

Optical Characterization of NiO Doped Fe₂O₃ thin Films Prepared by Spray Pyrolysis Method

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Abstract

In this paper, the Fe₂O₃ thin film were prepared with various ratios doping of NiO by spray pyrolysis method on glass substrate temperature 400 °C. The initial solution was including a 0.1 M/L for both NiCl₂ and FeCl₃ diluted with redistilled water and a few drops of HCl. The effect of NiO-doping on optical properties were studied. UV-Visible spectrophotometer in the range of (300-900) nm used to determine absorbance spectra. The transmittance increased with increasing NiO content in NiO:Fe₂O₃ thin films, same behavior of extinction coefficient and skin depth. The energy gap increased from 2.45 eV before doping to 2.86 eV after 3% NiO-doping. While the reflectance, absorption coefficient, and refractive index are decreased with increasing NiO content in Fe₂O₃ thin films.

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

1. INTRODUCTION

Iron oxides exist in many forms in nature, with magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃), and hematite (α -Fe₂O₃) being probably the most common [1]. These three oxides are also very important technologically. The iron oxide (Fe₂O₃ or hematite) is a semiconductor material with a narrow band gap (approximately 2.2 eV) and very good electrochemical stability in water. These properties make this material especially attractive when used as a photoanode to split the water into oxygen and hydrogen by sunlight [2-4]. Iron oxide (α -Fe₂O₃ or hematite) photoanode has received considerable attention on account of its abundance, stability and environmental compatibility, as well as its suitable band gap and valence band edge position. The preparation of hematite thin films was first reported by Bard and Hardee using CVD method [5-6]. Recently, Fe₂O₃ is found to have large third-order non-linear optical susceptibility and faster response time showing potential applications in optical computing [7].

The Fe₂O₃ thin film photoanodes for solar water splitting were prepared by spray pyrolysis of Fe (AcAc)₃ studied by Liang et al. [8]. Many researchers have worked on different techniques for fabricating Fe₂O₃ such as; Spray pyrolytic method [9-10], Sol-gel [11-12], spin-coating deposition [13], chemical vapor deposition [14], sputtering [15] and DC reactive magnetron sputtering [16], and pulsed laser deposition [17].

Present work is to study the effect of NiO content (0, 1, and 3%) on optical properties of NiO:Fe₂O₃ thin films that prepared by chemical spray pyrolysis method.

2. EXPERIMENTAL

Thin films of Fe₂O₃ doped by various ratios of NiO have been prepared by chemical pyrolysis technique, this technique is widely used for the large-scale production of films owing to its low production cost and simplicity of operation. 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 redistilled water and a few drops of HCl. Volumetric concentration of 1% and 3% was achieved the optimized conditions have been arriving at the following conditions; 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 10⁵ Nm⁻², and distance between nozzle and the substrate was about 30 cm ± 1 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 (300-900 nm) using UV-Visible spectrophotometer (Shimadzu Company Japan).

3. RESULTS AND DISCUSSIONS

The transmittance spectra were recorded by UV-Visible spectrophotometer in the range of (300-900) nm on glass substrate temperature for NiO:Fe₂O₃ thin films. The measured transmittance spectra of the NiO:Fe₂O₃ thin films are shown in Fig. 1. From this figure, it can show that the transmittance increases with increasing wavelength and there is Sharpe fall in the wavelength of 600 nm, and clearly increases of transmittance with increasing NiO-doped in the Fe₂O₃ thin films.

