Chapter-2

Methodology for the synthesis of iron oxide thin films on glass substrate
This chapter focuses on the synthesis of iron oxide thin films grown on the liquid-vapor interface which were transferred to the surface of the glass substrate. Since the field of nanoscience and technology is so new, there are still many fundamental questions that have yet to be answered regarding synthesis. The goal of this chapter is to better understanding the synthesis method used to grow iron oxide thin films and improve the precision and control which can be exerted over the entire range of materials to grow the different types of thin films using a particular type of synthesis setup. Since many of the results attained in this research work may be indicative of the experimental setup, this chapter begins with a section that details the specific equipment utilized for the synthesis of iron oxides thin films. This will be followed by an explanation of employed experimental procedure in general.

2.1 Synthesis setup for the formation of α-Fe₂O₃ thin film:

There are several processing parameters such as, reactant gas, polymers concentration, annealing temperature, which can be controlled and need to be selected properly before and/or during the synthesis. The thickness and the grain size of particle in thin films depend on the selection of reactants. In the experiments inert gas ‘argon (Ar)’ was used to produce an inert gas environment inside the reaction chamber.

The glass slide was cut in small pieces about 1cm². The preparation of glass substrate before the synthesis of thin films and nanostructures includes the following steps.

(i) Cutting of glass slide in small pieces.

(ii) Cleaning by CH₃COCH₃ and removal of pre-existing dust layer on its surface using dil. HF (10%) solution.

(iii) Rinsing heavily under running de-ionized water.

(iv) Drying in a stream of Ar gas.

2.1.1 Experimental procedure for the formation of α-Fe₂O₃ film

In order to make a precursor solution, FeCl₃.6H₂O (purity 99.99 %), as a source of Fe³⁺ ions, and FeCl₂ (purity 99.99 %) as a source of Fe²⁺ ions, were purchased from Sigma-Aldrich. The NH₃ solution (conc. 25 %) was purchased from E. Merck. The host polymer PVA (molecular weight = 125,000) was purchased from S. D. Fine Chemicals Limited, India.
A precursor solution with 24 mM FeCl₂ and 22 mM FeCl₃·6H₂O was initially prepared in distilled water. Then, a variable amount, as mentioned in the following discussion, of PVA was added to the precursor solution. The solution was stirred for 10 min at 80 °C and immediately transferred to a petri dish placed in an argon (Ar) chamber as shown in Fig. 2.1.

**Figure 2.1**: Schematic of the synthesis setup for the formation of α-Fe₂O₃ thin film.

A measured volume of NH₃ vapor was poured into the chamber containing the solution in the petri dish. After pouring NH₃ vapors, the chamber was kept sealed for 10 min to facilitate the chemical reaction between the NH₃ vapor and the PVA-containing precursor at the surface of the solution. The chemical reaction on the liquid vapor interface take place according to the following reaction:

\[
2\text{FeCl}_3 + \text{FeCl}_2 + 8\text{NH}_4\text{OH} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NH}_4\text{Cl} + 4\text{H}_2\text{O} \quad (2.1)
\]

\[
4\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6\text{Fe}_2\text{O}_3 \quad (2.2)
\]
Simultaneously, the formation of $\alpha$-$\text{Fe}_2\text{O}_3$ may also take place according to the following reaction:

$$2\text{FeCl}_3 + 6\text{NH}_4\text{OH} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{NH}_4\text{Cl} + 3\text{H}_2\text{O} \quad (2.3)$$

Consequently, the liquid–vapor interface converted into a thin floating film. The obtained film was transferred to the surface of distilled water filled in another petri dish. The film was then deliberately transferred to the surface of a glass substrate. The above experiment was repeated in order to observe the effect of NH$_3$ vapor concentration on the film morphology. The films were formed by using 2, 4, 6 and 8 % volume of NH$_3$ in the reaction chamber. Similarly, a second set of films was formed by varying the concentration of PVA in the precursor solution. The PVA concentrations were 8, 16, 32, 64 and 80 μM, while 6 % volume of NH$_3$ vapor was used inside the chamber. Then, in order to form $\alpha$-$\text{Fe}_2\text{O}_3$ films, the films obtained in the above experiments were annealed at 500 °C for 2 hours in an Ar gas environment. We also performed an experiment to study the effect of annealing temperature on surface morphology and property of $\alpha$-$\text{Fe}_2\text{O}_3$ thin film. For this experiment, the films were formed using 6 % NH$_3$ vapor and 32 μM concentration of PVA. The film was annealed at different temperature for 2 hours in Ar gas environment.

