Chapter-6

Effect of external magnetic field on the morphology of the iron oxide thin film
This chapter discusses the influence of external magnetic field on the morphology of the \(\alpha\)-Fe\(_2\)O\(_3\) thin film. Different properties of prepared iron oxide nanostructures have been explained in terms of their morphology, structural and magnetic properties. The effect of Ni\(^{2+}\) and Co\(^{2+}\) doping on the directional growth of structure over the surface of film is studied; also a suitable growth mechanism is presented. In this study, room temperature magnetization measurements revealed that the magnetization depends on the morphological attributes of the nanostructures. The chapter is summarized in last.

### 6.1 Results and discussion

The detailed experimental set up for the synthesis of the nanostructure is given in chapter 2. Figure 6.1(a) shows the SEM image of the \(\alpha\)-Fe\(_2\)O\(_3\) thin film formed without applying external magnetic field. Figures 6.1(b) to (d) show the pure and doped \(\alpha\)-Fe\(_2\)O\(_3\) films formed in the presence of magnetic field applied out of plane at liquid-vapor interface. Figure 6.1(b) is the SEM image of pure \(\alpha\)-Fe\(_2\)O\(_3\) thin film formed in the presence of magnetic field applied out of plane to the liquid-vapor interface. It clearly shows that the formations of cubic \(\alpha\)-Fe\(_2\)O\(_3\) nanostructure are due the induced magnetic moment in the magnetic grain of \(\alpha\)-Fe\(_2\)O\(_3\) due to external magnetic field. The nanoparticles formed in presence of external magnetic field have magnetic moment aligned in the direction of applied magnetic field. During annealing, the nanoparticles arrange themselves and the formation of nanostructure on the surface of thin film takes place. From this observation we see that morphologies and thus the properties can be tailored by changing the magnetic moment of \(\alpha\)-Fe\(_2\)O\(_3\) particles.

It is reported that the doping with Ni\(^{2+}\) and Co\(^{2+}\) improves the magnetic moment of the \(\alpha\)-Fe\(_2\)O\(_3\) [180] films. So we have doped \(\alpha\)-Fe\(_2\)O\(_3\) thin films with Ni\(^{2+}\) and Co\(^{2+}\) in order to study the effect of doping on the morphology and magnetic property of nanostructured \(\alpha\)-Fe\(_2\)O\(_3\) films. Figure 6.1(c) is SEM image of Ni\(^{2+}\) doped \(\alpha\)-Fe\(_2\)O\(_3\) thin film where one dimensional arrangement is observed. Similarly, the Co\(^{2+}\) doped \(\alpha\)-Fe\(_2\)O\(_3\) nanoparticles arrange themselves in one dimensional structure as shown in the corresponding SEM image (Fig. 6.1(d)). The large orientational growth of the micro rod is observed in the case of Co\(^{2+}\) doping.
Figure 6.1: SEM images of the $\alpha$-Fe$_2$O$_3$ thin films (a) without magnetic field, (b) undoped film formed with perpendicular magnetic field (out of plane), (c) doped with 15 % Ni$^{2+}$ in magnetic field applied out of plane and (d) doped with 15 % Co$^{2+}$ in magnetic field applied out of plane. All the films were obtained after annealing at 500 $^\circ$C.

Figure 6.2 shows typical XRD intensity patterns for pure and doped iron oxide thin film. From XRD, all the films are well crystalline and the position of diffraction peaks match with those of $\alpha$-Fe$_2$O$_3$ on comparison with the standard diffraction peaks of bulk $\alpha$-Fe$_2$O$_3$ (JCPDS no. 89-8104). Also, from the XRD data it is clear that there is no formation of the other secondary phases.
Figure 6.2: The XRD patterns of the pure and doped $\alpha$-Fe$_2$O$_3$ thin films.

Figure 6.3 shows the EDX of Ni$^{2+}$ and Co$^{2+}$ doped structures, these nanostructures have Ni$^{2+}$ and Co$^{2+}$ with the atomic percent of 15 and 14, respectively.

Figure 6.3: The EDX of (a) Ni$^{2+}$ doped and (b) Co$^{2+}$ doped $\alpha$-Fe$_2$O$_3$ structure formed on the surface of thin film.
For the pure and doped $\alpha$-Fe$_2$O$_3$ nanostructured films annealed at temperature 500 °C, the M–H measurement was done at room temperature using VSM technique. The pure and Ni$^{2+}$ doped samples show a superparamagnetic behavior as shown in Figs. 6.4(a) and (b). For the pure sample the saturation magnetization is achieved at the 6000 Oe while Ni$^{2+}$ doped $\alpha$-Fe$_2$O$_3$ film does not saturate even up to magnetic field of 17000 Oe. The magnetization value is found to increases with the Ni$^{2+}$ doping as shown in Fig. 6.4(b).

![Graphs showing M-H curves for (a) α-Fe$_2$O$_3$ (b) Ni$^{2+}$ doped α-Fe$_2$O$_3$ thin film respectively.](image)

**Figure 6.4:** The M-H curve for (a) $\alpha$-Fe$_2$O$_3$ (b) Ni$^{2+}$ doped $\alpha$-Fe$_2$O$_3$ thin film respectively.

