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Nickel Doping and Annealing Effects on the Structural and Optical Properties of Iron Oxide Thin Films

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In this paper, we studied the effect of Ni doped Iron Oxide (Fe_2O_3: Ni) with two different concentrations (0.8:0.2) and (0.9:0.1) thin films prepared by chemical spray pyrolysis method on glass substrates and also the annealing effect on the structural and optical properties of the deposited films. The crystal quality and surface morphology of the films were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), while the optical properties were studied calculated from transmission and absorption spectra. XRD results showed that α-Fe_2O_3 (Hematite) is the most abundant phase with strong peak [110] shown at 2θ=33.15°-33.17° with full width at half maximum (FWHM) of (0.446-0.27) degree for the three samples before annealing; and 2θ= 33.155°-33.175° with a FWHM of (0.37-0.23) degree after annealing at temperature 300°C. The band gap of the samples obtained from transmittance spectra was found to vary from 2.14 to 2.43 eV for pure Fe_2O_3 and Fe_2O_3: Ni with two different concentrations thin films before annealing; and from 2.33 eV to 2.64 eV after annealing. The results revealed that the structural and optical properties of the samples improved by increasing the Ni concentration and also after annealing.

Keywords: Fe_2O_3; Chemical spray pyrolysis; XRD; Optical properties
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1. Introduction

From the literature of the basic research, iron (III) oxide is a convenient material for the general study of polymorphism and the magnetic and structural phase transitions of nanoparticles. The existence of amorphous Fe_2O_3 and four polymorphs (alpha (α), beta (β), gamma (γ) and epsilon (ε) are appropriately known [1]. The most common numerous polymorphs, the hexagonal corundum structure "α" and cubic spinel structure "γ", have been found in nature as hematite and maghemite minerals. The other polymorphs such as the cubic bixbyite structure "β" and orthorhombic structure "ε", as well as nanoparticles of all forms, have been synthesized and extensively investigated in recent years [1,2].

Hematite (α-Fe_2O_3), the most frequent oxide with another fraction element like Nickel have entered many applications according to its optical and magnetic properties. From an optical point of view, α-Fe_2O_3 possesses a band gap (~2.2 eV) that lies in the visible range, and has a relatively high refractive index. Therefore, it has been investigated as a potential candidate for many optical applications, such as solar energy conversion, electrochromism, photocatalysis, interference filters, and photo-oxidation of water [3-5].

Fe_2O_3 has a number of additional properties, namely, low cost, abundance, non toxic, high resistivity toward corrosion in addition; it is also easy for synthesis [6-8]. Recently Fe_2O_3 nanostructures have attracted much attention in various morphologies such as nanoparticals, nanorods, nanosheets, nanowires and quantum dots [9-25].

Several methods have been reported for the preparation of iron oxide such as sol-gel method, Reactive evaporation, RF sputtering, atomic layer deposition, metal organic chemical vapor deposition (MOCVD) and chemical spray pyrolysis [25-31].

In this work, we I report the preparation Fe_2O_3: Ni with two different concentrations (0.8:0.2) and

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(0.9:0.1) thin films on glass substrates using (chemical spray pyrolysis method) and subsequently the properties of the deposited films were characterized by various tools. The structural properties of the samples were characterized by XRD, SEM, and EDX, while the optical properties were studied by transmission and absorption spectra.

2. Experimental work

Thin films of α-Fe_2O_3 and mixed with Ni have been prepared by chemical spray pyrolysis. Two kinds of aqueous solutions; 0.9 ml and 0.8 ml of Iron acetate $Fe(CO_2CH_3)_2$ ($CO_2CH_{3)2}$ to 0.1 ml and 0.2 ml of nickel acetate $Ni(CH_3COO)_2$ were chosen as the sources of iron and nickel respectively.

The substrates cleaning process was achieved by inserting the glass substrates in chromic acid for an hour then washed with distilled water. Prior to the deposition; these substrates were treated in an ultrasonic bath for 20 min. The selected optimum conditions were achieved by the following: substrate temperature 300^{o}C, the sprying rate was maintained at 5ml/min, the distance between the nozzle and the substrate was fixed at 29 cm and the spray time was kept at 7 seconds following by 2 minutes waiting to avoid excessive cooling. The thickness of deposited films and it was found to be in the range of (300±20 nm).

