

Fe₂O₃ thin Films prepared by Spray Pyrolysis Technique and Study the Annealing on its Optical Properties

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ABSTRACT

Fe₂O₃ thin films that doped by NiO were obtained on glass substrates by the chemical spray pyrolysis technique, and annealed at 450 °C and 500 °C. The effect of annealing on optical properties was studied by recording the absorbance spectra using UV-Visible spectrophotometer. The refractive index decreases with increasing annealing temperature, such as an optical band gap that decreases from 2.68 eV before annealing to 2.58 eV after annealing of 500 °C. Absorption coefficient and extinction coefficient increase with increasing annealing temperature.

Keywords: Fe₂O₃ thin film; Annealing; optical properties; Energy gap

1. INTRODUCTION

Iron oxide (Fe₂O₃) has been of considerable interest in its use as a photoelectrode because of small band gap of about 2.1 eV, low cost, and good stability in aqueous solution, but the reported photocurrent quantum efficiency of Fe₂O₃ is relatively low. Also the recombination of electrons and holes on account of low mobilities of holes and trapping of electrons by oxygen-deficient iron sites were considered to be responsible for the low conductivities and poor photocurrent efficiencies of Fe₂O₃ [1-5].

The hematite Fe₂O₃ was selected as a prototype due to its technological use as a catalyst [6-7], and photocatalyst [8], drug delivery vehicles [9], solar filters [10], recording media [11], spin valves [12], electrochromic devices [13], lithium-ion batteries [14], photo-electrochemical system for hydrogen generation [15]. However, the best photo response has been reported for hematite prepared by spray pyrolysis [16-17]. The electrochromic devices are made of amorphous oxides [18], while crystalline phase plays a major role in catalysts and sensors [19]; this is because the minor change in their chemical composition and crystalline structure could modify different properties of the metal oxides. The Present work is to study the effect of annealing temperature (before annealing, 450 °C, and 500 °C) on optical properties of NiO:Fe₂O₃ thin films that prepared by chemical spray pyrolysis method.

2. EXPERIMENTAL

Thin films of Nickel oxide doped Fe_2O_3 have been prepared by chemical pyrolysis technique. A laboratory designed glass atomizer was used for spraying the aqueous solution, which has an output nozzle about 1 mm. The films were deposited on preheated cleaned glass substrates at a temperature of 400 °C. A 0.1 M for both NiCl_2 (Sigma Aldrich UK) and FeCl_3 (Merck Chemicals Germany) diluted with redistilled water and a few drops of HCl were used to obtain the starting solution for deposition. Moreover, volumetric concentration of NiO 1% was achieved the optimized conditions have been arriving at the following parameters; spray time was 10 s and the spray interval 2 min was kept constant. The carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm^{-2} , and the distance between nozzle and substrate was about $30 \text{ cm} \pm 1 \text{ cm}$.

Thickness of the sample was measured using the weighting method and was found to be around 400 nm. Optical transmittance and absorbance were recorded in the wavelength range of (300-900) nm using UV-Visible spectrophotometer (Shimadzu Company Japan).

3. RESULTS AND DISCUSSIONS

Analysis of optical transmission spectra (T) and the reflectance (R) is one of the most productive tools for understanding the band structure and energy band gap (E_g) of both amorphous and polycrystalline materials. To study the effect of thermal annealing on the optical transmission of $\text{NiO}:\text{Fe}_2\text{O}_3$ thin films, the dependence of the transmittance on the wavelength (λ) in the spectral range of (300-900) nm, was recorded. Fig. 1 and Fig. 2 are representing the relationship between the transmittance and the reflectance with wavelength respectively.

From Fig. 1, it can notice that the transmittance increases with increasing annealing temperature until to the wavelength of 570 nm. While the reflectance decreases with increasing annealing temperature until to the wavelength 570 nm as shown in Fig. 2.

