CHAPTER IV
GROWTH AND CHARACTERIZATION
OF BINARY OXIDES

INTRODUCTION

The binary transition-metal oxides (BTMO) which form an important category of materials in fundamental physics as well as in technological applications have been attracting intense attention from the condensed matter community. They exhibit a rich variety of structural, magnetic, transport, and optical properties. The unusual properties of transition metal oxides are clearly due to many factors: (a) Unique nature of the outer d-electrons, (b) Electron correlation effects due to narrow electronic bands, (c) The polarizability of oxygen, (d) Instead of three-dimensional structures, they exhibit low-dimensional features etc. Due to the mentioned peculiarities, this class of materials has generated considerable interest due to their cheap synthesis methods, highly single crystalline surfaces and novel shapes. Their application in gas sensor technology has been explored experimentally and theoretically and in numerous cases, the developed devices show improved performance over the other traditional thin film sensors. Hence a devoted step has been taken to prepare and characterize NiO and Fe₂O₃ thin films for evaluating its suitability in the construction of ethanol gas sensor. Initially the spray pyrolysis depositions of the compounds are explained. Then the optimized film was chosen from the deposited films using the characterization methods adopted. This chapter therefore enumerate the various results obtained and the interpretations given to the variations in various structural, optoelectronic and magnetic properties.
4.1 NICKEL OXIDE THIN FILMS

Nickel (II) oxide is the chemical compound with the formula NiO (bunsenite) and is considered the only well-characterized oxide of nickel (although there being nickel (III) oxide, Ni$_2$O$_3$ and NiO$_2$). The mineralogical form of NiO is very rare and is classified as a basic binary metal oxide. NiO adopts the NaCl structure, with octahedral Ni (II) and O$^{2-}$ site. Like many other binary metal oxides, NiO is often non-stoichiometric. In nickel oxide this non-stoichiometry is accompanied by a color change, with the stoichiometrically correct NiO being green and the non-stoichiometric NiO being black. NiO, as one of the relatively few binary metal oxides that tend to be p-type, is a stable wide band gap (3.4 - 4.0 eV) material and can be used as a transparent p-type semiconducting layer [1].

As a kind of functional material, NiO thin films have been widely studied as a promising material for the possible applications to gas sensors [2], p-type transparent conducting electrodes [3], thermoelectric devices [4] and magnetoresistance sensors [5]. For controlling the crystallographic orientation, deposition of the films is very important [6]. In fact, the magnetic properties of NiO nanoparticles are very sensitive to size, crystal structure, and morphology, thus showing a wide variety of intriguing phenomena. Gao et al. synthesized NiO nanotubes and nanoparticles by a sol–gel technique followed by a heat treatment process [7]. They observed ferromagnetism at room temperature with obvious hysteresis loops and non-zero coercive fields.

Present work is therefore focused on fabricating NiO thin films by spray pyrolysis technique and to check its purity for device fabrications. The preparative method adopted for the deposition of NiO thin films and its structural, surface and magnetic properties that depend on process variables are described in this chapter.
4.1.1 Preparation of NiO Thin Films

Nickel oxide thin films have been prepared using 0.2 and 0.3 M nickel acetate dissolved in 100 % ethanol for different thicknesses by taking different volumes (25, 50 and 75 ml) of spray solution. This was then sprayed on to the heated substrates. Glass substrate was employed and it was pre-cleaned ultrasonically in ethanol, acetone and distilled water for 30 minutes respectively. It was reported that in spray pyrolysis deposition methods, the stoichiometry of the oxide films can be controlled by the partial oxygen pressure during the growth [8]. The oxygen atoms reaching the surface of the growing film depend upon the oxygen partial pressure, as a result the incorporation of oxygen atoms is reduced when the pressure is decreased. In this work, nickel oxide films have been grown under compressed air. Hence, the amount of oxygen in the compressed air leads to the preparation of dense, smooth and stoichiometric NiO films. The flow rate of the solution was fixed at 3.5 ml/min. and the carrier air flow rate was maintained at 0.4 kg/cm². The substrate temperature was kept constant at 450 °C and the substrate to nozzle distance was maintained at 30 cm during all depositions. Favorable deposition conditions for well adherent nickel oxide films are listed in Table 4.1.

