Structural and Optical Properties of Fe$_2$O$_3$ - NiO mixed Thin Films Prepared by Chemical Spray Pyrolysis

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ABSTRACT

Mixed Fe$_2$O$_3$ - NiO thin films have been prepared by chemical Spray pyrolysis technique onto glass substrate preheated to 450 °C. The thickness of thin films was found to be (400 ±20) nm. XRD measurements reveal that all the film exhibit polycrystalline hexagonal wrutzite with a preferred orientation along (104) plane for pure and 10 % and 20 % Ni, while for the rest the structure was amorphous. AFM analysis indicate a nanostructure for all the films. The optical energy gap was found to be increased from optical transitions seems to be direct and the optical energy gap seems to be increased from 2.5 to 2.69 eV as the percentage of NiO increase.

Keywords: Fe$_2$O$_3$; Spray pyrolysis technique; Structural; Optical properties

1. INTRODUCTION

Fe$_2$O$_3$ is one of the most important transition metal with a band gap of 2.2 eV. It received an extensive attention due to its good intrinsic physical and chemical properties, such as its low cost, stability under ambient conditions, and environmentally friendly properties [1]. (α-Fe$_2$O$_3$) is the most stable iron oxide compound material and is widely used in photoelectrodes, gas sensing, catalysts, magnetic recording, and medical fields [2]. Due to its great sensitivity for flammable gases, its fast speed of response and its long term stabilities; Photo electrochemical solar cell, due to its optical band gap, its high optical absorption coefficient; Negative electrode in rechargeable batteries. It is also used for water electrolysis in the presence of sunlight [3,4]. Nickel oxide is a transition metal oxide semiconductor, usually taken as a model for p-type material. NiO is having a wide band gap of 3.6 to 4.0 eV [5] and exhibit rhombohedral or cubic structure, but the most prominent structure was cubic structure [6]. NiO thin films have been studied for applications in electrochromic devices [7], electrode material for Li-ion batteries [8]. Recent works have shown that NiO is also a promising functional material for applications in resistive type gas sensors implementing thin NiO films [9].

Most attractive features of NiO are: (i) excellent durability and electrochemical stability, (ii) low materials cost, (iii) promising ion storage material in terms of cyclic stability, Fe_2O_3 and NiO films can be prepared by physical and chemical methods such as: spray pyrolysis [10], electron beam evaporation [11], pulsed laser deposition [12], plasma enhanced chemical vapor deposition [13] and reactive sputtering [14]. It is well known that the structural, optical, surface morphology and electrical properties of materials in thin film form depends on the deposition. This paper represents the fabrication of the mixed oxide Fe_2O_3-NiO thin film utlizing chemical spray pyrolysis in order to study their structure and optical properties.

2. EXPERMINTAL

Thin films of iron oxide have been prepared by chemical pyrolysis technique. The spray pyrolysis was done with a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of (450 °C). Best homogeneous films were obtained at this temperature. The chemical solution was achieved by adding (1.6221 g) of ($FeCl_3 \cdot 6H_2O$) a a source of Fe on 100 ml of deionized water to and was (2.377 g) of ($NiCl_2 \cdot 6H_2O$) a source of Ni on 100 ml of deionized water, homogeneous mixture of aqueous solution was achieved by using a magnetic stirrer. The optimized conditions were arrived at the following parameters, spraying time (5 sec), lasted by 2 minutes to avoid excessive cooling, deposition rate (8 ml/min), distance between nozzle and the substrate was (30 ±1 cm) and the carrier gas (filtered compressed air) was maintained at a pressure of 5 bar. Thickness of the samples was measured using the StellarNet TF method and was found to be around 400 ±20 nm. Optical transmittance and absorbance were recorded in the wavelength range (300-900 nm) using UV-Visible spectrophotometer (Shimadzu Company Japan).

3. RESULTS AND DISCUSSION

3. 1. Structural properties

Fig. 1 shows the XRD pattern for the as deposited thin films. (XRD) analyses show that (Pure, 10, 20 %) were polycrystalline in nature with a Rhombohedral wurtzite structure and a preferred orientation along (104) plane. A decrease in the values of the crystallization was noticed by the increase ratio of (NiO). All of the observed peaks can be assigned to Fe_2O_3, in accordance with data from (The **J**oint **C**ommittee on **P**owder **D**iffraction **S**tandard) (JCPDS) (0664-33 JCPDS no.) The ratios (30, 40, 50 %) NiO were Amorphous. The Grain size was calculated using the Scherrerr equation, and was found to be decreased with increasing (NiO) as shown in Figure (2).

Fig. 3 shows the AFM nicrograph for all the films under investigation. The atomic force microscope (AFM) images show that the average roughness and the square root of the average roughness square (RMS) of the films decreased with increasing (NiO) concentrations such as (Pure, 10, 20 %), and increases in the ratios (30, 40, 50 %) NiO. The average Grain size decreased with increasing (NiO) in pure and the ratios (10, 20 %) NiO while increases in (30, 40, 50 %) NiO as shown in the Table 1.
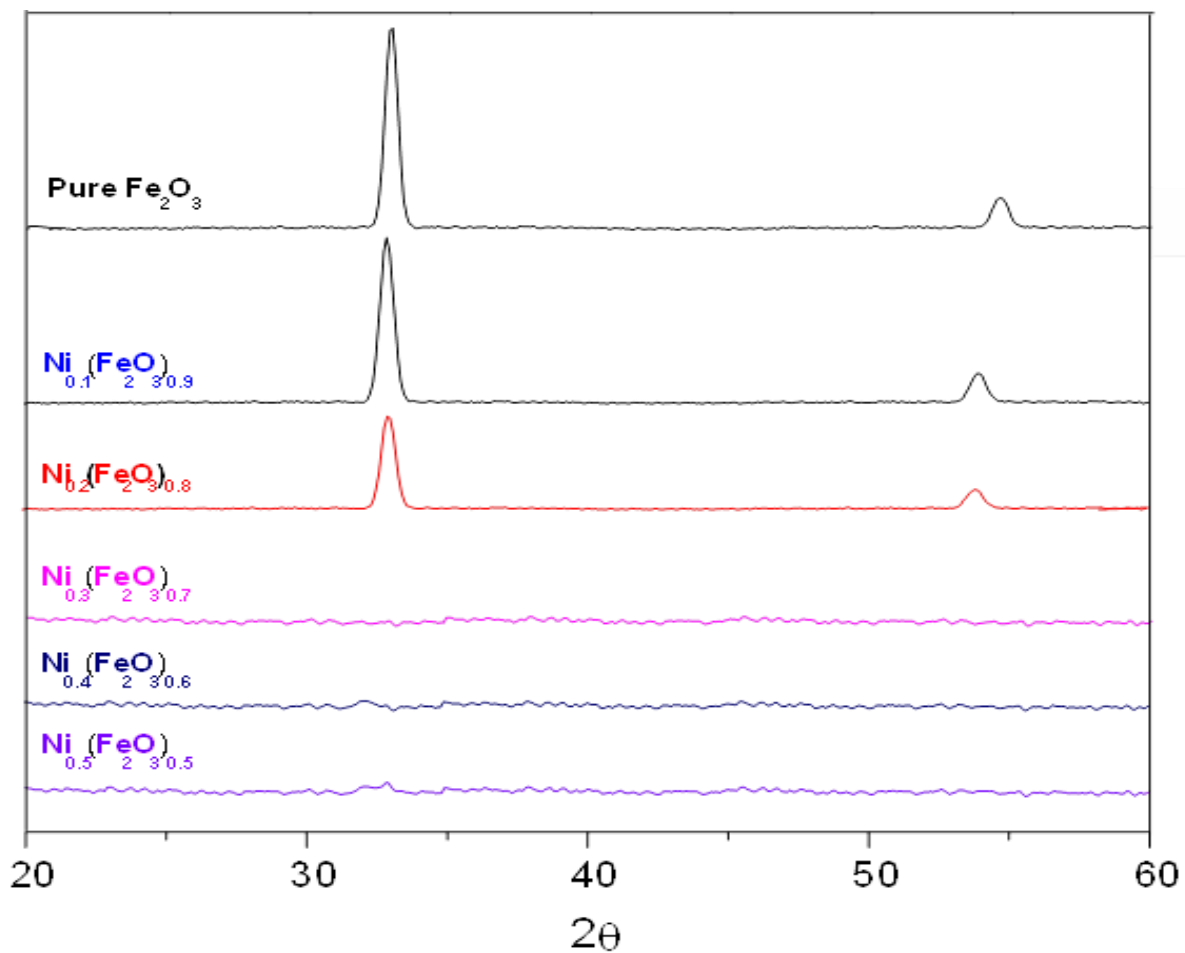
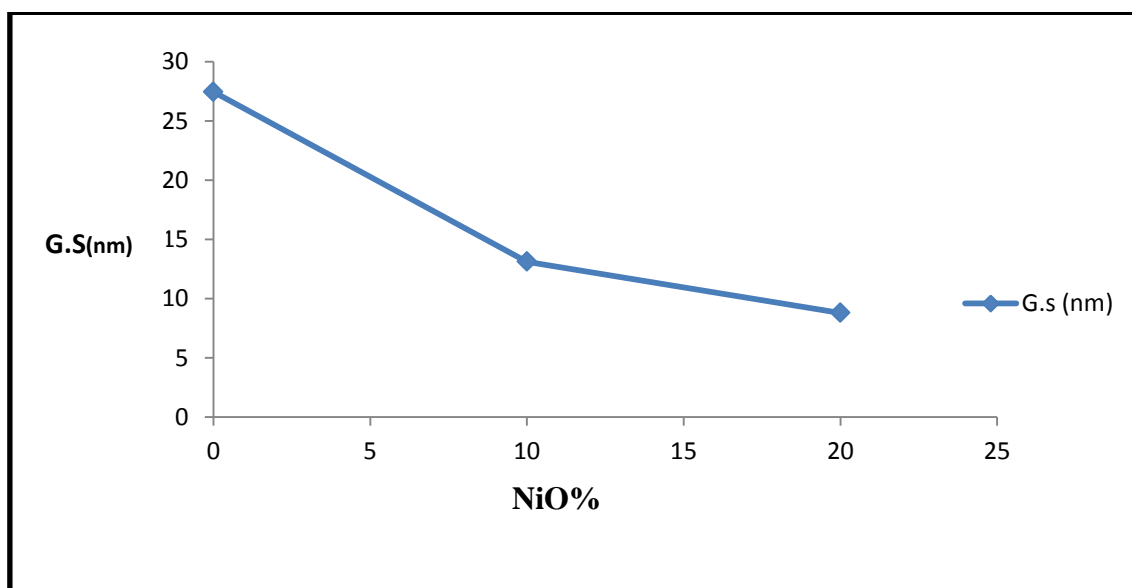**Fig. 1.** XRD patterns of films Fe_2O_3 and Fe_2O_3 - NiO.