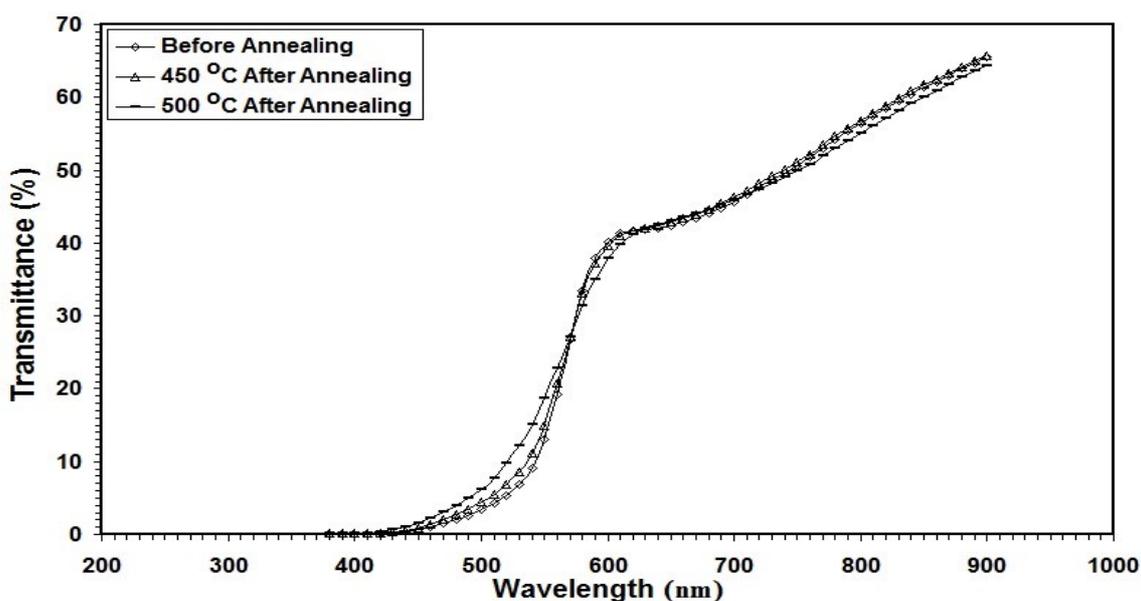


Fig. 1. Transmittance vs wavelength plot of NiO -doped Fe_2O_3 thin films with different annealing temperatures.

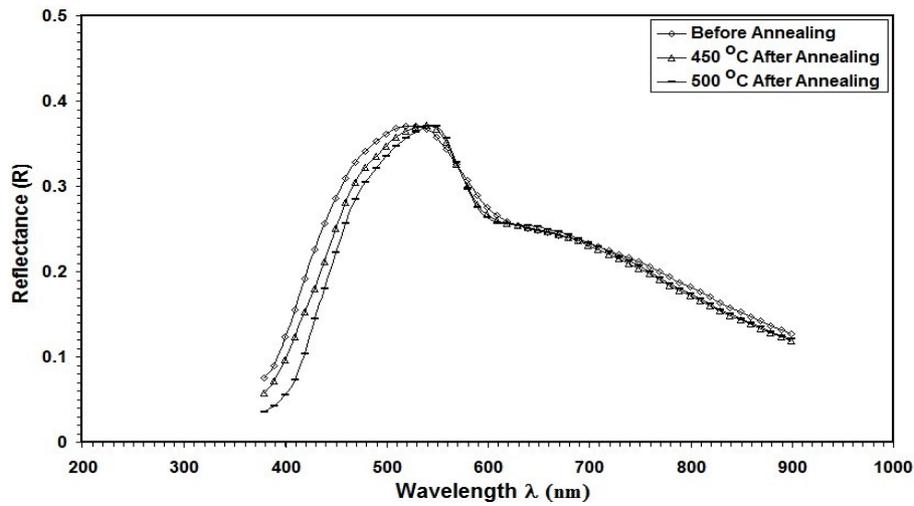


Fig. 2. Reflectance vs wavelength plot of NiO-doped Fe_2O_3 thin films with different annealing temperatures.

The absorption coefficient $\alpha(\lambda)$ of the annealed NiO: Fe_2O_3 thin films can be calculated by a simple method from transmittance spectra and defined as [20]:

$$T = \exp [-\alpha (\lambda) d] \quad (1)$$

Where T is the optical transmittance and d is the thickness of NiO: Fe_2O_3 thin films.