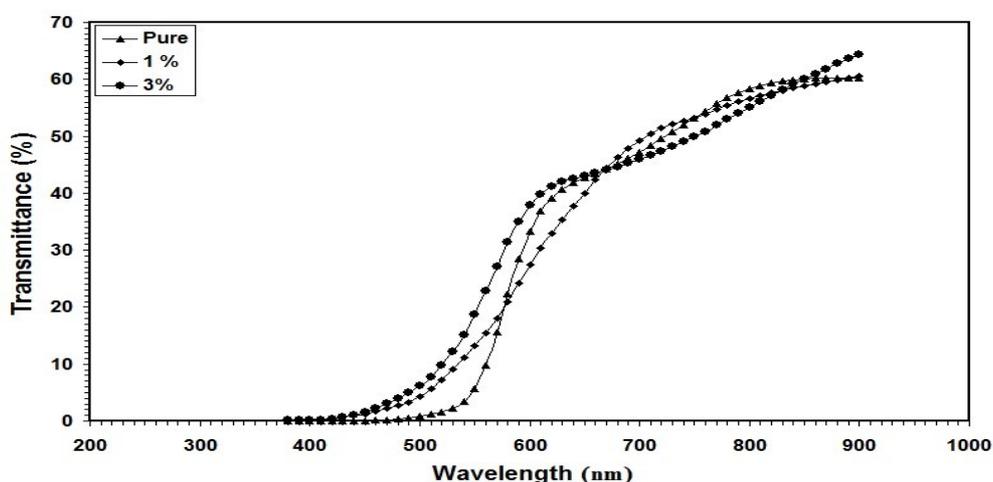


Fig. 1. The variation of optical transmittance spectra with wavelength for NiO:Fe₂O₃ thin films for deferent contain of NiO.

The reflectance (R) obtained from the expression [18]:

$$A + T + R = 1 \quad (1)$$

Where A is the absorbance and T is the transmittance. The measured reflectance spectra of the NiO:Fe₂O₃ thin films are shown in Fig. 2. From this figure, it can show that the reflectance decreases with increasing NiO-doped in the Fe₂O₃ thin films.

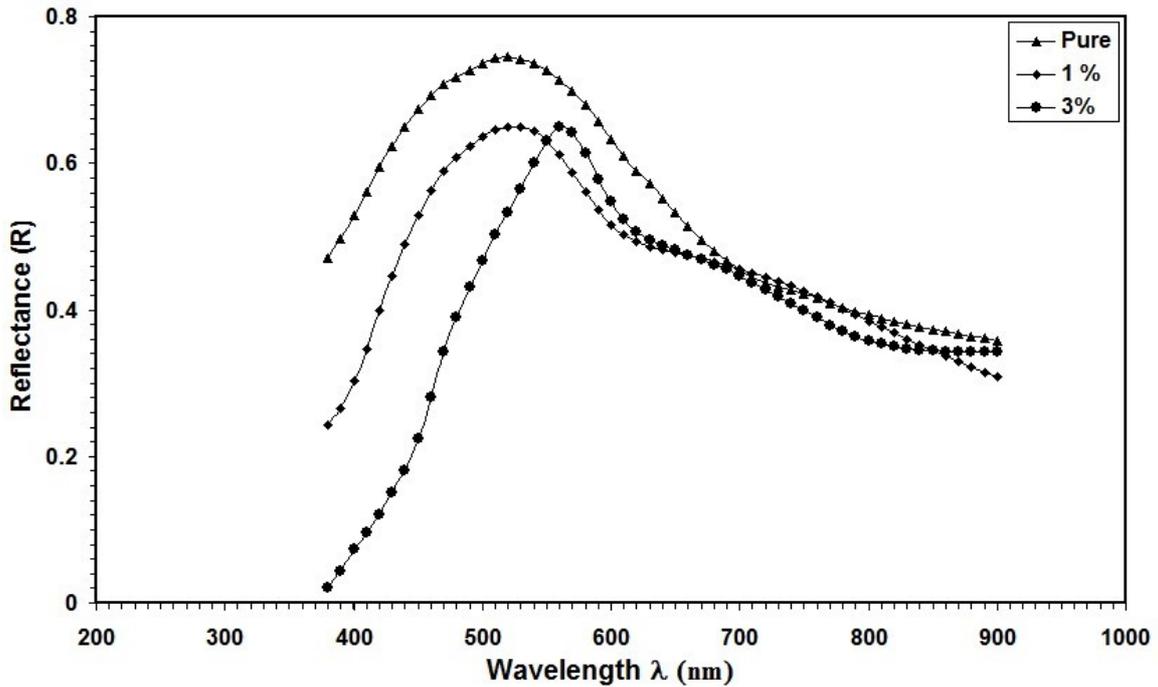


Fig. 2. The variation of optical reflectance spectra with wavelength for NiO:Fe₂O₃ thin films for different contain of NiO.

The absorption coefficient (α) was directly obtained from the absorbance (A) with wavelength (λ) values by using the relation [19].

$$\alpha = \frac{2.303 A}{t} \quad (2)$$

Where t is the thickness. Fig. 3 represent the plot of absorption coefficient vs. wavelength. From this figure, it can show that the absorption coefficient decreases with increasing NiO-doped in the Fe₂O₃ thin films, and gradually increased with increasing wavelength.