3. Results and discussion

Figures (1) and (2) show a typical XRD pattern for pure Fe_2O_3 and Ni doped Fe_2O_3 (Fe_2O_3: Ni) with two different concentrations (0.9:0.1) and (0.8:0.2), before and after annealing with 300^{o}C, the diffraction patterns were obtained with 2θ from 20^o to 60^o. X- ray analysis show that α-Fe_2O_3 (Hematite) is the most abundant phase and identified in all the prepared samples. The diffraction peaks before annealing were [104], [024] and [110] which represent the [113] reflection appeared; the [110] plane shows the strongest peak at 2θ=(33.15-33.17) degree with FWHM of 0.446^o-0.27^o for the three samples before annealing; and 2θ=(33.155-33.175) degree with a FWHM of 90.37-0.23) degree after annealing at temperature 300^{o}C in vacuum.

All the peaks were well matched with the standard data JCPDS (33-0664). The wide broadening of strong peaks indicate the nanostructure of the prepared films. According to the kinematical theory, XRD peaks get broadened when crystallites become smaller [32]. The average crystallite size (d) was calculated by using Scherrer's equation [33]:

$$d = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

where B is the FWHM of XRD, λ is the x-ray wavelength (Cu K_α=0.154 nm), θ is the Bragg diffraction angle, and K is a correction factor which is taken as 0.9

The XRD spectra in Fig. (1) show that as the Ni concentration increases the diffraction peak becomes sharper with decreased in FWHM, which indicating that the crystalline quality of the film is enhanced. The intensity and the FWHM of the diffraction peak are found to be dependent on the Ni concentration, in addition, the (110) peak location for the three films are nearly the same as shown in Fig. (1). As well; Fig. (2) also shows the annealing effects in improving the crystal quality of the three deposited thin films. Table (1) summarizes XRD data for the three films.

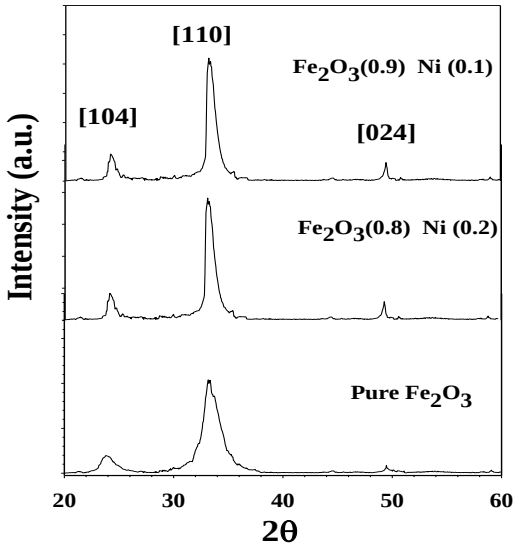

Fig. (1) XRD patterns for the three samples before annealing

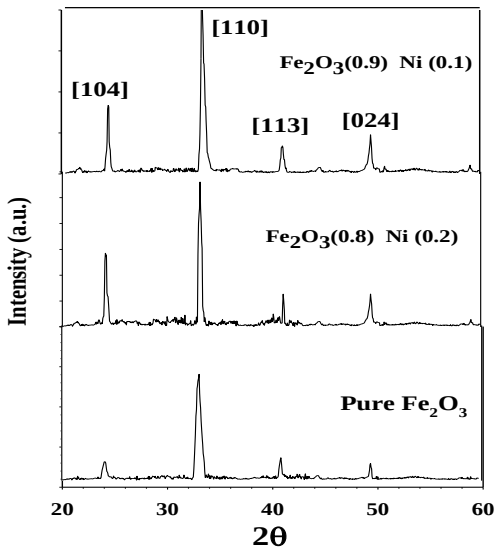

Fig. (2) XRD patterns for the three samples after annealing (300^{o}C)

Figures (3), (4) and (5) show the SEM images of the pure Fe_2O_3 and Ni doped Fe_2O_3 samples with two different concentrations respectively.