Prior to thin film depositions, the decomposition behavior of the precursor has been carried out using Perkin Elmer, Diamond TG/DTA to estimate the pyrolysis temperature range at which the precursor decomposes to the stable phase NiO. TG experiments were carried out at the heating rate of 20 °C/min in air ambient. Thickness of the prepared samples was measured using the Mitutoya surftest SJ-301, a stylus type surface roughness and thickness-measuring instrument. For measuring film thickness, the stylus was placed over the uncoated surface and made to move
towards the coating. The vertical displacement on reaching the coated film surface gave a vertical tilt that measures the thickness of the coating with an estimated error of ± 10 %. The thickness of the prepared thin film samples are in the order of 0.3 to 0.5 µm.

Table 4.1  Optimized deposition parameters for the preparation of NiO thin films

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>Nickel acetate</td>
</tr>
<tr>
<td>Solvent</td>
<td>100 % ethanol</td>
</tr>
<tr>
<td>Precursor concentration</td>
<td>0.2 &amp; 0.3 M</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>450 °C</td>
</tr>
<tr>
<td>Precursor volume</td>
<td>25, 50 &amp; 75 ml.</td>
</tr>
<tr>
<td>Precursor flow rate</td>
<td>3.5 ml/min.</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Air</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>0.4 kg/m²</td>
</tr>
<tr>
<td>Substrate-Nozzle distance</td>
<td>30 cm.</td>
</tr>
</tbody>
</table>

4.1.2 Thermal Decomposition of Nickel Acetate

The TGA/DTA thermogram of the nickel acetate tetrahydrate [Ni(CH₃COO)₂.4H₂O] was recorded in the temperature range 30 - 500 °C, which is shown in Fig. 4.1. Under experimental conditions, the thermogravimetry curve reveals weight loss in three regions within the entire temperature scan.

Region I lie in the temperature scale 80 - 160 °C, which accompanies with a weight loss of 30.45 % for the removal of four molecules of the hydrated water. This
decomposition is analogous to the observed endothermic peak centered at 120 °C in the DTA curve which can be ascribed by the following equation:

\[
\text{Ni(CH}_3\text{COO)}_2\cdot4\text{H}_2\text{O} \xrightarrow{(80-160 °C), \Delta m = 30.45 \%} \text{Ni(CH}_3\text{COO)}_2 + 4\text{H}_2\text{O} \quad (4.1)
\]

However, the coordinated water 4H\text{2O} is only 28.96 % in the initial compound Ni(CH\text{3COO)}_2\cdot4\text{H}_2\text{O}. The additional weight loss of about 1.49 % can be attributed to the hydrolysis of surface acetate groups to solid state nickel acetate by the evaluation of acetic acid and other organic effluents in gaseous phase as reported in the previous studies [9-11].

*Fig. 4.1 TG/DTA thermogram of the starting precursor Ni(CH\text{3COO)}_2\cdot4\text{H}_2\text{O}*

The second mass loss stage is observed in the temperature range 320 -360 °C with an endothermic peak in the DTA curve located at 358 °C. Due to the nonsymmetric nature of the peak, it is resolved into two peaks. Initial mass loss may
be attributed to the conversion of dehydrated nickel acetate into nickel carbonate by the release of acetone (endothermic reaction). Nickel carbonate is short lived due to the sudden deformation into nickel oxide by the release of CO₂ in gaseous phase, which is an exothermic reaction as revealed in the DTA plot centered at 327 °C. These two combined reactions can be represented as:

\[
\text{Ni(CH}_3\text{COO)}_2 \xrightarrow{(261-394 \degree \text{C})} \Delta m = 42.20 \% \rightarrow \text{NiCO}_3 (\text{NiO + CO}_2) + \text{CH}_3\text{COCH}_3 (4.2)
\]

Observe weight loss of 42.20 % in this stage is almost equal to the theoretical weight loss of 41.6 % for the generation of gaseous acetone and carbon dioxide. Residue of this decomposition stage supports the formation of solid phase of NiO as reported in the previous work [12, 13]. Hence from the decomposition analysis of the nickel acetate, the favourable process temperature for the formation of nickel oxide is above 400 °C and therefore in the present study NiO films were prepared at 450 °C.