Similarly the variation in optical properties of the films was studied with the variations of synthesis parameters i.e. (i) dose (vol. %) of NH$_3$ and (ii) concentration of PVA and (iii) the annealing temperature. The dose of NH$_3$ vapors was varied from 2% (40 cm$^3$) to 4% (80 cm$^3$) and then to 6% (120 cm$^3$) at fixed (32 μM) concentration of PVA. The concentration of PVA was varied from 8 to 32 and then to 80 μM for fixed dose of NH$_3$ at 6% (120 cm$^3$). The films formed in above two sets of experiments were annealed at 500 °C. In the third set, the films formed for fixed concentration (32 μM) of PVA and fixed dose of NH$_3$ (6% (120 cm$^3$)) were annealed, successively at 200, 400, 600, 800 and 1000 °C temperature. Thus formed films were characterized for structural and optical properties. The structural properties were obtained using X-ray Diffractometer (XRD, PANalytical’s X’Pert-PRO) and Transmission Electron Microscope (TEM) (JEOL, JEM 2100), morphological properties using Scanning Electron Microscope (SEM, Hitachi, S-4700) and thickness using Stylus profilometer. The optical properties were studied using UV-Vis-NIR double beam spectrophotometer (Perkin Elmer Lambda-750) in 250-900 nm wavelength range.
2.2 Synthesis setup for Fe$_3$O$_4$/$\gamma$-Fe$_2$O$_3$ thin films formation:

The Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ thin films in this work have been synthesized in a high temperature furnace by the way of a reduction/oxidation technique. In principle, the $\alpha$-Fe$_2$O$_3$ thin films can be converted into Fe$_3$O$_4$ thin film by heating in hydrogen gas flow in horizontal tube furnace. The Fe$_3$O$_4$ thin films can further be converted in to $\gamma$-Fe$_2$O$_3$ thin film by oxidation process heating in O$_2$ flow in horizontal tube furnace.

The furnace system used throughout of this work was comprised of two components: the furnace and the gas system. A schematic diagram of the entire system is shown in Figure 2.2 Metrex microprocessor controlled tube furnace was used for the conversion of $\alpha$-Fe$_2$O$_3$ thin films in to Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ thin film. Exposed heating element coils embedded into ceramic fiber insulation provided the furnace with the capability of heating up to 1100 °C in only 20 minutes. The heating rate of the furnace was controlled by a programmable controller. The digital program controller with one stored program of eight segments allows the desired temperature and time intervals. Each segments of the program consisted of temperature increment time, a temperature set point (ranging from 0 °C to 1100 °C), and temperature fall time.

![Diagram of the furnace](image)

**Figure 2.2:** Schematic diagram of the furnace.

A quartz tube measuring 40 inches in length and having a 1.75 inches outer diameter and 1.50 inches inner diameter can be placed inside the furnace. With the furnace measuring only 24
inches in length, the quartz tube protrudes out from the furnace, six inches on either side. Three inches tube collars lay at the open end of the tube furnace and the quartz tube is placed across the furnace which is supported by the collars. The size of the tube and the collars can be fixed in such a way that there remains no air gap between the tube and the collars. Each of the collars has the hole at their center to introduce the desired gas inside the furnace during the synthesis process.

![Diagram of gas control](image)

**Figure 2.3:** Schematic diagram of the gas control.

The gas flow control system has four separate tubes, which are marked from 0 to 800 ml min\(^{-1}\). The gases required for the reaction are connected separately to each of the tube through the gas connector pipes at the bottom of the tube and the upper end of each of the tube is connected to an outlet which is connected to the one end of the tube placed inside the furnace. The flow of the gas can be controlled through the screws at the bottom of each of the labels. The controlled gas is allowed to flow inside the quartz tube. The schematic diagram of the gas flow control is shown in the Fig. 2.3. The gas exits from the other end of the quartz tube and goes to the Si oil pot and finally the gas is exhausted.

