Chapter-5

Conversion of $\alpha$-Fe$_2$O$_3$ thin film in to Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ and their structural, morphological and magnetic properties
Chapter-5

Conversion of $\alpha$-Fe$_2$O$_3$ thin film into Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$...

In the beginning of this chapter the conversion of $\alpha$-Fe$_2$O$_3$ thin film into Fe$_3$O$_4$ and then to $\gamma$-Fe$_2$O$_3$ by reduction and oxidation process is described. Different characterizations of the prepared iron oxides thin films have been explained onwards in terms of their morphology, structural, phase purity and magnetic properties. The various structural parameters of the different iron oxide thin films have been calculated, and discussed in detail. The phase purity of the films is confirmed with the help of Raman spectroscopy. Next, an explanation of the observed magnetic properties is given. In last, there is a brief summary of the chapter.

5.1 Results and discussion

The $\alpha$-Fe$_2$O$_3$ thin film has been successfully converted into Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ thin films by reduction/oxidation process and the detail of the experimental set up is given in chapter 2. Typical XRD patterns obtained for $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ thin films have presented in Fig. 5.1. All iron oxide films are well crystalline and the position of diffraction peaks matched with those of the standard diffraction peaks of bulk $\alpha$-Fe$_2$O$_3$ (JCPDS no. 89-8104), magnetite Fe$_3$O$_4$ (JCPDS no. 89-0951) and maghemite $\gamma$-Fe$_2$O$_4$ (JCPDS no. 89-5892), respectively. The broadening of the peaks indicates the small size of crystallites. The average crystallites size ($D_{hkl}$) is estimated using Scherrer’s formula [160], $D_{hkl}=\frac{0.9\lambda}{\beta \cos \theta}$, where $\lambda=0.154$ nm corresponds to the wavelength of Cu K$_\alpha$ radiation and $\beta_{hkl}$ is the half-intensity width of the diffraction peak from the $(hkl)$ crystal planes. The average crystallite size calculated for $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ thin film samples are given in Table 5.1. Possible directions in which the films diffracted the beam of monochromatic X-rays are determined by Bragg’s condition [161]; $2d_{hkl} \sin \theta = n \lambda$, where $n$ is the order of diffraction, $\lambda$ is the wavelength of the incident X-rays, $d$ is the distance between planes parallel to the axis of the incident beam and $\theta$ is the angle of incidence relative to the planes in crystal. The lattice spacing ($d$) has been determined and found to be in very good agreement with the earlier reported values [162]. After heating in H$_2$ environment the $\alpha$-Fe$_2$O$_3$ phase changed to Fe$_3$O$_4$ which can be seen as shift in the XRD peak from $32.64^\circ$ to $35.47^\circ$ and disappearance of the (104) peak. As the Fe$_3$O$_4$ thin film is heated in O$_2$ atmosphere the XRD peak shifts to the higher values of $2\theta$ and another peak at $44.93^\circ$ is for $\gamma$-Fe$_2$O$_3$ (JCPDS no. 89-5892).
The magnitude of the preferred orientation factor \( f \) for a given plane (XRD peak) relative to other planes (peaks) in a material is calculated [161]. The preferred orientation factor \( f(104) \) of the (104) plane for the \( \alpha \)-Fe\(_2\)O\(_3\) thin film has been calculated by evaluating the fraction of (104) plane intensity over the sum of intensities of all peaks within a given measuring 2\( \theta \) range [109]. In \( \alpha \)-Fe\(_2\)O\(_3\) thin film \( f(104) = 0.782 \), for Fe\(_3\)O\(_4\) \( f(311) = 1 \) and in case of \( \gamma \)-Fe\(_2\)O\(_3\) \( f(311) = 0.667 \). Since \( f(104) \) is greater compared to other orientation factors in the \( \alpha \)-Fe\(_2\)O\(_3\) the films, it can be concluded that \( \alpha \)-Fe\(_2\)O\(_3\) thin films have the preferential orientation along (104) plane. Similarly the preferred orientation in Fe\(_3\)O\(_4\) and \( \gamma \)-Fe\(_2\)O\(_3\) is along (311) plane. From \((h \ k \ l)\) planes, the lattice constants \((a \& c)\) for \( \alpha \)-Fe\(_2\)O\(_3\) have been calculated using the relation [161];

\[
\frac{1}{d_{hk1}^2} = \left(\frac{4}{3}\right)(h^2 + hk + k^2/a^2) + (1/c^2),
\]

**Figure 5.1:** XRD patterns of the iron oxide thin films.
Conversion of $\alpha$-Fe$_2$O$_3$ thin film to Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$...