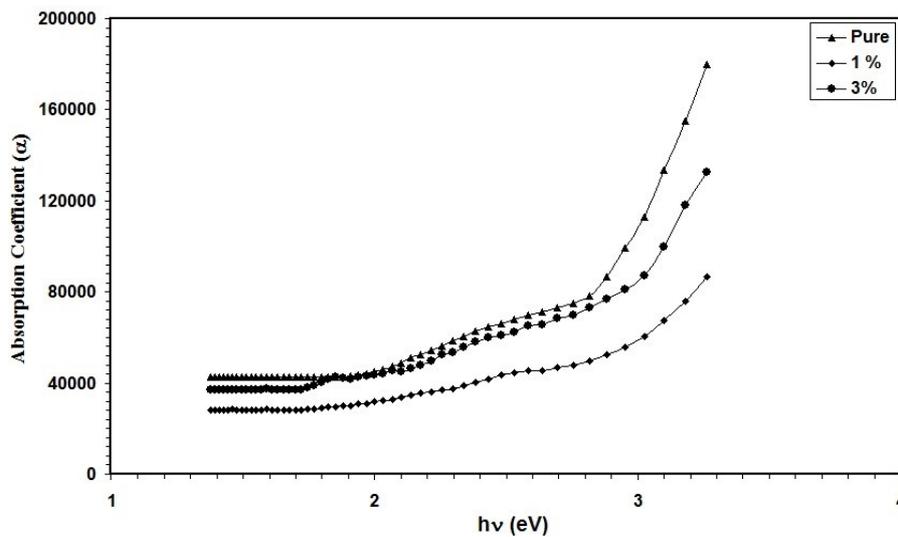


Fig. 3. The variation of absorption coefficient with wavelength for NiO:Fe₂O₃ thin films for different contain of NiO.

The optical absorption edge was analyzed by the following relationship [20],

$$\alpha h\nu = B (h\nu - E_g)^m \quad (3)$$

Where B is a constant and E_g is the optical band gap. The exponent m depends on the nature of the transition, $m = 1/2, 2, 3/2$ or 3 for allowed direct, allowed non-direct, forbidden direct or forbidden non-direct transitions, respectively.

A straight line is obtained by plotting $(\alpha h\nu)^{1/m}$ vs. $h\nu$. The intersection of this straight line on x-axis gives the value of optical band gap as in Figs. 4-6. From these figures it can notice that the optical band gap increases with increasing NiO contain in NiO:Fe₂O₃ thin films from 2.54 eV for undoped Fe₂O₃ film to 2.86 eV for 3% NiO-doped in NiO:Fe₂O₃ thin films.

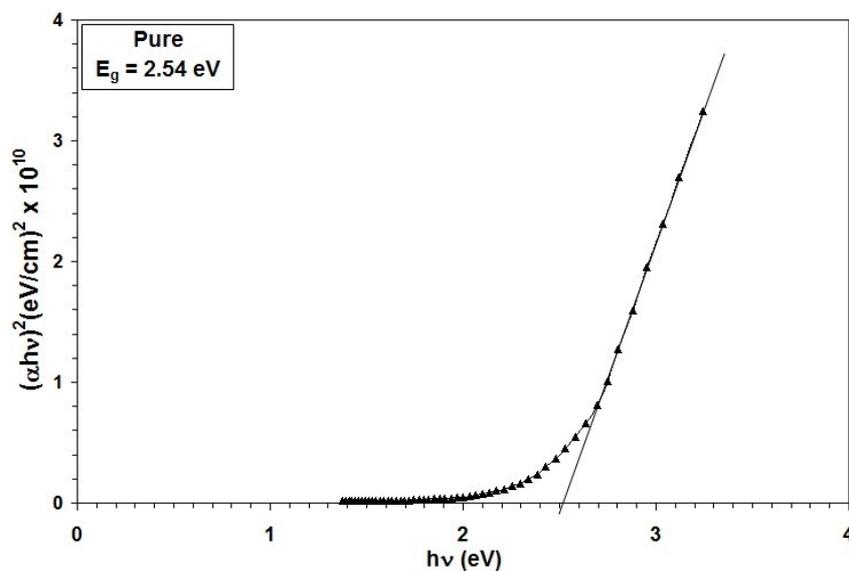


Fig. 4. The relationship of $(\alpha h\nu)^2$ vs $(h\nu)$ for Fe₂O₃ thin film.