Fig. 2. Grain size for films Fe_2O_3 and Fe_2O_3 - NiO.
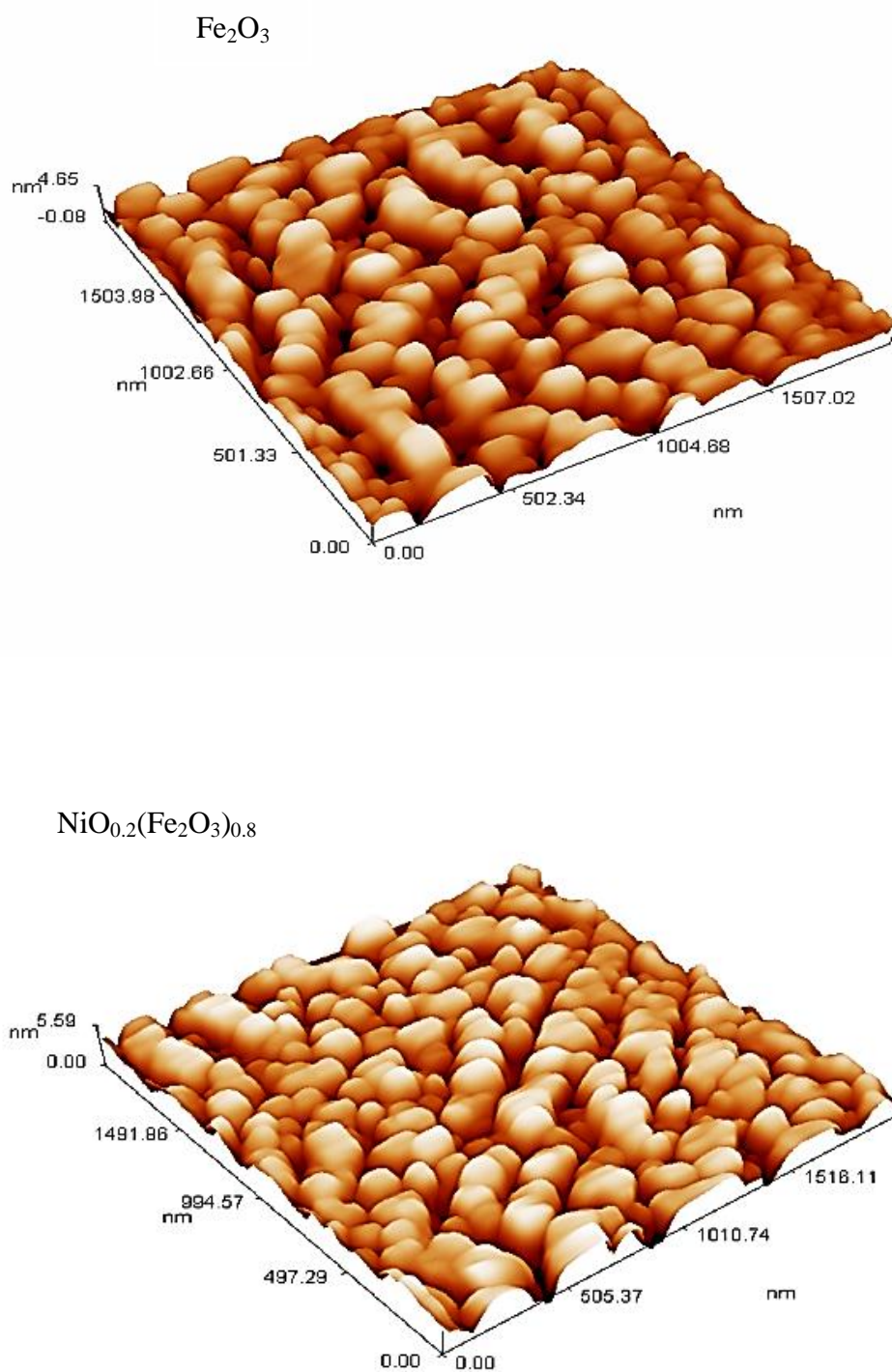
Fe_2O_3

$NiO_{0.2}(Fe_2O_3)_{0.8}$

Fig. 3. Three dimensional atomic force images of films Fe_2O_3 - NiO.

