Structural and Optical Characterization of Sprayed nanostructured Indium Doped Fe$_2$O$_3$ Thin Films

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Abstract: Nanostructured pure and Indium doped iron oxide thin films were deposited via spray pyrolysis technique (SPT). The effects of Indium (2 and % 4) concentration was studied. X-ray diffraction patterns disclosed that Fe$_2$O$_3$ films have a rhombohedral crystalline of α-Fe$_2$O$_3$ phase and their crystallite size was vary from (12.13 – 13.84) nm with Indium content. The strain(%) parameter decrease from 28.57 to 25.04, AFM images of films show changes in morphology with decreased in surface roughness from 2.75 nm to 1.7 nm with Indium 4% doping. The 3-D images and grain size distribution are illustrated that they exhibit spherical nano-grains ranged from 72.72 nm for pure Indium to 51.22 nm for 4% Indium doped Fe$_2$O$_3$. The transmittance decreases with increasing Indium concentration. The bandgap energy of Fe$_2$O$_3$ thin film was 2.75 eV and it decreases to 2.55 eV for Fe$_2$O$_3$:4% In.

Keywords: In-doped Fe$_2$O$_3$ thin films, spray pyrolysis technique, surface morphology, XRD, bandgap.

1-Introduction

Fe$_2$O$_3$ is a dark red material with bandgap 2.2 eV, non-toxic, high stability and low cost and The resistivity and activation energy of Fe$_2$O$_3$ at room temperature are 6.5x10$^5$ Ω.cm and 0.728 eV, respectively [1]. Fe$_2$O$_3$ was employed in many applications like thermopower, water splitting and solar cells, photoanode, and gas sensing [2-10]. Hematite was deposited for the first time via Bard and Hardee utilizing CVD technique [11-12].
The influence of substrate temperature affected structural, optical, and morphological properties of Fe$_2$O$_3$ thin film [13]. Numerous investigators were laboried on several methods for depositing Fe$_2$O$_3$ like; sol-gel [14-15], spray pyrolysis method [16, 17], thermal evaporation method [18], chemical vapor deposition [19], sputtering [20] and DC reactive magnetron sputtering [21], and pulsed laser deposition [22, 23]. This work aims to study the influence of Indium content (2, and 4%) on Structural and Optical Characterization of Fe$_2$O$_3$:In thin films deposited via SPT.

2-Materials and Methods
Fe$_2$O$_3$:In films were deposited via SPT. 0.1 M of FeCl$_3$ and InCl$_2$ resolved via deionised water with few drops of HCl. Volumetric ratio of 2% and 4% Indium was accomplished. The optimal parameters were: spray time was 8 s and time stopping period was 1 min substrate temperature was 400 °C, Air as a transporter gas was fixed at a pressure of 10$^5$ Nm$^{-2}$, and space between orifice and the substrate was 30 cm ±1 cm.

Film Thickness was estimated via gravimetric method and was 300 ± 25 nm. The structure of pure and Indium (2, 4%) doped Fe$_2$O$_3$ films were analyzed by (XRD) performed at PANalytical X-ray diffractometer in the range of 20° - 60° (2θ) at scanning rate of 0.05° /min, while the AFM was employed to obtain film topography. Transmittance spectra were achieved utilizing UV-Vis spectrophotometer.

3-Result and discussion
XRD patterns of the deposited films are shown in Figure (1), indicating that films were polycrystalline rhombohedral of α-Fe$_2$O$_3$ phase. Result agree with (ICDD No. 040-1139). The characteristic peaks (110), (113), (204), (111) and (220) corresponding to diffraction 2θ = 30.02°, 31.18°, 36.46°, 55.97° and 62.277°, From the figures, it is noticed that all the recorded membranes are polycrystallized with an ideal reflection at (113) plane at the angle of 2θ=31.26°.

The crystallite size $D$ was determined via Scherer relation [24, 25, 26]:

$$D = \frac{\lambda k}{\beta \cos \theta}$$  \hspace{1cm} (1)

where, $k$ is 0.9, $\lambda$ is X-ray wavelength, $\theta$ is Bragg’s angle, and $\beta$ is (FWHM). $D$ calculated for Fe$_2$O$_3$, Fe$_2$O$_3$:2% Indium and Fe$_2$O$_3$:4% Indium thin films found to be 12.13 nm, 13.09 nm and 13.84 nm respectively as listed in Table. 1

Other structural parameters such as dislocation density ($\delta$) and strain ($\varepsilon$) are also evaluated. $\delta$ gives number of defects in the films, the values of ($\delta$) and ($\varepsilon$) listed in Table. 1 shows the structural parameters estimated from [27, 28, 29]:

$$\delta = \frac{1}{D^2}$$ \hspace{1cm} (2)

$$\varepsilon = \frac{\beta \cos \theta}{4}$$ \hspace{1cm} (3)