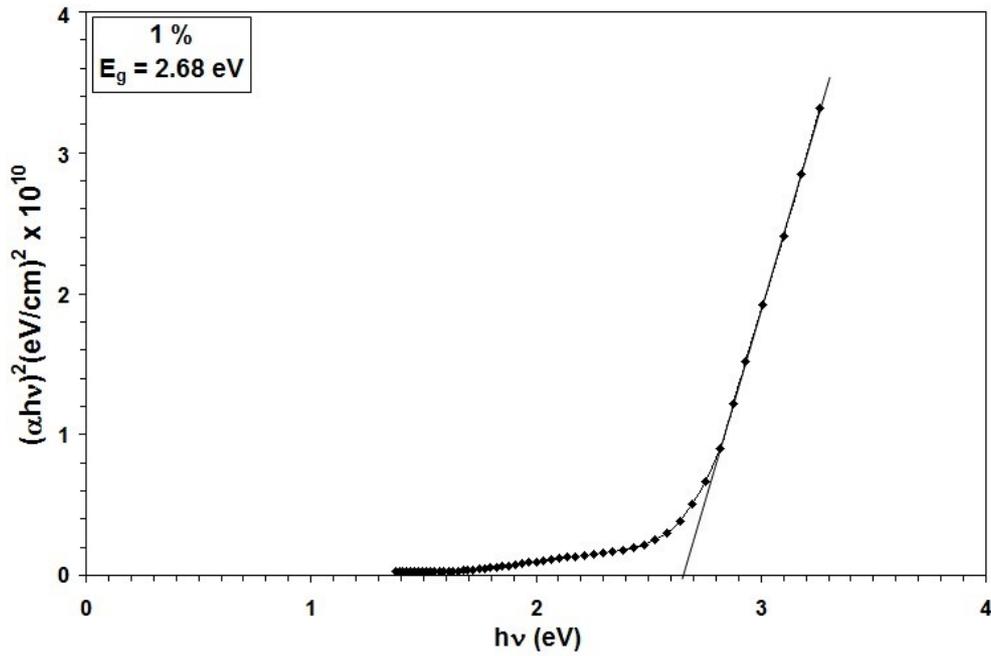


Fig. 5. The relationship of $(\alpha h\nu)^2$ vs $(h\nu)$ for Fe_2O_3 thin film with 1 wt.% of NiO.

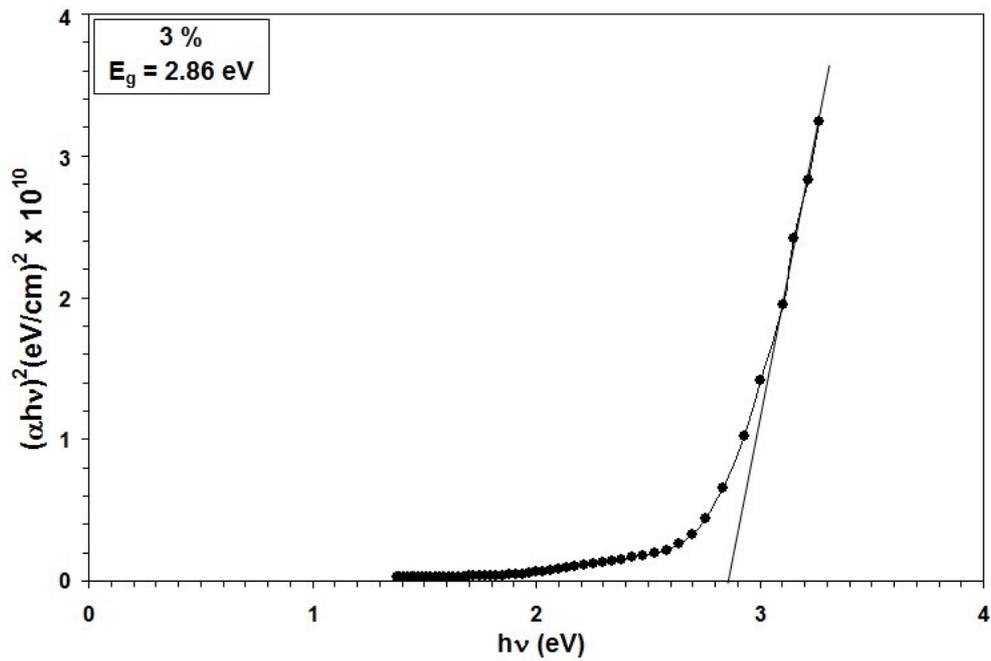


Fig. 6. The relationship of $(\alpha h\nu)^2$ vs $(h\nu)$ for Fe_2O_3 thin film with 3 wt.% of NiO.