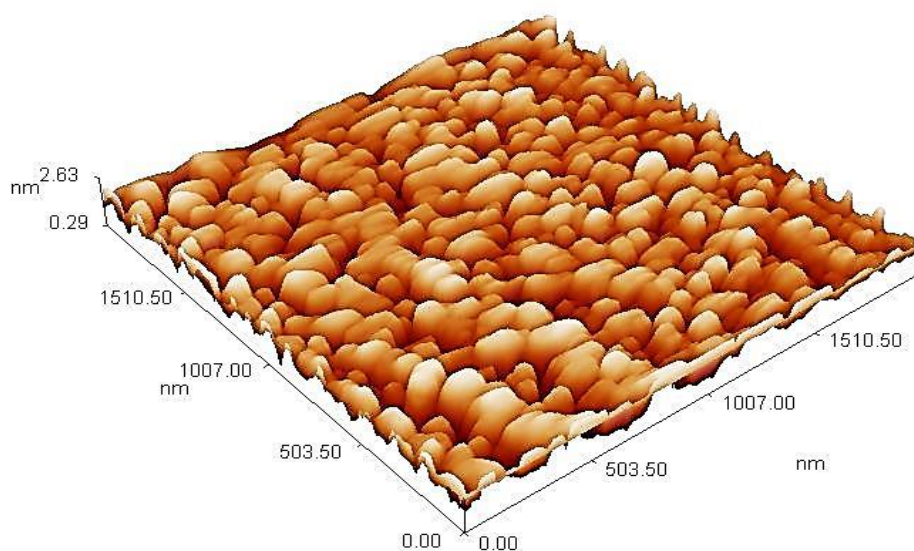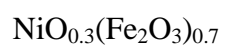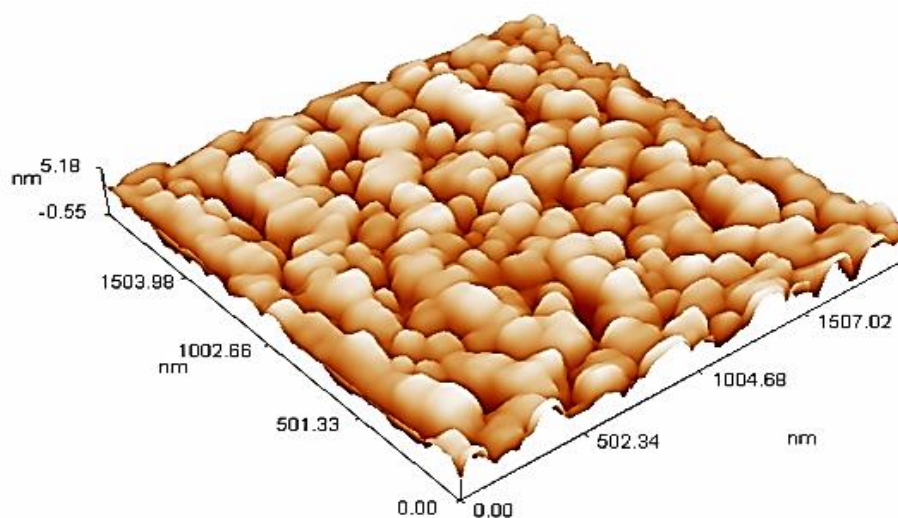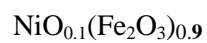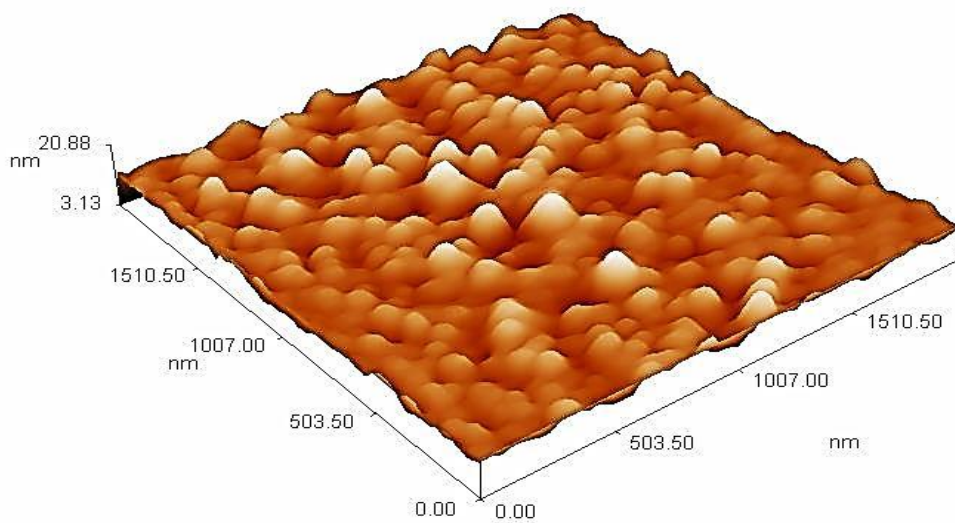$NiO_{0.1}(Fe_2O_3)_{0.9}$

$NiO_{0.3}(Fe_2O_3)_{0.7}$

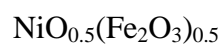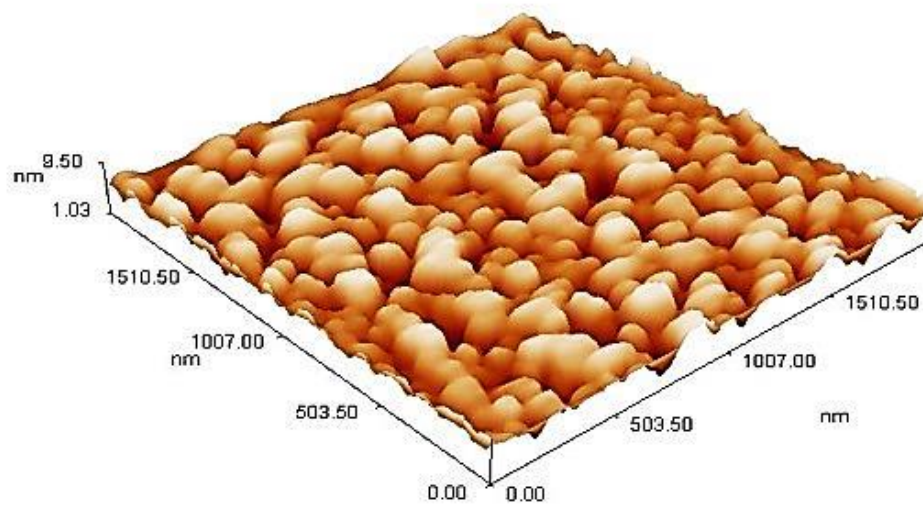**Fig. 3(continue).** Three dimensional atomic force images of films Fe_2O_3 - NiO.

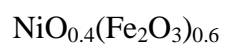$NiO_{0.4}(Fe_2O_3)_{0.6}$

$NiO_{0.5}(Fe_2O_3)_{0.5}$

Fig. 3(continue). Three dimensional atomic force images of films Fe_2O_3 - NiO.

Table 1. Average grain size, surface roughness and RMS values for the as deposited thin films.

Sample	Avg. Diameter (nm)	Surface Roughness (nm)	RMS (nm)
Fe_2O_3 (Pure)	92.83	0.832	1.03
Fe_2O_3 90 % - NiO 10 %	90.49	0.772	0.949
Fe_2O_3 80 % - NiO 20 %	82.58	0.756	0.944
Fe_2O_3 70 % - NiO 30 %	82.10	0.293	0.368
Fe_2O_3 60 % - NiO 40 %	82.42	1.11	1.4

3. 2. Optical properties

Figure (4) shows the optical transmittance spectra of Fe_2O_3 - NiO thin films in the wavelength range of (300-900) nm. The films are transparent in the visible and infrared region of the electromagnetic spectrum the transmittance increased as the NiO content increase The increase in optical transmittance can be attributed to the increase of structural homogeneity and crystallinity [15].
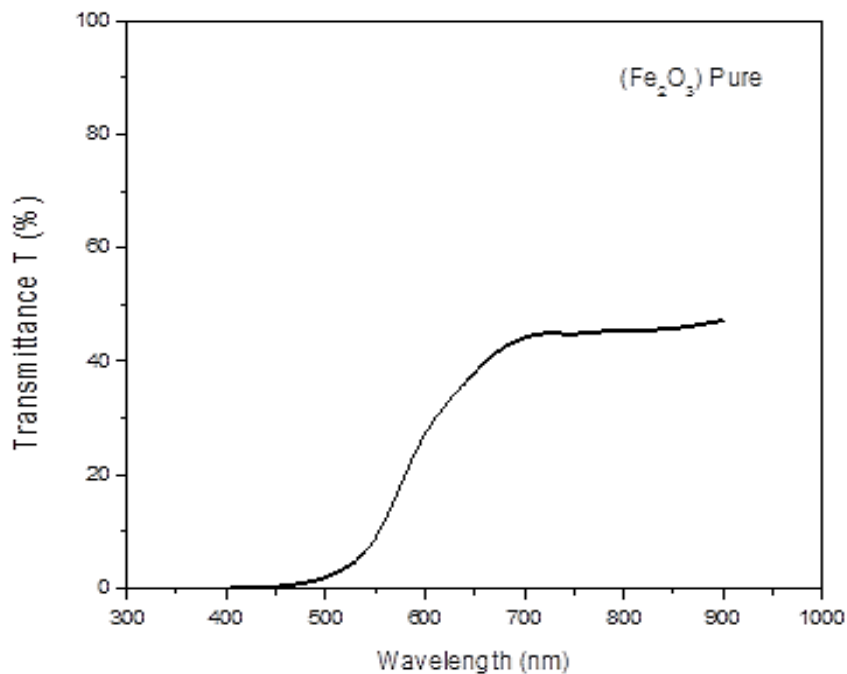