Table 5.1 Value of $2\theta$, grain size ($D_{hkl}$), lattice spacing ($d_{hkl}$), lattice parameter ($a=b, c$), strain ($\varepsilon_{str}$) and dislocation density ($\delta$) for iron oxide thin films from XRD result.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$ ± 0.02</th>
<th>$D_{hkl}$ (nm)</th>
<th>$d_{hkl}$ ± 0.0015</th>
<th>$a=b$ ± 0.0015 (Å)</th>
<th>$c$ ± 0.01 (Å)</th>
<th>strain ($\varepsilon_{str}$) ± 0.00013</th>
<th>dislocation density ($\delta$) ($10^{-15}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>33.17</td>
<td>13.8 ± 1.2</td>
<td>2.739</td>
<td>5.043</td>
<td>13.78</td>
<td>0.01027</td>
<td>2.13 ± 0.54</td>
</tr>
<tr>
<td></td>
<td>35.56</td>
<td>11.9 ± 0.7</td>
<td>1.936</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>35.47</td>
<td>9.2 ± 0.37</td>
<td>2.527</td>
<td>8.383</td>
<td>8.383</td>
<td>0.01255</td>
<td>2.45 ± 0.47</td>
</tr>
<tr>
<td>$\gamma$-Fe$_2$O$_3$</td>
<td>35.67</td>
<td>16.6 ± 1.2</td>
<td>2.514</td>
<td>8.338</td>
<td>8.338</td>
<td>0.0110</td>
<td>1.41 ± 0.24</td>
</tr>
<tr>
<td></td>
<td>44.93</td>
<td>21.4 ± 1.8</td>
<td>2.015</td>
<td>8.060</td>
<td>8.060</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lattice constant ($a$) for Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ samples have been determined by using [163]; $a = d_{hkl} (h^2 + K^2 + l^2)^{1/2}$, the lattice constants ($a& c$) of the iron oxide films are given in Table 5.1. The observed values of the lattice constants are in agreement with the values obtained in literature [162]. Due to the vacancy in the $\gamma$-Fe$_2$O$_3$ structure the lattice constant was found smaller than Fe$_3$O$_4$ thin films as evidenced from Table 5.1.

It is complex to distinguish between different iron oxide polymorphs (Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$) due to textural properties as the use of X-ray diffraction (XRD) alone cannot assure the presence of a specific phase. Additionally, it is known that the discrimination between Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ cannot be made by XRD because of the similar crystal structure. For a better analysis of iron oxide thin films, other techniques such as Raman spectroscopy and UV-visible spectroscopy have been used. Raman measurement was carried out to confirm the iron oxide phase (Fig. 5.2). The $\alpha$-Fe$_2$O$_3$ has irreducible vibrational modes at the first Brillouin zone center and represented by eq [74]; $\Gamma_{vib} = 2A_{1g} + 2A_{1u} + 3A_{2g} + 2A_{2u} + 5E_{g} + 4E_{u}$. The acoustic $A_{1u}$ and the $A_{2u}$ modes are optically silent, the symmetrical modes are Raman active, and the antisymmetric modes are infrared active [164-165]. Due to an inversion center in hexagonal crystal of $\alpha$-Fe$_2$O$_3$, no modes are both Raman and infrared active. The peaks seen at 229 cm$^{-1}$ and 499 cm$^{-1}$ are assigned to the $A_{1g}$ mode [166]. The remaining peaks at 294, 410, and 609 cm$^{-1}$ are assigned to the $E_{g}$ mode [166]. All lines typically described for $\alpha$-Fe$_2$O$_3$ can be identified as: 229 cm$^{-1}$ ($A_{1g}$), 294 cm$^{-1}$ ($E_{g}$), 410 cm$^{-1}$ ($E_{g}$), 499 cm$^{-1}$ ($A_{1g}$), and 609 cm$^{-1}$ ($E_{g}$) (Fig.5.2(a)). The additional line at 662 cm$^{-1}$...
has also been observed, but its origin is still under discussion in literature [167]. Bersani et al. has reported that this mode is thought to be activated by disorder within the \(\alpha\)-Fe\(_2\)O\(_3\) crystal lattice [168].

![Raman spectra](image)

**Figure 5.2**: Raman spectra for, (a) \(\alpha\)-Fe\(_2\)O\(_3\), (b) Fe\(_3\)O\(_4\), (c) \(\gamma\)-Fe\(_2\)O\(_3\) films and (d) is their transmission spectra.