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These Figures show that all the deposited films consist of some columnar structured grains with uniform particle size distribution which indicates that the films ware well grown. The grain size gradually increases and become more uniform in distribution with increasing the Ni concentration this can be explained as an addition in Ni can enhance the diffusion of elements and cause the particles to grow large and this result is in agreement with XRD results.

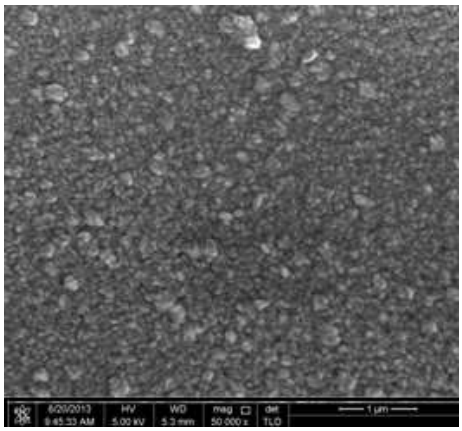

Fig. (3) SEM image of Fe_2O_3

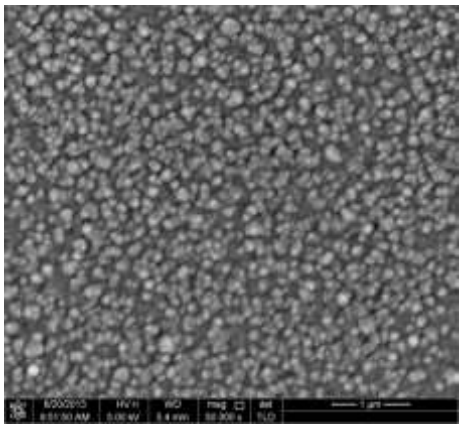

Fig. (4) SEM image of Fe_2O_3 (0.8): Ni (0.2)

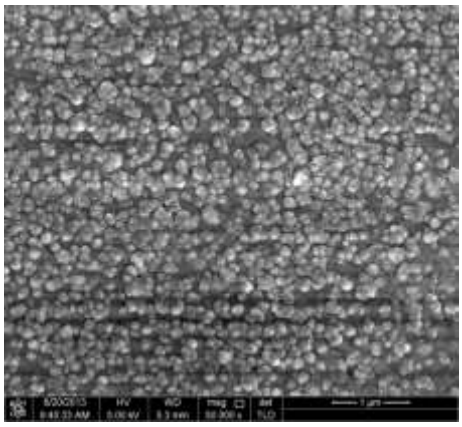

Fig. (5) SEM image of Fe_2O_3 (0.9): Ni (0.1)

The EDX of the samples are shown in Fig. (6a and b) which confirm the elemental composition of Fe_2O_3 and Ni doped Fe_2O_3 deposited on glass substrates. The presence of Si peak in spectrum is due to the glass substrate. It is clearly seen that the untapped undoped sample composed iron and oxygen; while the doped sample composed nickel in addition to iron and oxygen.

Figures (7) and (8) show the optical transmittance as a function of wavelength for the three prepared thin films before and after annealing at 300 ^oC.

Figure (7) shows that the threshold of the optical absorption shifts to shorter wavelength as the Ni concentration increase (Blue shift) and the transmittance increases sharply from 550 nm, it was shown that the value of transmittance increase for all the samples after annealing at 300^oC as shown in Fig. (8), in comparison with its value before annealing.

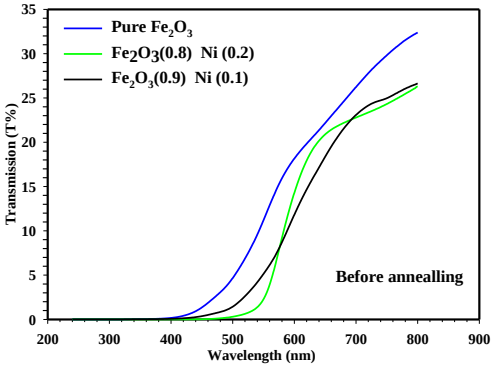

Fig. (7) Transmission spectra of the pure Fe_2O_3 and Ni doped Fe_2O_3 samples before annealing

Also, it can be seen that the transmission values of the film are low at short wavelengths (≤ 340nm) and high at long wavelengths. So, the films behaved as an opaque material because of their high absorbing properties at short wavelengths and as a transparent material at long wavelengths as shown in the figures.