The extinction coefficient (k) of the films was calculated using the expression [21]:

$$k = \alpha\lambda/4\pi \quad (4)$$

Where α is the absorption coefficient. The plot of extinction coefficient versus photon energy for the NiO:Fe₂O₃ films deposited at different content of NiO is shown in Fig. 7. It observes that the extinction coefficient increases for doped film than that of undoped films. With an increase in wavelength for all the films, the extinction coefficient decreases sharply until the wavelength of 600 nm to become the decreases gradually. In general, the k values increases with increasing doping ratio of NiO in NiO:Fe₂O₃ thin films.

The refractive index is an important parameter for optical materials and for photoelectronics applications [22]. Thus, it is important to determine optical constants of the films and the complex optical refractive index of the films. The refractive index of the films was determined from the following relation [23]:

$$n = \left[\frac{1+R}{1-R} \right] + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (5)$$

Where R is the reflectance and k is the extinction coefficient. The plot of refractive index versus wavelength for the NiO:Fe₂O₃ films is shown in Fig. 8. It observes that the refractive index decreased with increasing NiO content in the NiO:Fe₂O₃ thin films. It has been well established that the refractive index is closely correlated with film density; a higher refractive index implies a denser film.

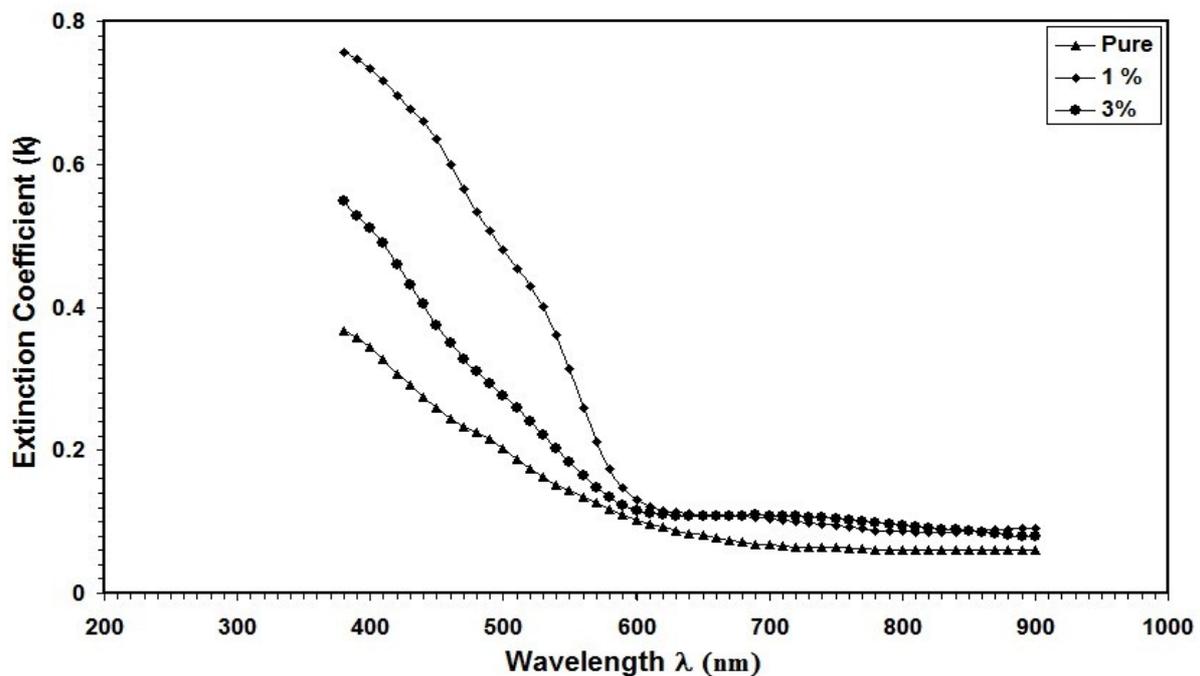


Fig. 7. The variation of extinction coefficient with wavelength for NiO:Fe₂O₃ thin films for different contain of NiO.