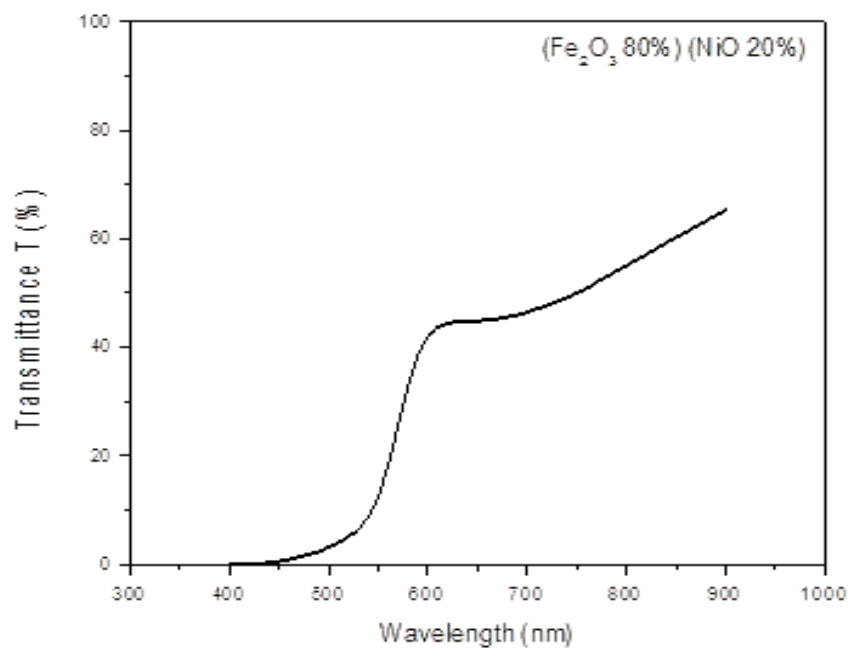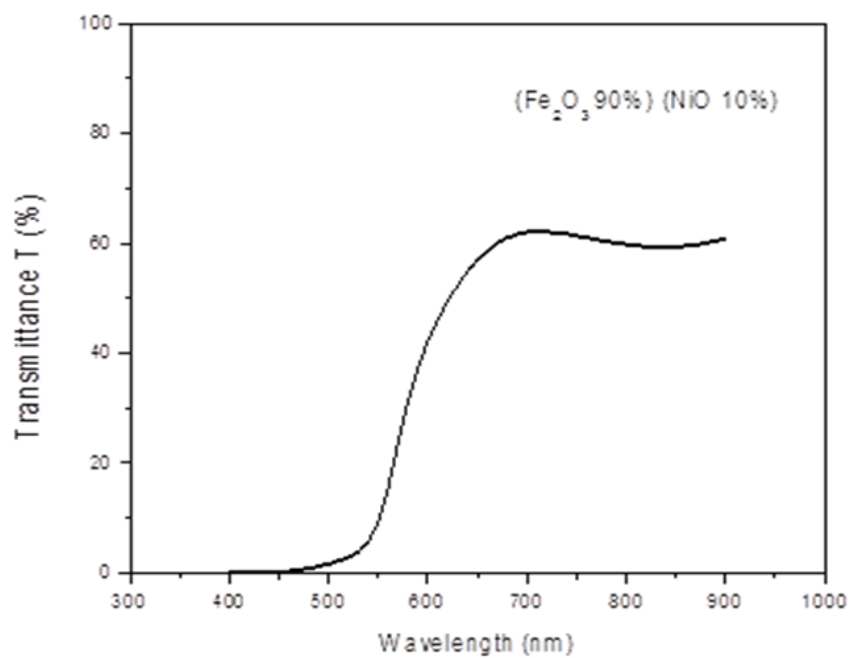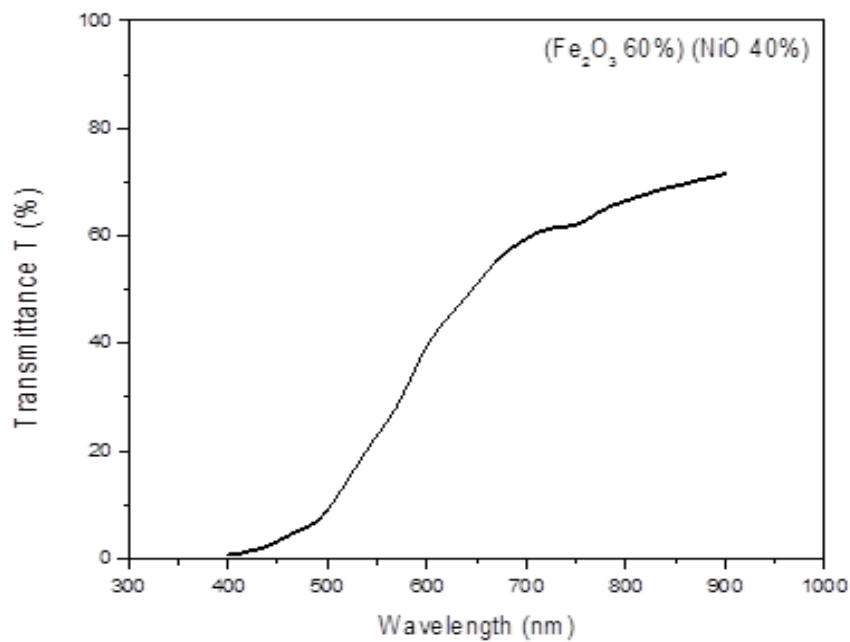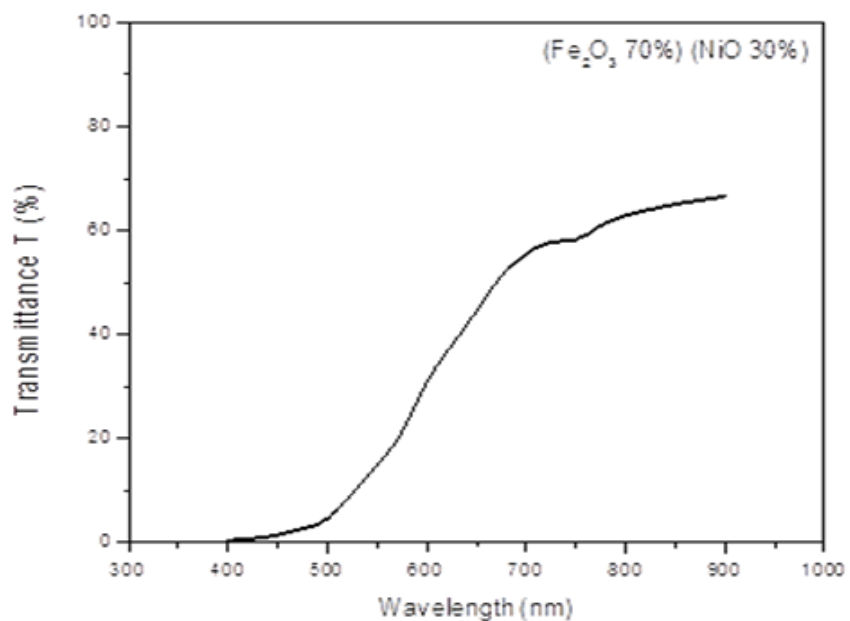**Fig. 4.** Variation of (T) as a function of wavelength for Fe_2O_3 - NiO films.

Fig. 4(continue). Variation of (T) as a function of wavelength for Fe_2O_3 - NiO films.

Fig. 4(continue). Variation of (T) as a function of wavelength for Fe_2O_3 - NiO films.
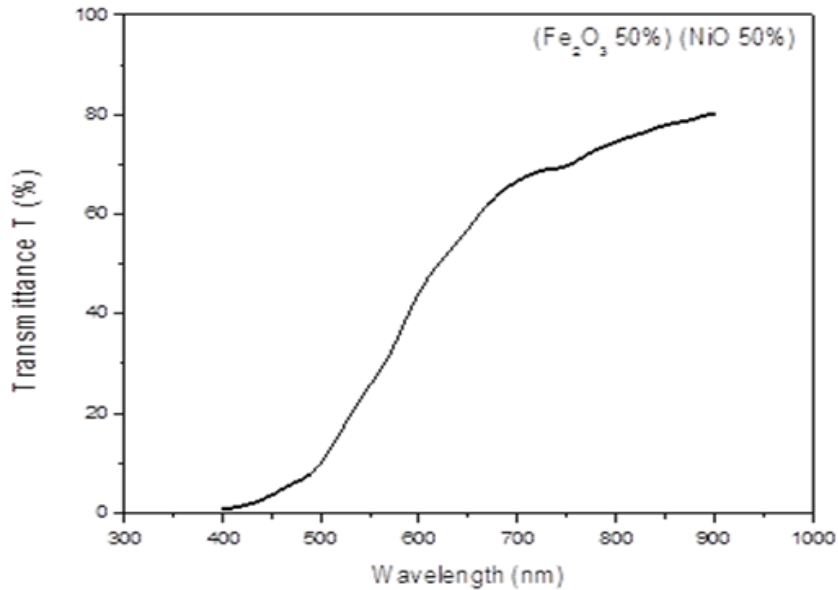
Fig. 4(continue). Variation of (T) as a function of wavelength for Fe_2O_3 - NiO films.