The \(\alpha\)-Fe\(_3\)O\(_4\) film converts to Fe\(_3\)O\(_4\) film according to thermal reaction (Eq. 2.4). During heating time, H\(_2\) gas was also introduced into the chamber. By adjusting the gas control valves, the rate of gases flow inside the chamber could be manipulated. The gases flow set point was
always achieved before the highest temperature was reached. Conversion of the $\alpha$-Fe$_2$O$_3$ into Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ is done by annealing the films as indicated below.

$$3 \alpha$Fe$_2$O$_3 + H_2 \xrightarrow{500^\circ C} 2 Fe_3O_4 + H_2O$$ (2.4)

$$4 Fe_3O_4 + O_2 \xrightarrow{350^\circ C} 6 \gamma$Fe$_2$O$_3$$ (2.5)

The reaction process were carried out by heating the $\alpha$-Fe$_2$O$_3$ film at the optimum temperature ($500^\circ C$) inside a quartz tube under flow of mixed gas ($H_2 : Ar = 50 : 100 \text{ cm}^3 \text{ min}^{-1}$) for 2 h, and then by cooling them down to room temperature at the rate of 5 $^\circ C \text{ min}^{-1}$ with flowing argon gas.

![Figure 2.4: Schematic diagram of synthesis of Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ thin films from $\alpha$-Fe$_2$O$_3$ thin film.](image)

For the formation of $\gamma$-Fe$_2$O$_3$ films the above prepared Fe$_3$O$_4$ film is heated in constant O$_2$ flow in quartz tube at 400$^\circ$C for 2 h. A designated flow of the gases and temperature set point were chosen prior to the synthesis process. The furnace was heated at a heating rate of 5 $^\circ C \text{ min}^{-1}$. The system was held at constant flow of gases and temperature for a designated time period, after which the furnace was programmed to cool down to the room temperature. Once the furnace got the room temperature, the flow of the gas into the reaction chamber was stopped.

For the morphology and structural characterizations of the prepared iron oxide films Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD) techniques were used. The phases of iron oxide thin films were analyzed with Raman Spectroscopy and UV-Visible spectrophotometer. The magnetic characterization has been carried out by Vibrating Sample Magnetometer (VSM).
2.3 Synthesis setup for nanostructure formation

The $\alpha$-Fe$_2$O$_3$ thin film was prepared on liquid vapor interface using previous method discussed above. A precursor solution with 24 mM FeCl$_2$ and 22 mM FeCl$_3$.6H$_2$O containing 64 $\mu$M of polyvinyl alcohol (PVA) was prepared initially. The solution was stirred for 10 minutes at 80 °C and immediately it was transferred to a petri dish placed in argon (Ar) chamber. The solution was kept in the ice chamber in order to reduce the thermal fluctuation at the precursor surface. The precursor solution as prepared in above procedure was taken in a petridish and placed below the pole of the electromagnet having pole diameter 2 inches. An external magnetic field of 8000 gauss was then applied in out of plane to the liquid vapour interface. The gap between the solution surface and electromagnet pole was kept is 2.5 mm.

Then a measured volume of NH$_3$ vapor was poured into the chamber containing the solution in the petri dish and was kept sealed for 10 minutes to facilitate the chemical reaction between NH$_3$ vapor and precursor in presence of the external magnetic field. Consequently, the liquid-vapor interface converted into a thin floating film which was transferred surface of a glass substrate. The film on the glass substrate was annealed in air at 500 °C in furnace. The schematic for the nanostructure formation on the surface of the film is shown in Fig. 2.5.

![Figure 2.5](image_url)

**Figure 2.5:** Schematic representation of the nanostructure formation.
The same procedure is repeated for the film doped with 15 mole % of Ni$^{2+}$ and Co$^{2+}$ with respect to Fe$^{3+}$ in precursor solution. The as prepared nanostructured thin films were the characterized by XRD, FESEM, EDAX and VSM techniques for their structural morphological and magnetic properties.