The extraneous peak, at 662 cm\(^{-1}\) in the Raman spectra is representative of disorder within the crystal lattice and not of the residual Fe\(_3\)O\(_4\) contamination [74]. The line at 1315 cm\(^{-1}\) was occurred due to 2\(^{nd}\) order scattering process. This peak at 1315 is specific for the two-phonon or two-magnon scattering process in hematite [167-170].

The Fe\(_3\)O\(_4\) possesses spinel structure and, the normal modes of vibration for the first Brillouin zone center are expected to be given by eq [74]; \(\Gamma_{vib} = A_{1g} + E_{1g} + T_{1g} + 3T_{2g} + 2A_{2u} + \)
$2E_u + 4T_{1u} + 2T_{2u}$, The Raman spectra of the Fe$_3$O$_4$ thin film has been shown in Fig. 5.2(b). This spectrum agrees well with reported spectra in the literature without any feature that indicate either $\gamma$-Fe$_2$O$_3$ or $\alpha$-Fe$_2$O$_3$ contamination [16]. The pronounced Fe$_3$O$_4$ feature at $668$ cm$^{-1}$ is attributed to $A_{1g}$ mode. The feature at $315$ and $535$ cm$^{-1}$ are weak in both spectra and are assigned to $T_{1g}$ vibrational mode [74,167,171].

The expected vibrational modes of the first Brillouin zone center of $\gamma$-Fe$_2$O$_3$ spinel structure are also given by given by eq. $\Gamma_{vib} = A_{1g} + E_{1g} + T_{1g} + 3T_{2g} + 2A_{2u} + 2E_u + 4T_{1u} + 2T_{2u}$ [74]. The Raman spectrum of the $\gamma$-Fe$_2$O$_3$ film has been given in Fig. 5.2(c). The Raman active phonon modes frequency of $\gamma$-Fe$_2$O$_3$ is known to vary with preparation method and the distribution of vacancies within the $\gamma$-Fe$_2$O$_3$ crystal unit cell [74]. However, the spectra present in Fig. 5.2(c) matches with Raman spectra for $\gamma$-Fe$_2$O$_3$ which has been reported previously in literature [172]. The $\gamma$-Fe$_2$O$_3$ film has three observed Raman active phonon modes at $350$ cm$^{-1}$ ($E_g$), $395$ ($T_{2g}$), $507$ cm$^{-1}$ ($T_{2g}$), $670$ ($A_{1g}$) and $700$ cm$^{-1}$ ($A_{1g}$), that exhibit a broad scattering response [74,171,173]. The additional peaks at $599$ and $804$ cm$^{-1}$ (red arrow) are contributed by the small amount of $\alpha$-Fe$_2$O$_3$ phase present in the $\gamma$-Fe$_2$O$_3$ thin films. Figure 5.2(d) shows the transmission spectra of the iron oxide thin films. Both $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ thin films have absorption edge in the visible region while in case of Fe$_3$O$_4$ thin film no absorption edge is observed.

Figure 5.3 shows the TEM micrographs of the iron oxide thin films. Figure 5.3(a) is the TEM images of the $\alpha$-Fe$_2$O$_3$ thin film and Fig. 5.3(b) is the HRTEM image with lattice spacing $0.2715$ nm which resembles with the XRD result. Figure 5.3(c) and 5.3(d) show the TEM and HRTEM images of the prepared Fe$_3$O$_4$ thin film. From image (Fig. 5.3(c)) it is clear that the film has uniform morphology and the lattice spacing (Fig. 5.3(d)) corresponds to the (311) plane of the Fe$_3$O$_4$ which also matches with the XRD data. Fig. 5.3(e) and 5.3(f) show corresponding TEM and HRTEM images for $\gamma$-Fe$_2$O$_3$ film.
Figure 5.3: TEM images (a) & (b) for α-Fe₂O₃, (c) & (d) for Fe₃O₄ and (e) & (f) are for Fe₂O₃ films respectively. The inset in (a), (c) and (e) is the selected area electron diffraction (SAED) of the iron oxide thin films respectively.
Conversion of $\alpha$-Fe$_2$O$_3$ thin film into Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$.

The inset in Figs. 5.3(a), 5.3(c) and 5.3(e) are the selected area electron diffraction (SAED) patterns of $\alpha$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ thin films and indicate that the films are composed of nanocrystallites. In the insets the dotted circles denote the crystal planes and radius of the circles is inversely proportional to inter planar spacing.