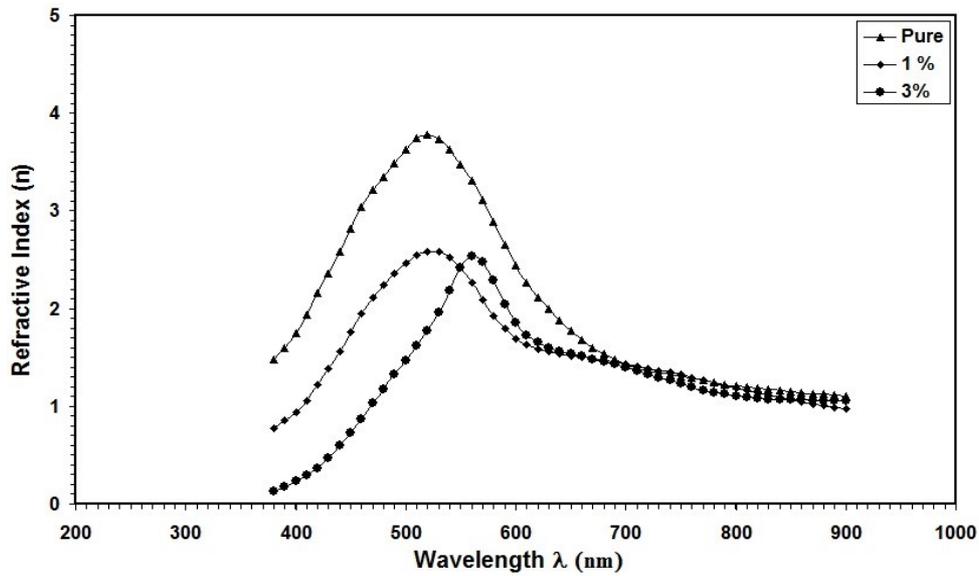


Fig. 8. The variation of refractive index with wavelength for NiO:Fe₂O₃ thin films for different contain of NiO.

The skin depth (χ) represents the electromagnetic wave will have amplitude reduced after traversing a thickness can be calculated by using the following relation [24]:

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

Fig. 9 represent the plot of skin depth versus wavelength. From this figure, It can show that the increases of skin depth with increasing wavelength, and the slightly change with increasing NiO content in NiO:Fe₂O₃ thin films.

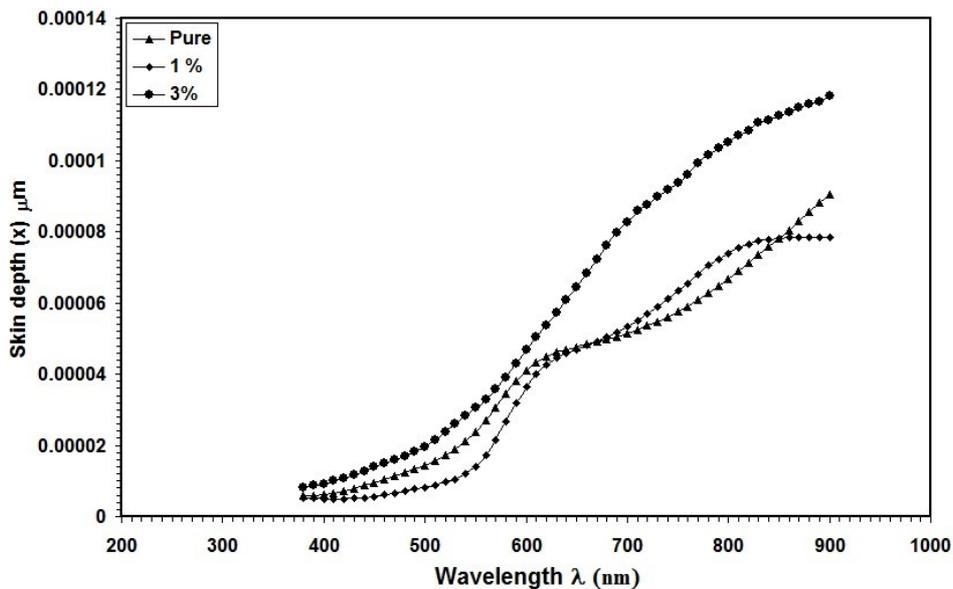


Fig. 9. The variation of skin depth with wavelength for NiO:Fe₂O₃ thin films for different contain of NiO.

4. CONCLUSION

The Fe₂O₃ thin film prepared with various ratios doping of NiO by spray pyrolysis method on glass substrate temperature 400 °C. UV-Visible spectrophotometer was used to recording the transmittance spectra. From studying the optical properties we found the transmittance increased with increasing NiO content in NiO:Fe₂O₃ thin films, same behavior appears for extinction coefficient and skin depth. The energy gap increased from 2.45 eV before doping to 2.86 eV after 3% NiO-doping. While the reflectance, absorption coefficient, and refractive index are decreased with increasing NiO content in Fe₂O₃ thin films.

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