A plot of absorption coefficient vs. wavelength is shown in Fig. 3. From this figure, it can notice that the absorption coefficient is increased gradually with photon energy until 2.1 eV, while the increases of α become sharply at incident photon energy greater than 2.1 eV. In addition, from this figure, it can show clearly the α increases with increasing annealing temperature, and the high values of α refer to the allowed direct transition for all prepared NiO: Fe_2O_3 thin films.

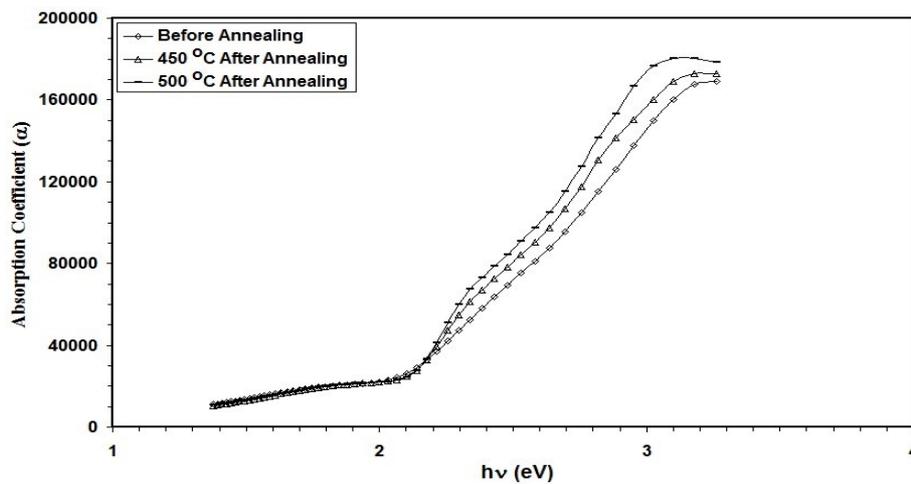


Fig. 3. Absorption coefficient vs wavelength plot of NiO-doped Fe_2O_3 thin films with different annealing temperatures.

There are many different methods for determining the optical band gap (E_g). Yadav et al. [21], Dghoughi et al. [22], Pejova and coworkers [23], Ismail et al. [24] determined the band gap from the relation between the absorption coefficient (α) and the energy of incident light $h\nu$ [24]:

$$(\alpha h\nu)^n = B (h\nu - E_g) \quad (2)$$

Where $h\nu$ is the photon energy, B is a constant, and n represents the transition type ($n=2$ for direct transition, $n=1/2$ for indirect transition). The values of the direct optical band gap (E_g) values of the NiO:Fe₂O₃ thin films were obtained from the intercept of $(\alpha h\nu)^2$ vs. $h\nu$ curves plotted as shown in figs. 4-6. From these figures it can notice that the optical band gap decreased from 2.68 eV before annealing to 2.58 eV after 500 °C annealing temperature for NiO:Fe₂O₃ thin films, this result refer to the broadening of secondary levels that product by NiO-doping to the Fe₂O₃ thin films.

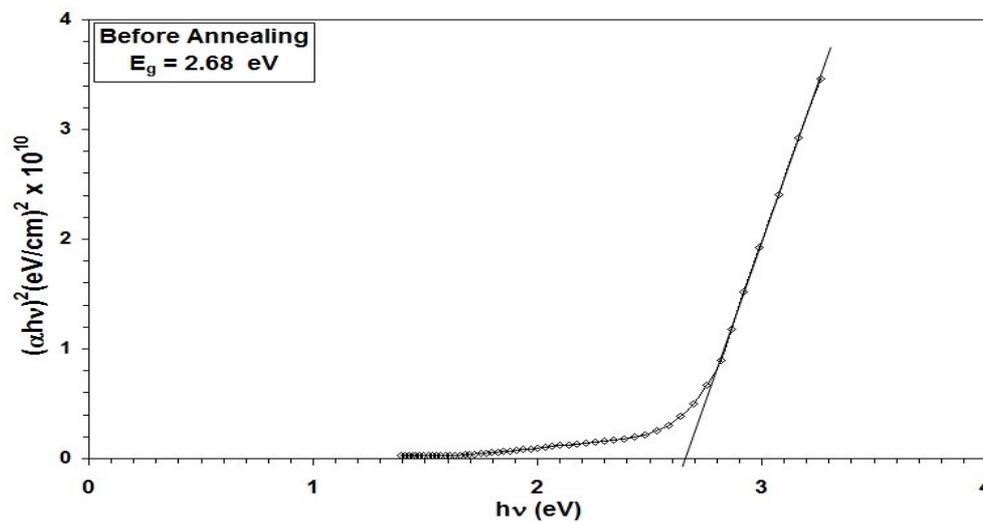


Fig. 4. $(\alpha h\nu)^2$ vs $h\nu$ plot of NiO-doped Fe₂O₃ thin films before annealing.