Since Fe_2O_3 and Ni doped Fe_2O_3 is considered as a direct band gap semiconductor [34-37], the optical energy gap of Fe_2O_3 and Fe_2O_3: Ni thin films can be calculated by using the well-known Tauc relation [33]:

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \qquad (2)$$

where α is the absorption coefficient, A is a constant, h is Planck's constant, ν is the frequency of light and E_g is the [optical] band gap energy and n= ½ (for direct transition mode materials) [33]

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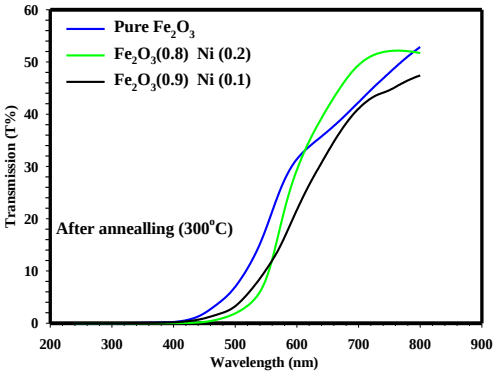

Fig. (8) Transmission spectra of the pure Fe_2O_3 and Ni doped Fe_2O_3 samples after annealing with 300°C

The band gap could be derived by extrapolating the linear portion of the graphs of the hν axis. From the plot the E_g value was determined to be 2.14 eV, 2.23 eV and 2.45 eV for pure Fe_2O_3 and Fe_2O_3: Ni with two different concentrations thin films before annealing; and 2.33 eV, 2.43 eV and 2.64 eV for the three samples after annealing. The results show that the band gap is slightly red-shifted by increasing Ni doping concentration.

Figures (9) and (10) show the Tauc plot of $(\alpha h\nu)^2$ versus $h\nu$ for the three samples before and after annealing respectively, it can be seen a linear dependence of $(\alpha h\nu)^2$ versus $h\nu$.

Our results are in agreement with those reported by Salim [38] who prepared Fe_2O_3 on Si substrates.

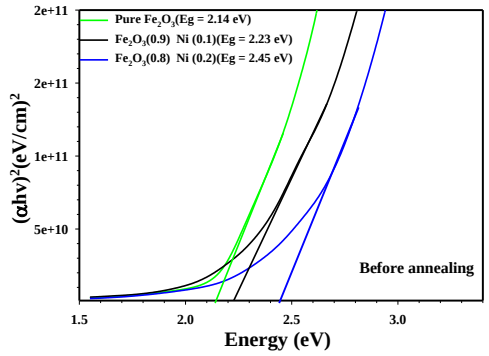

Fig. (9) Tauc plots of the deposited pure Fe_2O_3 and Fe_2O_3:Ni with two different concentrations thin films before annealing

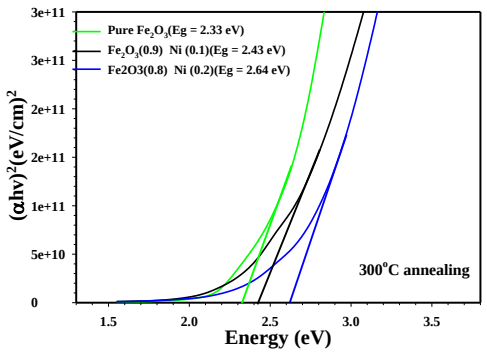

Fig. (10) Tauc plots of the deposited pure Fe_2O_3 and Fe_2O_3:Ni with two different concentrations thin films after annealing in 300°C