The Co$^{2+}$ doped $\alpha$-Fe$_2$O$_3$ thin film shows the ferromagnetic behaviour with the large coercivity values of 1000 Oe (Fig. 6.5). The coercivity is an extrinsic property of a magnet, which depends not only on the spin carrier but also on the shape and size of the magnet. The larger coercivity and remanence for Co-doped sample can be attributed to their enhanced shape and magneto-crystalline anisotropy [181]. Magnetic properties of $\alpha$-Fe$_2$O$_3$ doped with Co$^{2+}$ ions have stronger spin-order interaction than that of the Fe$^{2+}$ ions [182]. The Ni$^{2+}$ and Co$^{2+}$ doping decompensate the antiferromagnetic order of the lattice, leading to an enhancement of effective magnetic field seen by Fe$^{3+}$ nucleus [119]. So the higher coercivity and remanent magnetization are due to the shape anisotropy of Co$^{2+}$ doped Fe$_2$O$_3$ structures, which prevent them from magnetizing in directions other than along their easy magnetic axes, leading to a higher coercivity. Due to this large value of magnetocrystalline anisotropy, large directional growth occurs in Co$^{2+}$ doped samples.
Figure 6.5: The M-H curve for Co\textsuperscript{2+} doped α-Fe\textsubscript{2}O\textsubscript{3} nanostructured film.

We also studied the effect of parallel magnetic field. Figure 6.6(a) shows the corresponding SEM images of Co\textsuperscript{2+} doped α-Fe\textsubscript{2}O\textsubscript{3} thin film formed in presence of magnetic field applied parallel to the liquid-vapour interface, the obtained film after annealing is shown in Fig. 6.6(b).

Figure 6.6: The SEM images of Co\textsuperscript{2+} doped α-Fe\textsubscript{2}O\textsubscript{3} thin films (a) unannealed and (b) annealed at 500 °C formed with the external magnetic field applied parallel (in plane) to the liquid-vapour interface.
The formation of worm-like nanostructure of the Co\(^{2+}\) doped \(\alpha\text{-Fe}_2\text{O}_3\) on the surface of the thin film takes place on annealing. Similar structures were formed for pure and Ni\(^{2+}\) doping. This is due to the crack formed on the film surface during synthesis in the presence of the external magnetic field.

### 6.1.1 Formation mechanism

**Mechanism of the nanostructure formation**

To investigate the growth mechanism of nano, microstructure formation, the Co\(^{2+}\) doped \(\alpha\text{-Fe}_2\text{O}_3\) thin films were formed by annealing at different temperature. The films were formed in various applied magnetic field. There was no nanostructure formed on the film surface which indicates that nanostructure formation takes place during the annealing process. We annealed Co\(^{2+}\) doped \(\alpha\text{-Fe}_2\text{O}_3\) thin films at 100, 300 and 500 °C temperature to investigate the formation mechanism of structure. At the lower annealing temperature, only the nanoparticles aggregation was observed while with the increasing of annealing temperature, more and more nanoparticles agglomerate and resulted in the nanostructure formation of nano to micro size range as shown in Fig. 6.7.

Penn et al. [183] attributed “oriented attachment” as the main driving force to decrease the high surface energy through self-organization. According to the “oriented attachment” nanoparticles would fuse together with their high-energy surfaces under crystallographic fusion and elimination of the high-energy faces under energy gain, which is not observed in our samples. In our case, the applied external magnetic field induced magnetic moment which plays an important role for the aggregation (orientational attachment). The nanoparticle would further attract free-standing nanoparticle due to the induced magnetic moment and attach on their surface to repeat the fusion process to grow bigger [184].
Figure 6.7: The SEM images of the $\text{Co}^{2+}$ doped $\alpha$-Fe$_2$O$_3$ thin films (a) unannealed and annealed at (b) 100 °C, (c) 300 °C and (d) 500 °C temperature.

In the SEM image, we can see that initially there is no formation of the nanostructure on the surface of the thin film (Fig. 6.7(a)). When the film is annealed at 100 °C temperature smaller grains starts agglomerated (Fig 6.7(b)). As we further increase the annealing temperature to 300 °C, one dimensional nanostructure emerges the larger growth takes place and at the 500 °C temperature they grow to several micrometer length (Figs. 6.7(c)-6.7(d)). Thus from the SEM images it is clear that a directional growth takes place during the annealing process.

Further, the formation mechanism can be explained with the help of the schematic diagram (Fig. 6.8). In case when the iron oxide film was prepared in absence of magnetic field, small grains formed inside the film might be having their magnetic moment oriented in random directions which when annealed at higher temperature remained the same. While in second case when the external magnetic field was applied, the grain nucleated in presence of magnetic field might be having their magnetic moment in the direction of magnetic field.
**Figure 6.8:** Schematic for the nanostructures formation on the iron oxide thin film in presence of the external magnetic field.

When these thin films were annealed at higher temperature, the PVA get evaporated and the magnetized grains arrange themselves due to the magnetocrystalline anisotropy to reduce their magnetocrystalline anisotropy energy. So a directional growth of the nanostructure occurs.

**6.2 Summary**

The effect of external magnetic field during the synthesis on the morphology of \(\alpha\)-Fe\(_2\)O\(_3\) thin film has been studied and it is found that nanostructure grows during the annealing process. The applied magnetic field aligns the magnetic moment in its direction. And in annealing process the magnetized grains rearrange themselves by the orientational attachment process to form the directional nanostructures. From the VSM characterization, \(\alpha\)-Fe\(_2\)O\(_3\) and Ni\(^{2+}\) doped \(\alpha\)-Fe\(_2\)O\(_3\) films are found superparamagnetic while Co\(^{2+}\) doped film was ferromagnetic. The magnetic moment of \(\alpha\)-Fe\(_2\)O\(_3\) films is found to be enhanced with the Ni\(^{2+}\) and Co\(^{2+}\) doping. In case of the Co\(^{2+}\) doping, one dimensional growth is due to the large value of magnetocrystalline anisotropy.