Annealing Effects on the some Optical Properties of Fe$_2$O$_3$ Thin Films Doped by NiO

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Abstract. Nickel oxide doped Fe$_2$O$_3$ thin films have been prepared by spray pyrolysis technique on glass substrate. The initial solution was including a 0.1 M/L for both NiCl$_2$ and FeCl$_3$ diluted with re-distilled water and a few drops of HCl. The effect of annealing temperature on some optical properties was studied, using UV-Visible spectrophotometer to determine transmittance and absorbance spectra at a thickness of 400 nm. The reflectance increased with increasing annealing temperature, the same behavior observed for absorption coefficient $\alpha$, extinction coefficient $k$ and refractive index $n$, while the transmittance decreases slightly with increasing annealing temperature and the optical energy gap was decreased from 2.86 eV before annealing to 2.70 eV at 500 ºC annealing temperature .

Introduction

Iron oxide (Fe$_2$O$_3$) has an optical energy gap ($E_g$), which averages 2 eV, absorbing ~40% of the sunlight. Additionally, it is low cost, non-toxic and exhibits a chemical stability over a broad pH range [1], it is quite stable against photo-corrosion [2]-[3], but its high resistivity at room temperature [4]. An efficient n-Fe$_2$O$_3$ semiconductor can be used as an important front layer to protect a Si or an amorphous Si solar cell to be used in the back to supply the required photovoltage for efficient water-splitting reaction [5]; these characteristics create an attractive material for photocatalytic applications.

The energy conversion efficiency of $\alpha$-Fe$_2$O$_3$ is not very good due to its high electron–hole recombination rate. In order to improve the conversion efficiency, many proposed to add a small amount of a third element [6]-[9]. The influence of the deposition temperature is related to the structural, optical, and morphological properties of the Fe$_2$O$_3$ [10]. Many researchers have worked on different techniques for fabricating Fe$_2$O$_3$ such as; sol-gel [11]-[12], Spray pyrolytic method [13], thermal evaporation method [14], chemical vapor deposition [15], sputtering [16] and DC reactive magnetron sputtering [17], and pulsed laser deposition [18].

Jandow [19] had prepared Fe$_2$O$_3$ thin films doped by 1% and 2% volume concentration of Ni and study the effect of annealing temperature at 300 ºC on their optical properties. It was found that the optical energy gap increase after annealing, while Abass[20] was used the same technique to prepare Fe$_2$O$_3$ thin films with 1% volume concentration of NiO at annealing temperature of 400 ºC and 500ºC. It was found the optical properties were decreased after annealing showing a red shift.

The aim of the Present work is to study the effect of annealing temperature at 400 ºC, and 500 ºC on optical properties of NiO:Fe$_2$O$_3$ thin films that was prepared by chemical spray pyrolysis method.
Materials and method

NiO-doped Fe₂O₃ thin films 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 NiCl₂ (Sigma Aldrich UK) and FeCl₃ (Merck Chemicals Germany) diluted with re-distilled water and a few drops of HCl were used to obtain the starting solution for deposition. The volume concentration of NiO was 5%. The optimum conditions which were used for spraying the solution were: spray time was 8 seconds and the spray interval (one minute) was kept constant, nitrogen was used as a carrier gas maintained at a pressure of 10⁵ Nm⁻², and the distance between nozzle and the substrate was about 29 cm ±1 cm.

The prepared films were annealed at a temperature of 450 and 500 °C. Thickness of the sample was measured using the gravimetric method and was found to be around 400 nm. Optical transmittance and absorbance were recorded in the wavelengths range (380-900nm) using UV-Visible spectrophotometer (Shimadzu Company Japan).

Results and Discussions

The optical transmittance of as-deposited and annealed films of Fe₂O₃: NiO in the wavelengths range (300-900) nm was investigated. The transmittance of Fe₂O₃: NiO films were shown in Fig. 1, the transmittance was found to increase sharply in the wavelength of 540 nm, and then gradually increases with wavelength. In addition, the transmittance decreased with increasing annealing temperature.

![Transmittance spectra of NiO-doped Fe₂O₃ thin films](image)

Fig. 1: Transmittance spectra of NiO-doped Fe₂O₃ thin films Prepared with different annealing temperatures.

Fig. 2 shows reflectance spectra for NiO-doped Fe₂O₃ thin film. The plot displayed a sharp decrease in reflectance at wavelengths less than 560 nm, while gradually decreases with wavelengths more than 560 nm. In addition, the reflectance increased with increasing annealing temperature.
Fig. 2: Reflectance spectra of NiO-doped Fe$_2$O$_3$ thin films prepared with different annealing temperatures.

The absorption coefficient was determined from the transmittance data (obtained at normal incidence). The variation of absorption coefficient of various annealing temperature for NiO:Fe$_2$O$_3$ was shown in Fig. 3, indicates an increase in the absorption coefficient with photon energy for all the samples. The absorption coefficient decreases with increasing annealing temperature.

Fig. 3: Absorption coefficient for NiO-doped Fe$_2$O$_3$ thin films prepared with different annealing temperatures.

The variation of extinction coefficient with wavelength was shown in Fig. 4. From this figure, the extinction coefficient decreased with increasing annealing temperature until 550 nm, and then there is no change of extinction coefficient with annealing temperature.

The refractive index (n) can be determined from a transmittance spectrum as a function of the photon energy. Fig. 5 shows the plot of n vs. λ, that’s clearly show an increase in refractive index with increasing annealing temperature until the wavelength of 560 nm, while there was no effect of refractive index with annealing temperature of wavelengths more than 560 nm.
The optical band gap of the NiO:Fe$_2$O$_3$ films was estimated from the plot of $(\alpha h\nu)^2$ versus $h\nu$ as shown in the Figs. 6-8. The optical energy gap was determined by extrapolating the linear portions of the plot at $(\alpha h\nu)^2 = 0$. This plot gives $n = \frac{1}{2}$ according to Tauc relation, which indicates that the direct transition dominates in the films. From the figures 6-8, it can be noticed that the optical band gap was decreased from 2.86 eV before annealing to 2.70 eV at 500 ºC annealing temperature.
Fig. 6: $(\alpha h\nu)^2$ vs. $(h\nu)$ for NiO-doped Fe$_2$O$_3$ thin films before annealing.

Fig. 7: $(\alpha h\nu)^2$ vs. $(h\nu)$ for NiO-doped Fe$_2$O$_3$ thin films at 450°C annealing temperature.
Fig. 8: $(\alpha h\nu)^2$ vs. $(h\nu)$ for NiO-doped Fe$_2$O$_3$ thin films at 500°C annealing temperature.

**Conclusion**

Fe$_2$O$_3$: NiO thin films have been successfully prepared by spray pyrolysis technique on glass substrate with 5% volume concentration of NiO. Optical properties are determined using UV-Visible spectrophotometer by recording the transmittance and absorbance spectra. The reflectance increased with increasing annealing temperature. The same behavior was noticed for $\alpha$, $k$, and $n$, while the transmittance decreases with increasing annealing temperature and the optical energy gap was decreased from 2.68 eV before annealing to 2.70 eV at 500 ºC annealing temperature showing a red shift behavior.

**References**