Figure (5) shows the absorbance of Fe_2O_3 - NiO films .It is clear that the films have high absorption at short wavelength, the figure show that the absorption decreases with increasing ratios of Nickel.

The change of reflectance as a function of wavelength in the range (300-900) nm is shown in Fig (6) It is seen from the figure that the reflectance decreases with the increased of nickel ratio. The optical band gap of the films is determined by applying Tauc model [16] in the high absorption region by the relation [16]

$$\alpha \, h\nu = B_o \, (h\nu - E_g)^r \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

where $h\nu$ is the photon energy, E_g is the optical energy gap, B_o is a constant. For direct transition r = 1/2 or 2/3 and the former value was found to be more suitable for Fe_2O_3 thin films.

The optical energy gap is determined by plotting $(\alpha h\nu)^2$ as a function of photon energy as shown in Fig. 7.

The value of the optical energy gap were increase with the increasing of nickel content. it is well known that the energy gap of the semiconductor increases with the decrease of the grain.
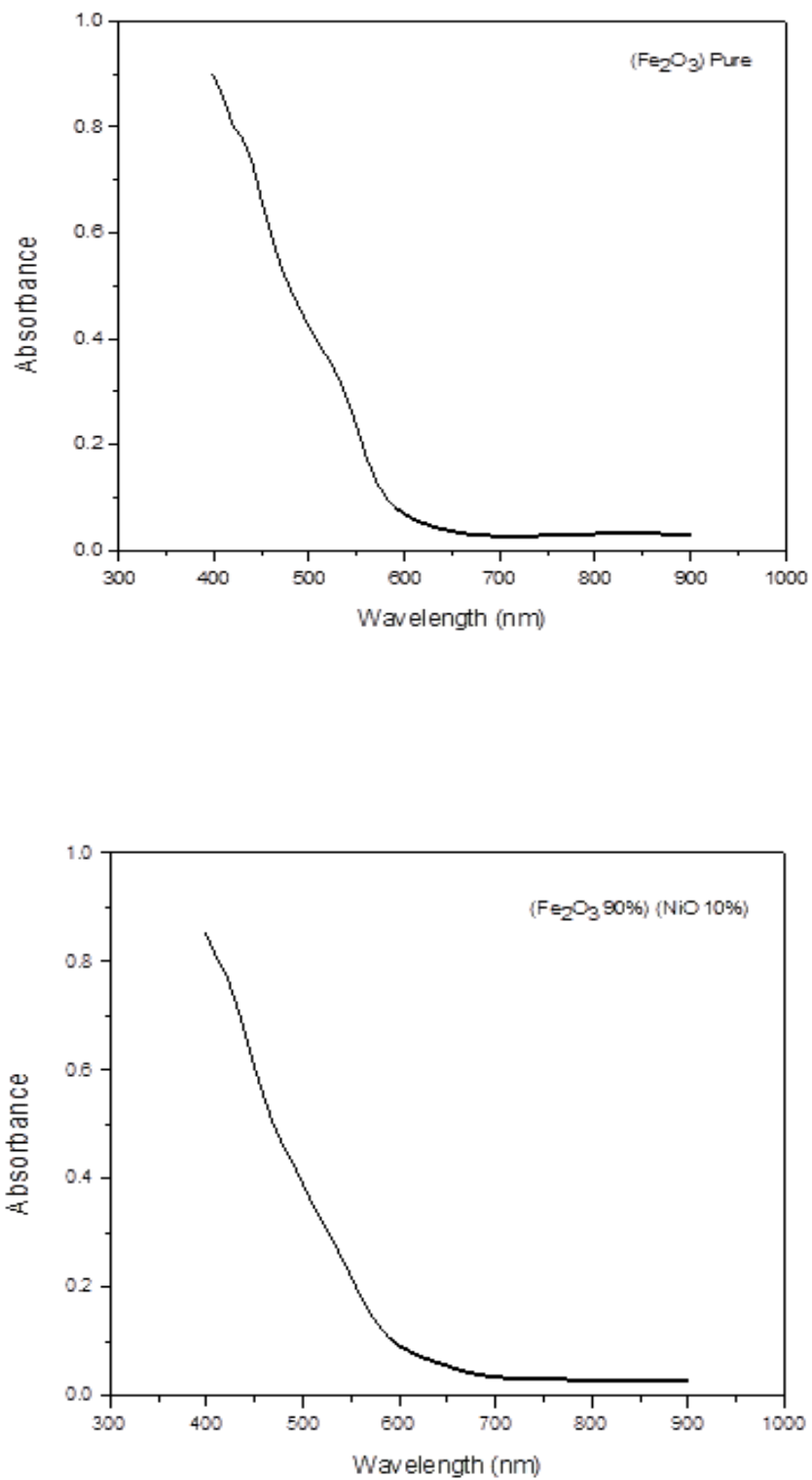
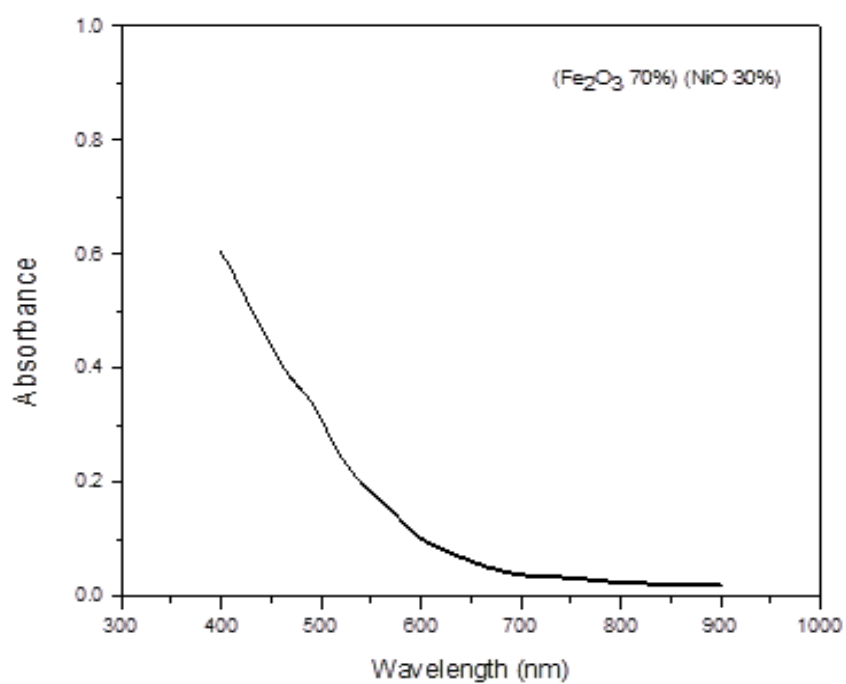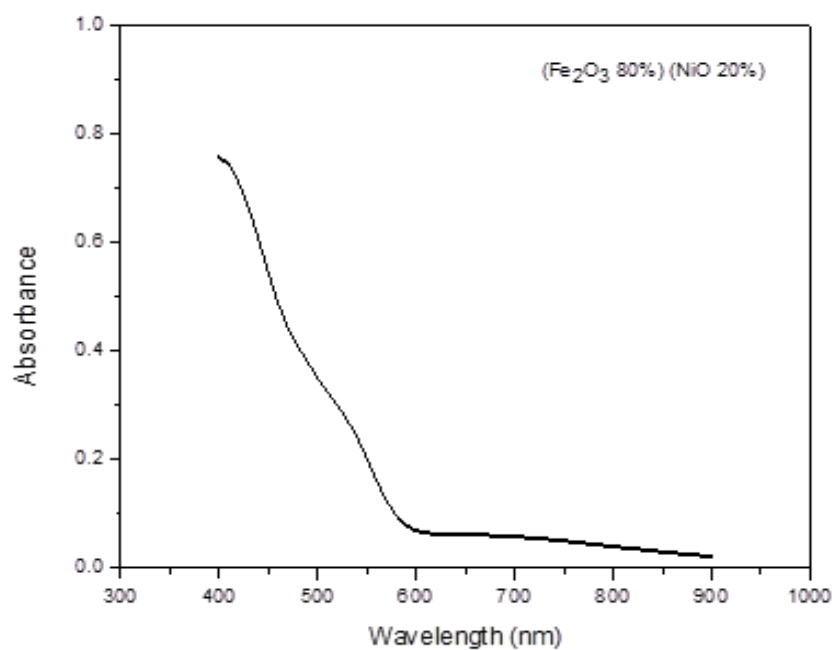**Fig. 5.** Absorbance versus wavelength for Fe_2O_3 - NiO thin films.