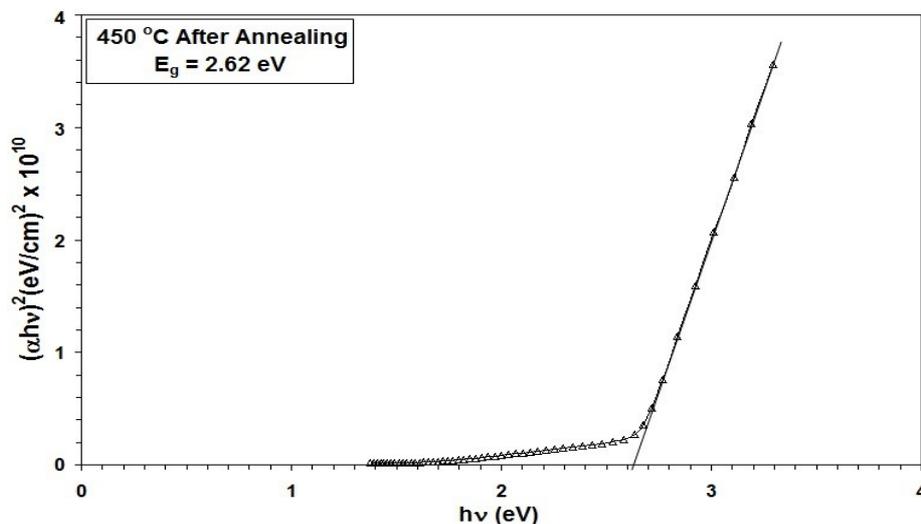


Fig. 5. $(\alpha h\nu)^2$ vs $h\nu$ plot of NiO-doped Fe₂O₃ thin films after 450 °C annealing temperatures.

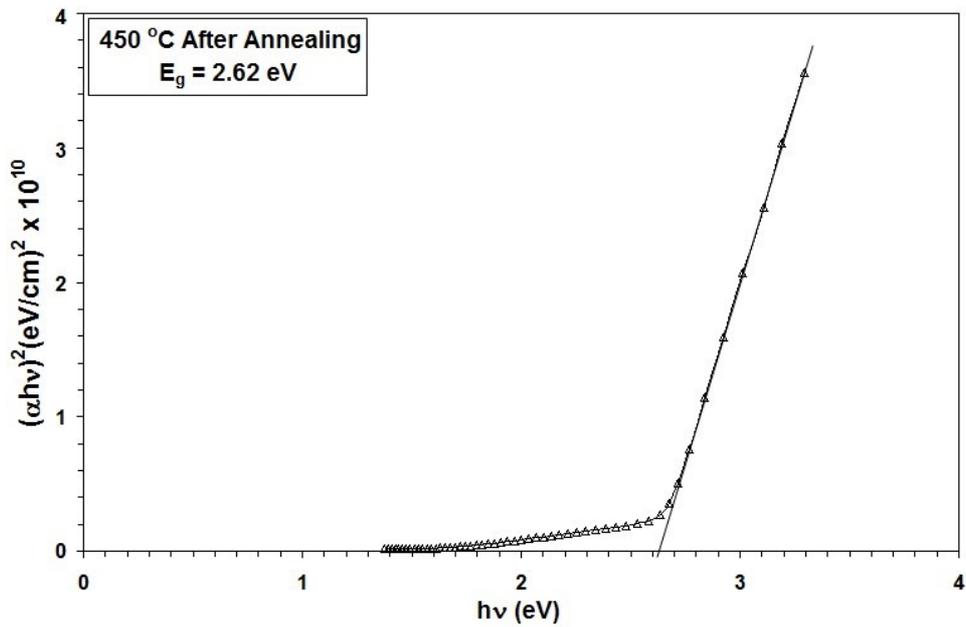


Fig. 6. $(\alpha h\nu)^2$ vs $(h\nu)$ plot of NiO-doped Fe_2O_3 thin films after 500°C annealing temperature.