Table (1) X-ray diffraction data summary of Fe_2O_3 and Fe_2O_3: Ni with two different concentrations (0.8:0.2) and (0.9:0.1) respectively, before and after annealing with 300°C

Substrate	Pure Fe_2O_3	Fe_2O_3(0.8)/Ni (0.2)	Fe_2O_3(0.9)/Ni (0.1)
2θ (°) before annealing	33.150	33.160	33.170
2θ (°) after annealing	33.155	33.165	33.175
FWHM (°) before annealing	0.446	0.271	0.297
FWHM (°) after annealing	0.370	0.190	0.230
Crystallite size (nm) before annealing	18.394	30.272	20.664
Crystallite size (nm) after annealing	22.163	43.172	35.664

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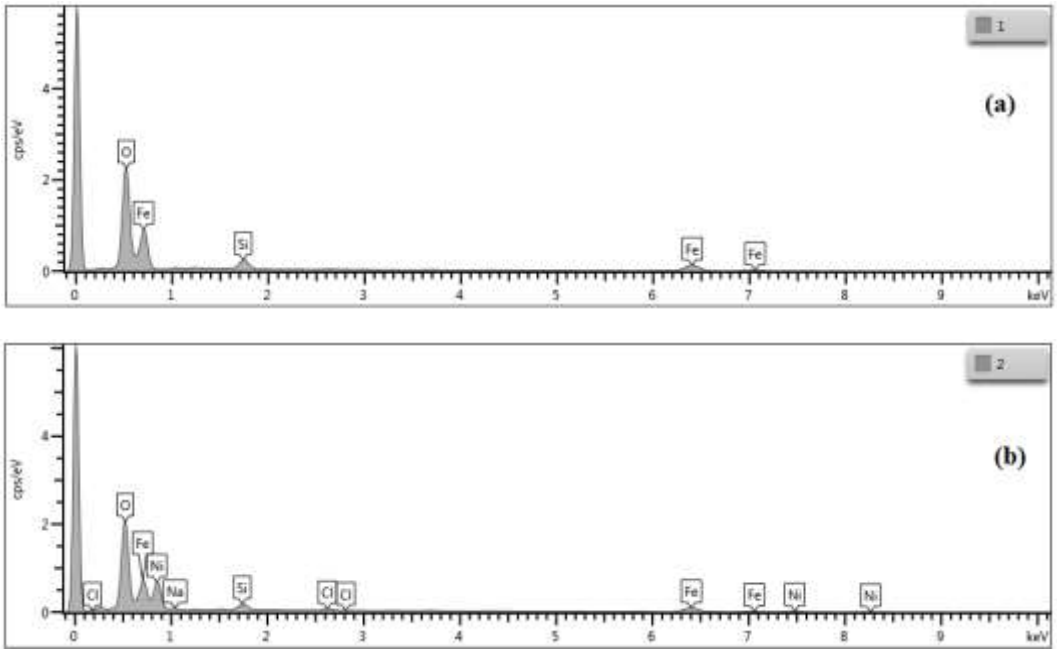

Fig. (6) EDX images of (a) pure Fe_2O_3 and (b) Ni doped Fe_2O_3 thin films

4. Conclusions

The effects of Fe_2O_3:Ni with two different concentrations (0.8:0.2) and (0.9:0.1) thin films prepared by chemical spray pyrolysis method and also the annealing effect on the structural and optical properties of Fe_2O_3 have been investigated. XRD results showed that α-Fe_2O_3 (Hematite) is the most abundant phase and identified in all the prepared samples with strong peak [110] plane shown at 2θ= 33.15°- 33.17° with FWHM of 0.446°- 0.27° for the three samples before annealing; and 2θ=33.155°-33.175° with a FWHM of 0.37°-0.23° after annealing at temperature 300°C. The band gap of the samples obtained from transmittance spectra measurement was found to vary from 2.14 eV to 2.43 eV for pure Fe_2O_3 and Fe_2O_3:Ni with two different concentrations thin films before annealing; and from 2.33 to 2.64 eV for the three samples after annealing with 300°C. The results revealed that the structural and optical properties of the samples improved by increasing the Ni concentration and also after annealing.

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