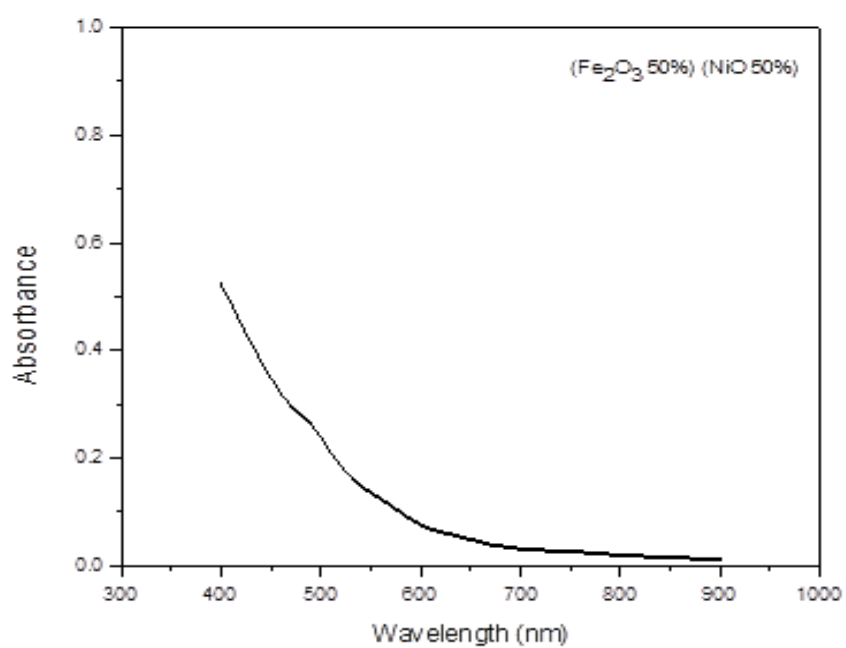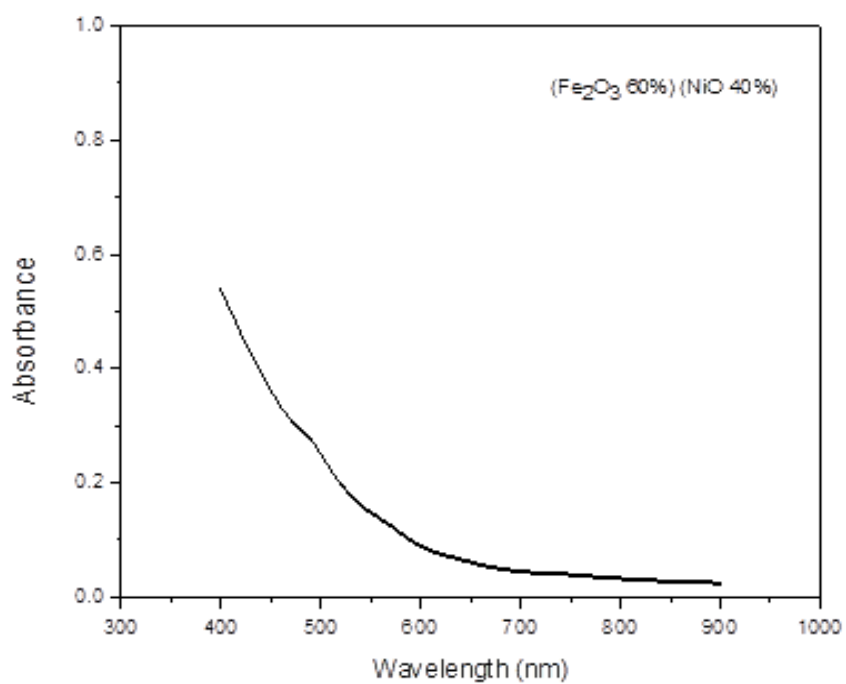**Fig. 5(continue).** Absorbance versus wavelength for Fe_2O_3 - NiO thin films.

Fig. 5(continue). Absorbance versus wavelength for Fe_2O_3 - NiO thin films.
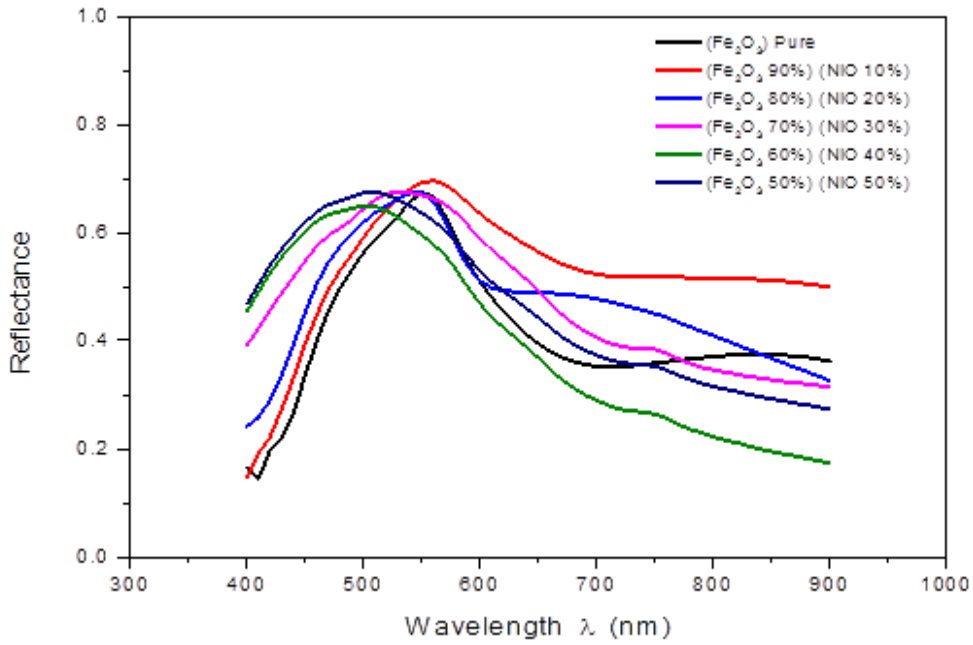
Fig. 6. The reflectance versus wavelength for Fe$_2$O$_3$ - NiO thin films.