Fig. 7 shows the extinction coefficient of NiO: Fe_2O_3 thin films recorded in the range of (300-900) nm at different annealing temperatures. It can be observed from this figure that the extinction coefficient decreases sharply with the increase of wavelength for all prepared films until the wavelength of 600 nm, and its value increases with the increase of annealing temperatures.

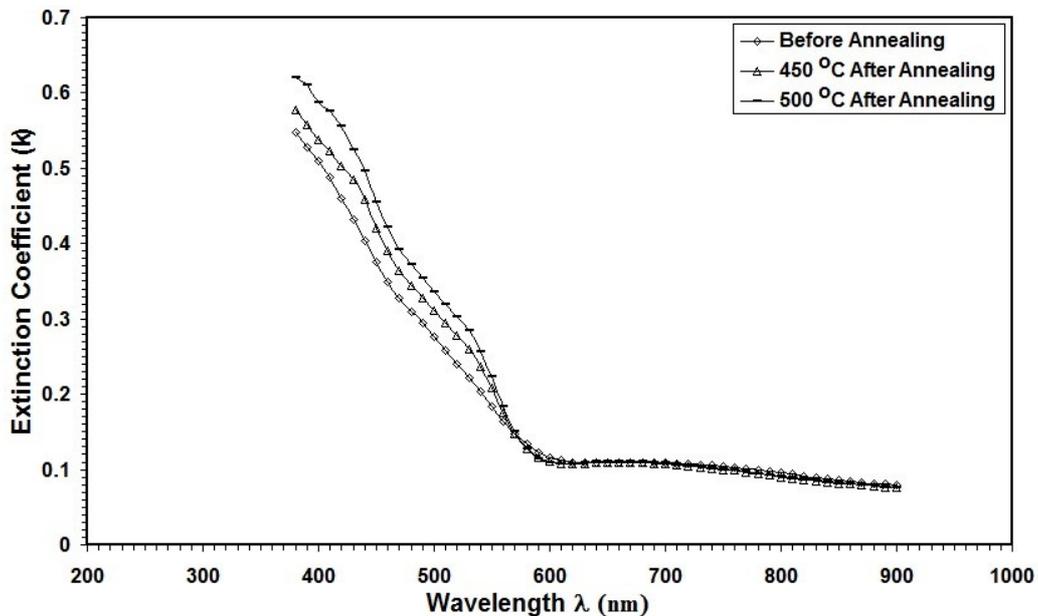


Fig. 7. Extinction coefficient vs wavelength plot of NiO-doped Fe_2O_3 thin films with different annealing temperatures.

The refractive index dispersion plays an important role in the research of optical materials, because it is a significant factor in optical communication and in designing devices for spectral dispersion. The refractive index of the film was calculated approximately from the following relation [25]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (3)$$

Where n is the refractive index and k is extinction coefficient. Fig. 8 shows the variation of refractive index with wavelength for different annealing temperature of NiO:Fe₂O₃ films. From this figure, it is clear that n decreases with increasing annealing temperature, that mean the density is decreased of this films.