Figure (2) represents each of the FWHM, Grain size, $\delta$ and Strain of the deposited films.

| Samples  | (hkl) Plane | 2θ (°) | FWHM (°) | Grain size (nm) | Optical bandgap (eV) | Dislocations density ($\times 10^4$)(lines/m$^2$) | Strain ($\times 10^4$) |
|----------|-------------|--------|----------|-----------------|-------------------|---------------------------------|------------------|
| Fe$_2$O$_3$ pure | 113 | 31.18 | 0.68 | 12.13 | 2.75 | 66.96 | 28.57 |

Table 1. Grain size, optical bandgap and structural parameters of the prepared films.
| Sample       | Peak       | 2θ  | d (Å) | d (Å) | d (Å) | d (Å) |
|--------------|------------|-----|-------|-------|-------|-------|
| Fe$_2$O$_3$: 2% In | 113       | 31.00 | 0.63  | 13.09 | 2.65  | 58.36 | 26.48 |
| Fe$_2$O$_3$: 2% In | 113       | 30.70 | 0.59  | 13.84 | 2.55  | 52.20 | 25.04 |

**Figure 1.** XRD-patterns crystalline size of the prepared films.
Figure 2. FWHM (a) Grain size (b) Dislocation (c) Strain (d) of the prepared films.

AFM images were presented in Figure. (3), it can be seen films exhibit spherical nano-grains ranged from 87.36 nm for pure Fe₂O₃ to 65.03 nm for 4% In doped Fe₂O₃ nm respectively.

The influence of Indium doping on AFM parameters namely grain size, surface roughness (Rₘ) and root root-mean-square (Rₘᵋ) are shown in Figure. 3( a₃, b₃, and c₃) respectively. Table (2) represent the values of AFM parameters.
Figure 3. AFM images of the prepared films (a1, b1 and c1), granularly distributed (a2, b2 and c2) and variation of AFM parameters via doping (a3, b3 and c3).

Table 2. AFM parameters of the deposited films.

| Samples      | Average Particle size (nm) | Roughness Average (nm) | R. M. S. (nm) |
|--------------|---------------------------|------------------------|--------------|
| Fe₂O₃ pure  | 72.72                     | 2.75                   | 3.18         |
| Fe₂O₃: 2% In| 58.57                     | 2.11                   | 2.47         |
| Fe₂O₃: 2% In| 51.22                     | 1.70                   | 2.03         |

Figure (4) represents the transmittance against wavelength, which decreases from 68% to 62% with the increase of doping. The absorption coefficient ($\alpha$) was determined from absorbance ($A$) via the relation \[30, 31, 32\].

$$\alpha = \frac{2.303 A}{t}$$ (4)

Where $t$ is the thickness. Figure 5 displays $\alpha$ vs. wavelength. $\alpha$ decreases with increasing In content, suffer an exponential increase with wavelength.

The optical bandgap $E_g$ was evaluated from next relation \[33, 34, 35\]:
where, $h\nu$, $G$ are photon energy and proportional constant respectively.

Figure (6) show The bandgap value of pure and Indium doped Fe$_2$O$_3$ film is be 2.75 eV, 2.65 eV and 2.55 eV respectively as displayed in Table 1. The exponential edges may be assigned to a reduction of long-range order or existence of defects [36, 37].

Figure 4. Transmittance for the prepared films.
Figure 5. $\alpha$ Vs $h\nu$ of the prepared thin films.

Figure 6. $(\alpha h\nu)^2$ Vs $h\nu$ of the prepared thin films.
4-Conclusions

Nanostructured of undoped and Indium doped Fe$_2$O$_3$ films were prepared using CPT. XRD results indicate that the deposited films have rhombohedral crystalline phase of a-Fe$_2$O$_3$ phase hematite. Increasing the Indium doping ratio improve the (113) preferential orientation, XRD analysis confirmed the Fe$_2$O$_3$ nanostructure for all samples. The crystallite size for pure Fe$_2$O$_3$ show an increase from 12.13 nm to 13.84 nm on doping, whereas the strain(%) parameter decrease from 28.57 to 25.04, AFM images of the films show changes in morphology with decreased in surface roughness from 2.75 nm to 1.70 nm with Indium 4% doping. The 3-D images and grain size distribution are given in, they exhibit spherical nano-grains ranged from 72.72 nm for pure Fe$_2$O$_3$ to 51.22 nm for 4% Indium doped Fe$_3$O$_5$. The transmittance decreases with increasing Indium content, The optical bandgap of the Indium-doped Fe$_2$O$_3$ films slightly changed in the range 2.75–2.55 eV.

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