Fig. 7. Variation of vs. photon energy for Fe$_2$O$_3$ - NiO thin film.
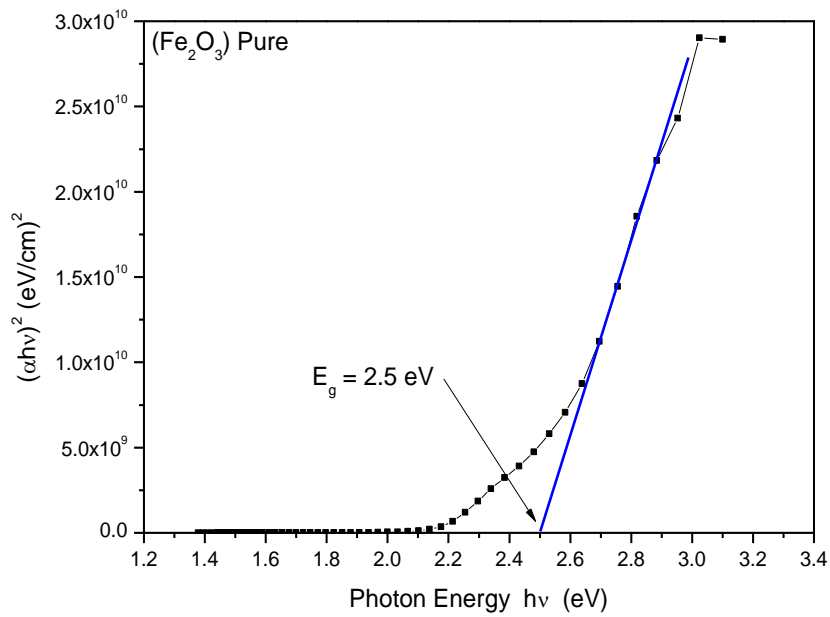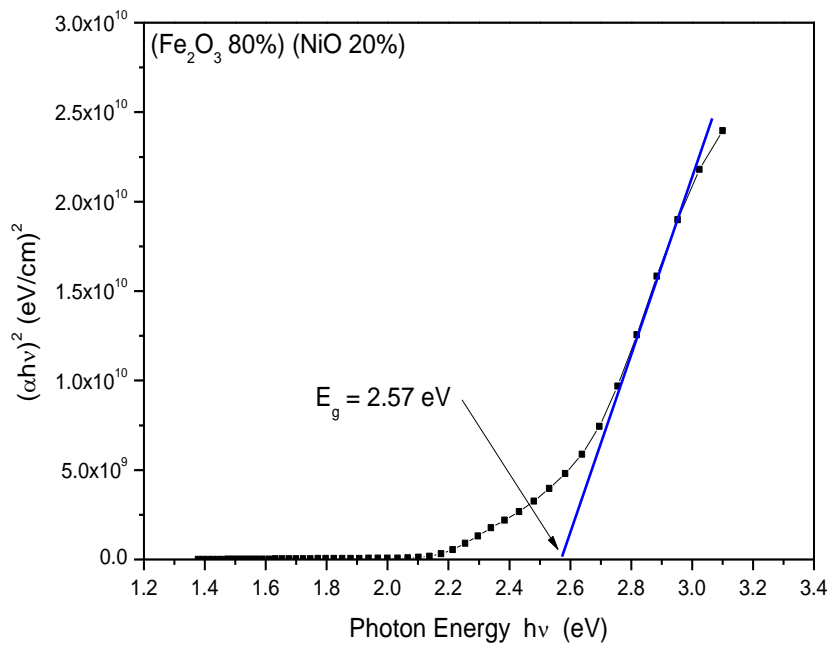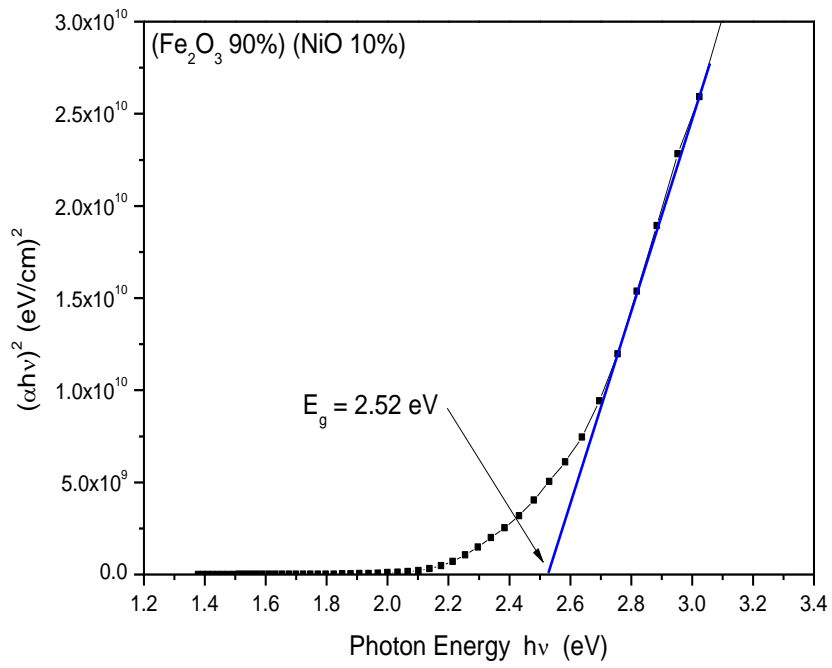
Fig. 7(continue). Variation of vs. photon energy for Fe_2O_3 - NiO thin film.
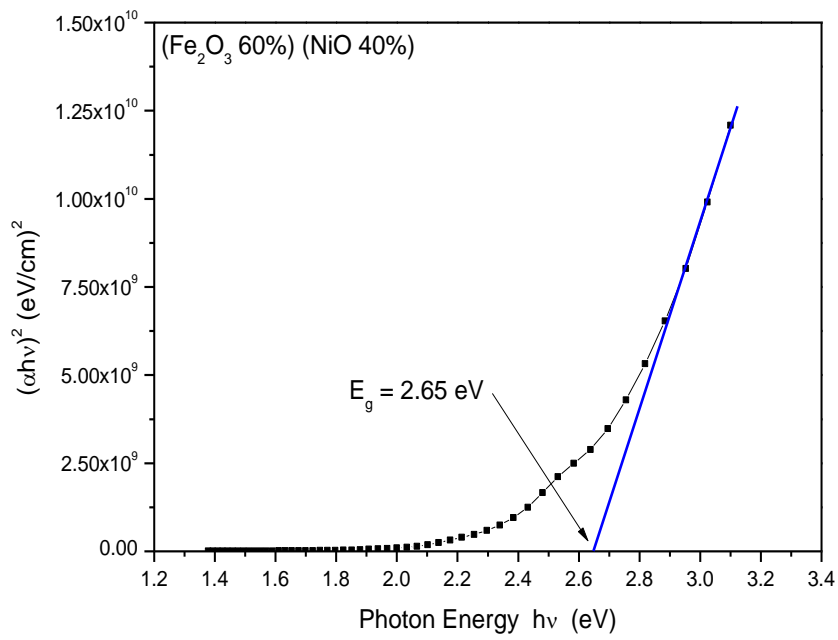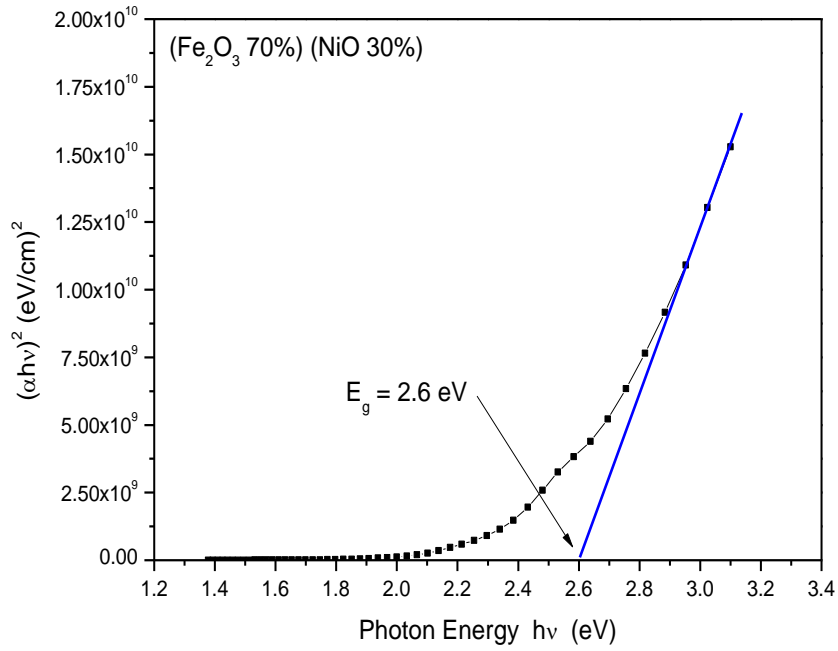
Fig. 7(continue). Variation of vs. photon energy for Fe_2O_3 - NiO thin film.
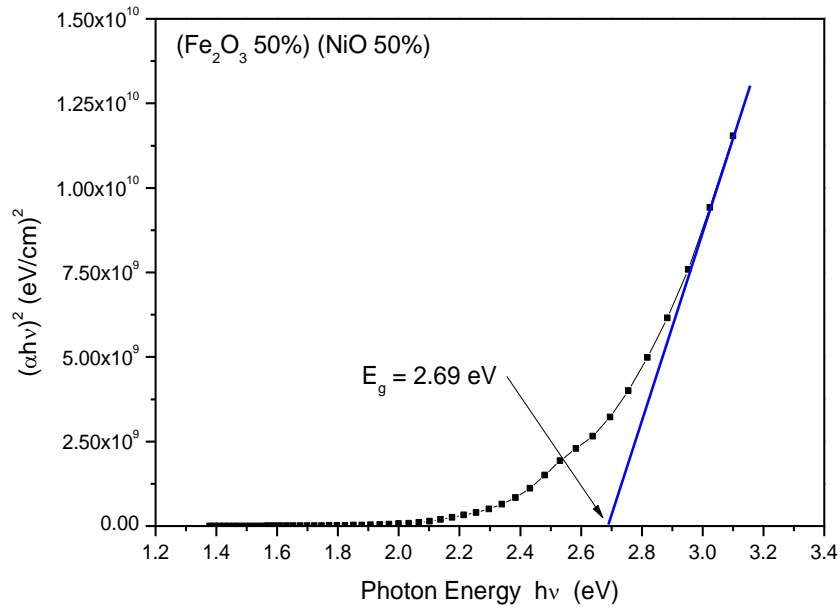
Fig. 7(continue). Variation of vs. photon energy for Fe_2O_3 - NiO thin film.

