Chapter-7

Summary and future suggestions
7.1 Summary and important findings

A novel method is developed for the formation of the $\alpha$-Fe$_2$O$_3$ thin films on the liquid-vapor interface i.e the interface of the precursor solution and NH$_3$ vapors. X-ray diffraction studies suggest the formation of nanostructured $\alpha$-Fe$_2$O$_3$ thin films and the persistence of the corundum hexagonal structure. The study of NH$_3$ vapor doses on the reaction suggest that the thickness and roughness of $\alpha$-Fe$_2$O$_3$ thin film increases with the increasing dose of NH$_3$ in the reaction chamber. Initial PVA concentration in precursor solution also affects the film morphology, and the particle size is found to decrease with the increasing concentration of PVA due to the capping effect. Transmission electron microscopy shows that the $\alpha$-Fe$_2$O$_3$ thin films synthesized via this novel technique have spherical particles with narrow particle size distribution for the films synthesized at a particular condition. In case of synthesis parameter, annealing temperature the particle size inside the film can be tuned. The effect of annealing temperature on the magnetic property of $\alpha$-Fe$_2$O$_3$ film is also studied and $\alpha$-Fe$_2$O$_3$ films are found to be superparamagnetic in nature and follow the Langevin function for superparamagnetism. In MT measurement of $\alpha$-Fe$_2$O$_3$ films, suppression in Morin transition temperature is due to the small size of $\alpha$-Fe$_2$O$_3$ nanocrystals inside the $\alpha$-Fe$_2$O$_3$ films.

Since the optical properties of $\alpha$-Fe$_2$O$_3$ thin films are also important due to its band gap in visible region the effect of the synthesis parameter on the optical band gap and the refractive index is studied. The red shift in the band gap is observed with the increasing dose of NH$_3$ and annealing temperature while with increasing concentration of PVA causes a blue shift in the optical band gap. The refractive index of $\alpha$-Fe$_2$O$_3$ thin film is found to increase with the increasing doses of NH$_3$ and annealing temperature while it decreases with the increasing concentration of PVA. For lower annealing temperature the $\alpha$-Fe$_2$O$_3$ films follow the quantum confinement effect as calculated from effective mass approximation while for higher values of annealing temperature, the experimental values of $\alpha$-Fe$_2$O$_3$ film deviate from the theoretical value, indicating deviation from quantum confinement effect. The observed change in the optical band gap with the synthesis parameter is found to depend on the change in the lattice symmetry and the change in crystallinity of the $\alpha$-Fe$_2$O$_3$ films. The refractive index is correlated with the packing density of the $\alpha$-Fe$_2$O$_3$ films which changes with the change in the synthesis parameters.

The prepared $\alpha$-Fe$_2$O$_3$ film was then converted into Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ film by the reduction and oxidation process. The XRD study of these films reveals that Fe$_3$O$_4$ and $\gamma$-
Fe₂O₃ films exhibit spinel phase. The dislocation density and strain of Fe₃O₄ film are found to be larger than both of the α-Fe₂O₃ and γ-Fe₂O₃ films, due to the small crystallite size in magnetite thin film. Also the observed large magnetocrystalline anisotropy is due to the large magnetic moment. The Raman study reveals that α-Fe₂O₃ and Fe₃O₄ films have high phase purity without any other phase while γ-Fe₂O₃ film shows the presence of α-Fe₂O₃. The grain size is found smaller in Fe₃O₄ film as compare to parent α-Fe₂O₃ film since Fe₃O₄ has smaller lattice constant and there is loss of oxygen during reduction process. Further the roughness of Fe₃O₄ and γ-Fe₂O₃ films is found larger than that of α-Fe₂O₃ film as the aggregation of magnetic nanoparticle starts at elevated temperature due to the large magnetic moment in the nanoparticle. The VSM study is used to find the magnetic nature of iron oxide thin films. The α-Fe₂O₃ film is found superparamagnetic while Fe₃O₄ and γ-Fe₂O₃ thin films are ferromagnetic in nature. The magnetization value of Fe₃O₄ film is observed comparable to that of the bulk magnetization. The large value of magnetization in case of Fe₃O₄ film indicates less crystallographic defect and less antiphase boundary.

Also, the effect of external magnetic field during the synthesis on the morphology of α-Fe₂O₃ film is studied. The magnetic field is applied both in plane and out of plane to the liquid-vapour interface. The formation of the nanostructure on the surface of film is found on the application of external magnetic field. The nanoparticles in the presence of magnetic film have induced magnetic moment in the direction of applied field which helps in the directional growth during the annealing process. When the film was heated in the furnace these magnetised nanoparticle arrange themselves due to the induced magnetic moment and the formation of nanostructure took place. The effect of Ni²⁺ and Co²⁺ doping on the growth of nanostructure is also studied. One dimensional nanostructure are formed in case of doping. The nanostructure formation takes place during the annealing process, and the size of nanostructures depend on the annealing temperature and annealing time. The directional growth is probably due to the increase in the magnetization or magnetic moment of nanoparticles inside the films which on annealing at elevated temperature gets align to induced the one dimension growth of nanostructures.

This is the first report which highlights the development of novel method for the formation of α-Fe₂O₃ thin film on the liquid-vapour interface. This approach offers several advantages because of control of synthesis parameters on the properties of the thin films. This is the first study where the external magnetic field is applied on the liquid-vapour interface and one dimensional growth of nanostructures is observed. The changes observed
in the magnetic and optical properties of α-Fe₂O₃ films with the variation of synthesis parameters suggest that this could be a very useful way to design novel magnetic and optical materials.

Future suggestions

- In future attempts, this technique could develop a tool/synthesis procedure to obtain thin films with large surface area and of better quality in smaller time frames. This means these reaction methodologies can be utilized to produce material (thin films) at large scale.
- This synthesis method can be used for the formation of better quality thin films of other metal oxide such as ZnO, NiO, Ce₂O₃, CoO, AZO thin films etc. and their properties can be controlled by changing the synthesis parameter.
- Further, the magnetic measurements suggest that the magnetic moment in α-Fe₂O₃ films is larger than the bulk value while in Fe₃O₄ film it is same as that of the bulk Fe₃O₄ so these films can be investigated for the magnetic field sensor and spintronics based application.
- In this thesis, optical properties of α-Fe₂O₃ are studied in detail. It would be interesting to study the prepared α-Fe₂O₃ thin films for other application such as photocatalytic, water photo catalysis and sensor activity etc.
- Since α-Fe₂O₃ film and its nanostructures have great application in lithium-ion batteries, sensors and water purification, the prepared pure and doped nanostructures can be further studied for these applications. Also, due to their magnetic nature they can be used for spin transport applications.