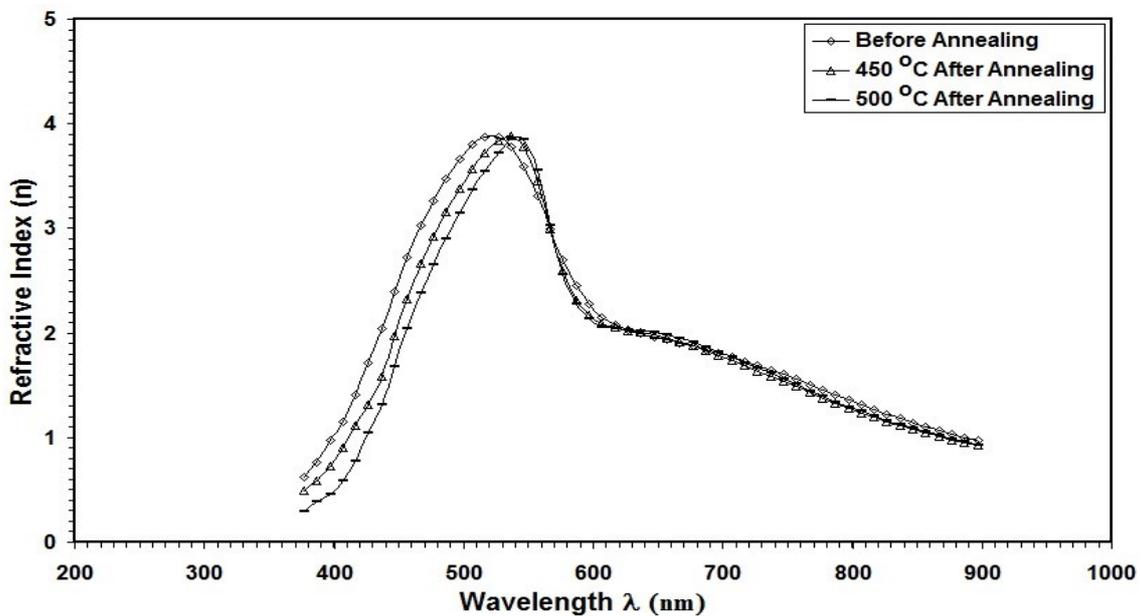


Fig. 8. Refractive index vs wavelength plot of NiO-doped Fe₂O₃ thin films with different annealing temperatures.

The skin depth (χ) that represent the electromagnetic wave will have amplitude reduced after traversing a thickness as the formula [26]:

$$\chi = 1 / \alpha \quad (4)$$

A plot of skin depth versus wavelength is shown in Fig. 9. It can see from this figure, the increases of skin depth with increasing wavelength, and the slightly change with increasing annealing temperature.

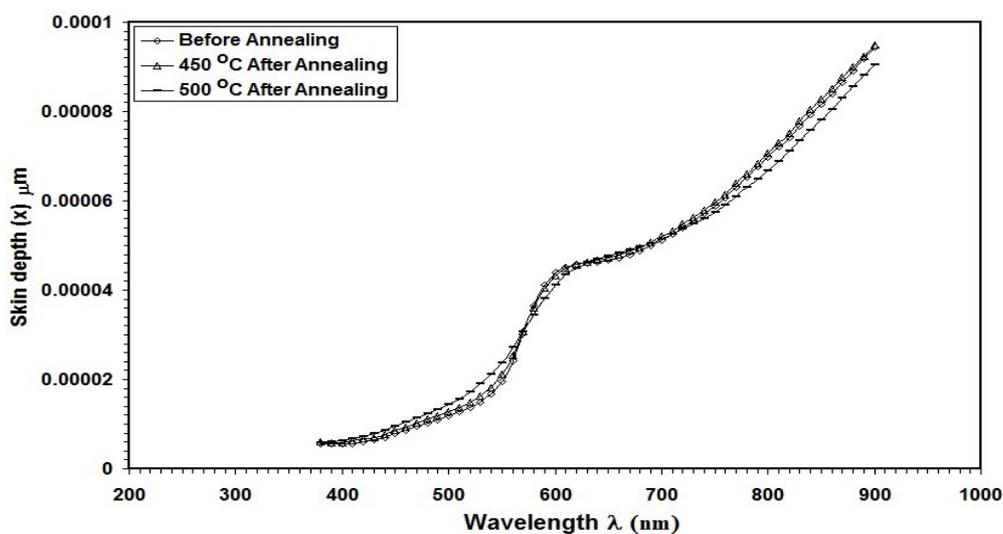


Fig. 9. Skin depth vs wavelength plot of NiO-doped Fe₂O₃ thin films with different annealing temperatures.

4. CONCLUSION

We have been using chemical spray pyrolysis to deposited Fe₂O₃ thin film doped by NiO and study the effect of annealing on its optical properties. The refractive index decreases with increasing annealing temperature, such as optical band gap that decreases from 2.68 eV before annealing to 2.58 eV after annealing of 500 °C. Absorption coefficient and extinction coefficient increase with increasing annealing temperature, also the slight change of skin depth for all deposited NiO:Fe₂O₃ thin films.

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