The thickness of the film is measured with profilometer and is found to be 415, 398 and 408 nm for $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ films, respectively. The Fe$_3$O$_4$ thin films are thinner than both the $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ films because of magnetite inverse spinel crystal structure that possesses a smaller unit cell than $\alpha$-Fe$_2$O$_3$ (due to the loss of oxygen) and it is free of vacancies unlike $\gamma$-Fe$_2$O$_3$. The surface morphology of the three iron oxide thin films is also studied with AFM (Fig. 5.4). From the AFM image of $\alpha$-Fe$_2$O$_3$ film (Fig. 5.4(a)) it is clear that the film has uniform morphology and the average grain size is found to be about 18 nm (Fig. 5.5(a)). The root means square ($rms$) roughness is measured from AFM data (Fig. 5.4(b)) and is found to be 4.35 nm. Figure 5.4(c) shows the AFM image of the Fe$_3$O$_4$ thin films and the average grain size as obtained from AFM data (Fig. 5.5(b)) for Fe$_3$O$_4$ thin film is 15.4 nm which is in agreement with XRD result. The $rms$ roughness of the Fe$_3$O$_4$ thin films is 4.602 nm as shown in Fig. 5.5(d).
Figure 5.4: (a) & (b) 2D and 3D AFM image of the α-Fe₂O₃ thin film, (c) & (d) is the 2D and 3D AFM image of the Fe₃O₄ thin film, (e) & (f) are the 2D and 3D AFM image of the γ-Fe₂O₃ thin film. The entire AFM scan measurement is at 2 x 2 μm scale.
The average grain size decreases in case of Fe$_3$O$_4$ due to the loss of oxygen from α-Fe$_2$O$_3$ grains during reduction process. Figure 5.4(e) shows the AFM image of the γ-Fe$_2$O$_3$ film. The aggregation of the particles increases due to the magnetic nature of grain. The annealing in presence of the oxygen also increases the particle size due to the inter-diffusion of the small grains. The average grain size for γ-Fe$_2$O$_3$ thin films is 27 nm (Fig. 5.5(c)) which is close to the XRD result. Also, the roughness for the γ-Fe$_2$O$_3$ thin film increases due to the aggregation of the nanoparticles in the thin film (or large size grains) and is found to be 8.21 nm as shown in Fig. 5.4(f).

![Figure 5.5: Grain size distribution as obtained from the AFM data for (a) α-Fe$_2$O$_3$, (b) Fe$_3$O$_4$ and (c) γ-Fe$_2$O$_3$ thin films.](image)

**5.2 Magnetic Properties**

Figure 5.6 shows the room temperature M-H curve for the three iron oxide (α-Fe$_2$O$_3$, Fe$_3$O$_4$ and γ-Fe$_2$O$_3$) thin films. The corresponding magnetic parameters are given in Table 5.2. The α-Fe$_2$O$_3$ film shows a super paramagnetic behavior at room temperature (Fig 5.6(a) and Fig. 5.6(b)). The observed saturation magnetization for α-Fe$_2$O$_3$ film has value 18 emu/cm$^3$ that is higher than that of the bulk value (~1 emu/cm$^3$) of α-Fe$_2$O$_3$. In α-Fe$_2$O$_3$ film the antiparallel spins arrangement gives the lowest magnetic contribution. In previous chapter 3 we have discussed the presence of γ-Fe$_2$O$_3$ phase in prepared α-Fe$_2$O$_3$ films. To get rid of γ-Fe$_2$O$_3$ impurity we have annealed α-Fe$_2$O$_3$ thin films in oxygen to convert any gamma phase into α-Fe$_2$O$_3$. There is no peak of the gamma phase in XRD (Fig. 5.1) as well as in Raman spectra (Fig. 5.2(a)). So the surface spin canting is the main cause of the increased magnetic moment. If the
surface spins canting increases, an increase of surface magnetism is expected. Bhowmik et al. [174] has proposed a core-shell model for antiferromagnetic nanoparticles (AFNs) where the core is essentially antiferromagnetic and the shell consists of frustrated spins. The situation, where spins of the particle are highly frustrated, is consistent with Neel’s prediction of superparamagnetism in an antiferromagnetic nanoparticle [174-175]. The varying magnetic properties of the α-Fe₂O₃ are reported with the particle size due to change in lattice symmetry [140].