Figure 8 illustrates the variation of (ε_r) as a function of photon energy. It is clear from the figure that (ε_r) decrease with increasing of (NiO) content. Figure (9) illustrates
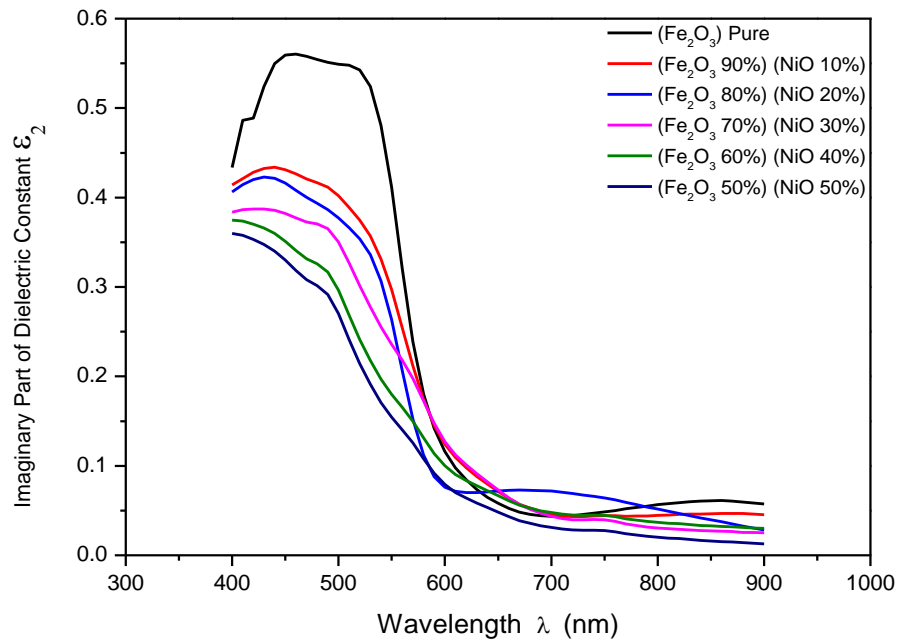
Fig. 8. Variation of ε_r as a function of wavelength for Fe_2O_3 - NiO films.

the variation of (ε_i) as a function of wavelength. The figure shows a decrease of (ε_i) with increasing of wavelength and that, (ε_i) decrease with increasing ratio of (NiO).

Fig. 9. Variation of ε_i as a function of wavelength for Fe_2O_3 - NiO films.

Fig. 10. Refractive index as a function of wavelength for Fe_2O_3 - NiO thin films.

The refractive indices (n) of the thin films were determined from equation (2) [18-32]. As shown in Fig. (10), the refractive indices of the films are influenced by the NiO content. The refractive indices decrease as the NiO content increases and the refractive index decrease as the wavelength increases.
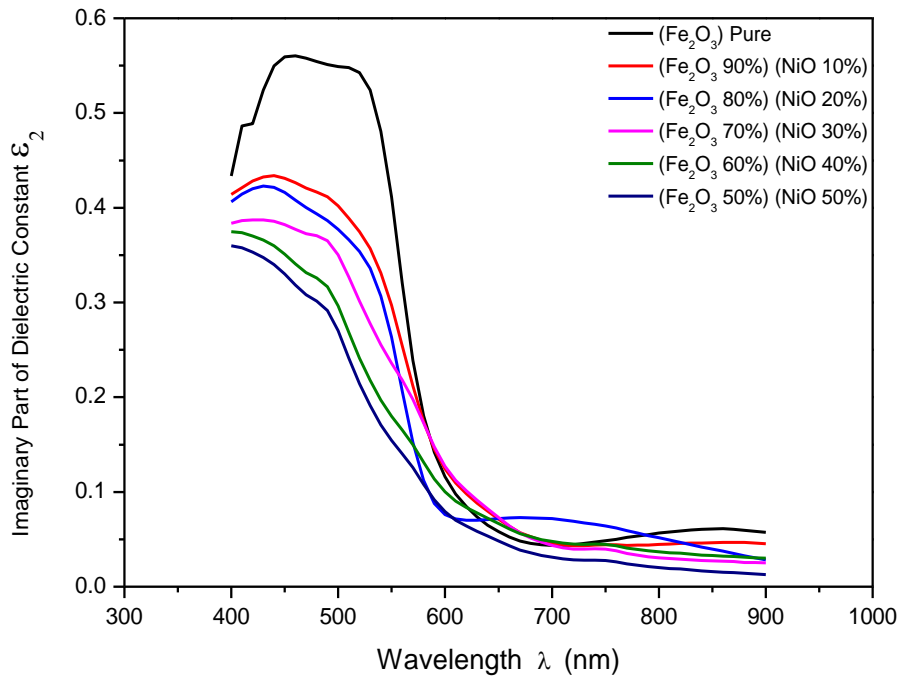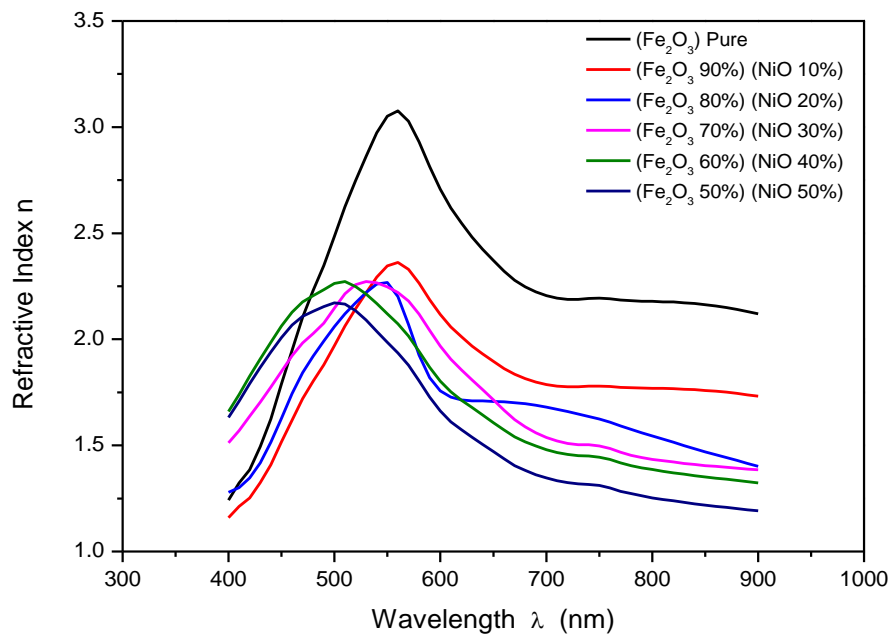
$$n_o = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k_o^2} \ldots\ldots\ldots(2)$$

where (n) is the refractive index , (R) is the reflectance.

4. CONCLUSIONS

Fe$_2$O$_3$ thin films were prepared using a spray pyrolysis technique onto a glass substrate at temperature of 450 °C. X-ray diffraction (XRD) analyses show that Fe$_2$O$_3$ and the ratio of (10, 20 %) were polycrystalline in nature with a Rhombohedral wurtzite structure and a preferred orientation along (104) plane. A decrease in the values of the crystallization was noticed by the increase ratio of (NiO).

The rest ratios (30, 40, 50 %) NiO have now been amorphous.

The atomic force microscope (AFM) images show that the average roughness and the square root of the average roughness square (RMS) of the films decrease with increasing (NiO) concentrations (Pure, 10, 20 %) and increases in the ratios of (30, 40, 50 %) NiO.

From UV-Visible spectrometer, the absorption spectrum was measured also, the optical constant such as real and imaginary dielectric constant were determined and indicated that they decreased with the increase of the wavelength and the of ratio of (NiO) and the value of the optical energy gap increase with increasing ratio of NiO.

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