Annealing Effects on the some Optical Properties of Fe₂O₃ Thin Films Doped by NiO

Nadir Fadhil Habubi^{1*}, Sami Salman Chiad¹, Khalid Haneen Abass²,
Mahmood Muwafaq Abood¹

¹Al_Mustansiriyah University, College of Education, Physics Department, Baghdad, (IRAQ)

² University of Babylon, College of Education for Pure Sciences, Department of Physics,
Babel, (IRAQ)

*nadirfadhil@yahoo.com, samichiad2003@yahoo.com, kalidhanin@yahoo.com,
mahmood_moafaq@yahoo.com

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Abstract. Nickel oxide doped Fe₂O₃ thin films have been prepared by spray pyrolysis technique on glass substrate. The initial solution was including a 0.1 M/L for both NiCl₂ and FeCl₃ 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 α , 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 °C annealing temperature .

Introduction

Iron oxide (Fe₂O₃) 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-Fe₂O₃ 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 α -Fe₂O₃ 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 Fe₂O₃ [10]. Many researchers have worked on different techniques for fabricating Fe₂O₃ 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 Fe₂O₃ thin films doped by 1% and 2% volume concentration of Ni and study the effect of annealing temperature at 300 °C 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 Fe₂O₃ thin films with 1% volume concentration of NiO at annealing temperature of 400 °C and 500°C. 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 °C, and 500 °C on optical properties of NiO:Fe₂O₃ thin films that was prepared by chemical spray pyrolysis method.

Materials and method

NiO-doped Fe_2O_3 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 NiCl_2 (Sigma Aldrich UK) and FeCl_3 (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 10^5 Nm^{-2} , and the distance between nozzle and the substrate was about $29 \text{ cm} \pm 1 \text{ cm}$.

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 Fe_2O_3 : NiO in the wavelengths range (300-900) nm was investigated. The transmittance of Fe_2O_3 : 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.

Fig. 1: Transmittance spectra of NiO-doped Fe_2O_3 thin films Prepared with different annealing temperatures.

Fig. 2 shows reflectance spectra for NiO-doped Fe_2O_3 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_2O_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_2O_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_2O_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.

Fig. 4: Extinction coefficient for NiO-doped Fe_2O_3 thin films prepared with different annealing temperatures.

Fig. 5: Refractive index for NiO-doped Fe_2O_3 thin films prepared with different annealing temperatures.

The optical band gap of the $\text{NiO}:\text{Fe}_2\text{O}_3$ 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 °C annealing temperature.

Fig. 6: $(\alpha h\nu)^2$ vs. $(h\nu)$ for NiO-doped Fe_2O_3 thin films before annealing.

Fig. 7: $(\alpha h\nu)^2$ vs. $(h\nu)$ for NiO-doped Fe_2O_3 thin films at 450°C annealing temperature.

Fig. 8: $(\alpha h\nu)^2$ vs. $(h\nu)$ for NiO-doped Fe_2O_3 thin films at 500°C annealing temperature.

Conclusion

Fe_2O_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 α , 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 °C annealing temperature showing a red shift behavior.

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