertical axis respectively and their values were calculated from the plot of  $(n^2-1)^{-1}$  vs.  $(1/\lambda^2)$  as shown in Figure 8.

Table 2 summarizes the values of  $E_o$ ,  $E_d$ ,  $n(0)$ ,  $\epsilon_\infty$ ,  $S_o$  and  $\lambda_o$  for the as-deposited and annealed  $\text{Fe}_2\text{O}_3:\text{Ni}$  thin films.



**Figure 7.**  $(n^2-1)^{-1}$  versus  $(h\nu)^2$  for  $\text{Fe}_2\text{O}_3:\text{Ni}$  thin films before and after annealing at 450 and 500°C.

The single-oscillator parameters  $E_0$  and  $E_d$  is related to the imaginary of  $\epsilon_i$  of the complex dielectric constant. The  $\epsilon_i$  parameter includes the desired response information about the electronic and optical properties of the used material. It was found that their values decrease as the annealing temperature increases as shown in Table 2. This might be due to the dependence of these moment on the complex dielectric constant[29].



**Figure 8.**  $(n^2-1)^{-1}$  versus  $(1/\lambda^2)$  for  $\text{Fe}_2\text{O}_3:\text{Ni}$  thin films before and after annealing at 450 and 500°C.

**Table 2** The optical parameters of  $\text{Fe}_2\text{O}_3:\text{Ni}$  thin films for different annealing temperatures

Sample	$E_d$ (eV)	$E_0$ (eV)	$E_g$ (eV)	$\epsilon_\infty$	$n(o)$	$M_{-1}$	$M_{-3}$ (eV <sup>-2</sup> )	$S_0 \times 10^{13}$ (m <sup>-2</sup> )	$\lambda_0$ (nm)	$U_E$ (meV)
Before annealing	43.8	5.70	2.85	8.69	2.94	7.69	0.236	2.89	588	451
After annealing (450 °C)	30.0	5.48	2.74	6.55	2.56	5.55	0.185	3.08	519	523



After annealing (500 °C)	20.5	5.34	2.67	4.84	2.20	3.84	0.134	3.20	472	595
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#### 4. CONCLUSION

Fe<sub>2</sub>O<sub>3</sub>:Ni thin films have been deposited by spray pyrolysis technique on glass substrate with 3% doping of Ni. XRD pattern reveals that all the deposited films were polycrystalline with a preferred orientation along (104) plane. It was found that the optical absorbance decreased as well as the dielectric constants and dispersion parameters such as E<sub>d</sub>, E<sub>o</sub>, ε<sub>∞</sub>, n(0), λ<sub>o</sub>, M<sub>-1</sub>, and M<sub>3</sub> decreased with increasing annealing temperature in contrary with the values of S<sub>o</sub>. The determined Urbach energy increased and the energy gap decreased from 2.74 to 2.67 eV with the increasing of annealing temperature.

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