![M-H plots](image)

**Figure 5.6:** (a) M-H plots (b) enlarged image of the iron oxide thin films at room temperature.

The Fe₃O₄ film is observed ferromagnetic in nature (Fig. 5.6(a) and Fig. 5.6(b)). The saturation magnetization ($M_s$) and coercivity ($H_c$) (Table 5.2) are larger than the reported values for the Fe₃O₄ films [47,177]. Lin et al. [178] has reported $M_s$ equal to 305 emu/cm³ and coercivity equal to 400 Oe in the films prepared by the reduction of α-Fe₂O₃ form films of thickness 150 nm. The magnetization is found to be decreases with thickness of the Fe₃O₄ thin films in literature [178]. These values are much lower than the values observed in this study. The high value of $M_s$ indicates less crystallographic defect (antiphase boundaries) in Fe₃O₄ thin film [47,177]. The observed high values of coercivity are due to the crystalline and/or stress induced anisotropy. Crystalline anisotropy arises because the Fe₃O₄ films exhibit preferred orientation in the [311] direction. Stress-induced anisotropy arises because of the internal stress build-up.
Conversion of $\alpha$-Fe$_2$O$_3$ thin film in to Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$... during the growth of the films whose thermal expansion coefficient differs from that of the substrates. But the substrate temperature as well preparation method does affect the density of antiphase boundaries (APBs). For example in the epitaxial films, the average size of antiphase domain has been found to range from 30 nm for the sputter deposited film at 500 °C to 300 nm for the molecular beam epitaxially grown film at 225 °C [179]. In our case transition of the $\alpha$-Fe$_2$O$_3$ to Fe$_3$O$_4$ has been done at 500 °C so we expect reduced antiphase boundary.

Table 5.2. Value of saturation magnetization ($M_s$), coercivity ($H_c$) and remanent magnetization ($M_r$) for iron oxide thin films from VSM result.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_s \pm 2.04$ (emu/cm$^3$)</th>
<th>$H_c$ (Oe)</th>
<th>$M_r \pm 2.04$ (emu/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>18</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>414.5</td>
<td>317</td>
<td>124.35</td>
</tr>
<tr>
<td>$\gamma$-Fe$_2$O$_3$</td>
<td>148</td>
<td>400</td>
<td>52</td>
</tr>
</tbody>
</table>

Also in case of the $\gamma$-Fe$_2$O$_3$ thin film the magnetization and coercivity values are 148 emu/cm$^3$ and 400 Oe, respectively (Table 5.2). These values are smaller than the reported values by Ishii et al. [31]. Using standard values of the magnetization (bulk values) of the two phases, i.e., 1 emu/cm$^3$ for $\alpha$-Fe$_2$O$_3$ and 430 emu/cm$^3$ for $\gamma$-Fe$_2$O$_3$, the concentration of the $\alpha$-Fe$_2$O$_3$ inside the film has been estimated using the formula, $M_s = (x) (M$ of $\alpha$-Fe$_2$O$_3$) + (1-$x$) ($M$ of $\gamma$-Fe$_2$O$_3$). The magnetization measurement considering the bulk value of the both phase the concentration of $\alpha$-Fe$_2$O$_3$ phase in the $\gamma$-Fe$_2$O$_3$ thin film comes out to be 66%. While considering the magnetization value for $\alpha$-Fe$_2$O$_3$ 18 emu/cm$^3$ the concentration of the $\alpha$-Fe$_2$O$_3$ phase is found to be 68% in $\gamma$-Fe$_2$O$_3$ thin film. But there is no peak of the $\alpha$-Fe$_2$O$_3$ phase in XRD spectra of $\gamma$-Fe$_2$O$_3$ thin film. Also, in Raman spectra there are very small peaks observed which may be due to the conversion of the $\gamma$-Fe$_2$O$_3$ phase in to $\alpha$-Fe$_2$O$_3$ phase by laser heating. Thus the decrease in the magnetization value can be explained in terms of the vacancy of the Fe$^{3+}$ ion at octahedral position in $\gamma$-Fe$_2$O$_3$ structure. It indicates that there is less vacant site in the sample prepared in our case which results in the less saturation magnetization of $\gamma$-Fe$_2$O$_3$ thin film.
Chapter-5  Conversion of $\alpha$-Fe$_2$O$_3$ thin film into Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$……

5.3 Summary

The $\alpha$-Fe$_2$O$_3$ thin film has been successfully converted into Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ thin films by reduction/oxidation process. The films have been found to exhibit a pure phase as confirmed from the XRD and Raman analysis. All the three iron oxide thin films have uniform morphology and corresponding grain size has been found to be 12.8, 9.2 and 18.5 nm for $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$, respectively. $M-H$ measurement of the $\alpha$-Fe$_2$O$_3$ film indicates the existence of superparamagnetism with saturation magnetization value of 18 emu/cm$^3$, while the Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ have been found to be ferromagnetic in nature. The high value of magnetization in $\alpha$-Fe$_2$O$_3$ thin film has been explained on the basis of the uncompensated surface spins of small $\alpha$-Fe$_2$O$_3$ nanoparticle. A higher value of the magnetization in Fe$_3$O$_4$ film indicates the efficacy of our process to attain high quality films with less anti-phase boundaries or crystal defects.