4.1.3 Thickness and Structural Characterization

The nickel acetate dissolved in ethanol was atomized through specially designed glass nozzle that produces fine aerosol like droplets. The droplet size was so adjusted by controlling the air and solution flow rate such that the pyrolytic decomposition takes place in the close vicinity of the substrate due to temperature gradient formed between the substrate and the atomizer. At the optimized deposited conditions, uniformly coated nickel oxide films were obtained.

The thickness variation of NiO films deposited at 450 °C using 0.2 and 0.3 M nickel acetate solutions are shown in Fig. 4.2. For both the precursor concentrations, the thickness variations have a similar trend with the volume of precursor sprayed.
Initially the growth rate is linear because of greater amount of reactants participating in the deposition process. On further increasing the precursor volume, deposition begins to decrease, showing the phenomenon of reactant saturation effect. Growth rate for two solutions of different concentrations are therefore not exactly in proportion. Moreover, the growth of oxide films is governed by two growth mechanisms, the Rideal-Eley and Langmuir-Hinshelwood mechanisms [14]. In the present case, thickness of the film increases with concentration and therefore the growth rate follows the Rideal-Eley mechanism. According to this mechanism, the growth rate is governed by the metal ion containing species, which is available plenty on increasing the concentration of the precursor. After attaining a specific thickness, due to precursor saturation effect, the thickness of the film remains almost constant.

![Graph](image)

**Fig. 4.2 Thickness variation of NiO films deposited using 0.2 and 0.3 M**

The X-ray diffraction spectra of NiO films deposited on corning 7059 microscopic glass plates for different thicknesses by spraying different volumes of 0.2 M precursor at 450 °C is shown in Fig. 4.3.
As seen, the nickel oxide film deposited for the thickness of 0.316 µm is amorphous without any peaks in the recorded 2θ region. However, films deposited for the thickness of 0.426 µm show a peak which begins to arise at 2θ = 43.09°. This is assigned to the (200) peak of cubic NiO. On increasing the thickness to 0.441 µm, well crystallized phase of NiO is observed. On comparing the interplanar distances (d_{hkl}) with the standard JCPDS data (No. 65-2901), they are found in good agreement. The peaks corresponding to the 2θ values 37.09, 43.19, 62.72, 75.31 and 79.28 are assigned to the Miller indices (111), (200), (220), (311) and (222) respectively. The orientation of the film is dominant along the (200) plane. The calculated unit cell parameter of the system (4.1945 Å) is perfectly matched with the standard value (4.194 Å). NiO films deposited for the thickness of 0.441 µm is therefore considered as an optimized film with good crystallinity and possessing single phase. From the
overall observations, it is clear that the thickness of film plays a vital role in deciding the crystallinity of the nickel oxide films.

Crystallite size can be estimated from the broadening of the peak measured in terms of full width at half maximum (FWHM). This is inversely proportional to the average crystallite size (D) as predicted by the well-known Scherrer’s formula [15] and the microstrain for the films processed for the thickness 0.441 µm are respectively 58.6 nm and 2.51 x 10^{-3} (Table 4.2).

### Table 4.2 Structural parameters of prepared NiO thin film for different film thicknesses

<table>
<thead>
<tr>
<th>Films Thickness (µm)</th>
<th>Lattice parameter (a) (Å)</th>
<th>Grain size (D) nm</th>
<th>Microstrain (ε) x10^{-3}</th>
<th>Dislocation density (δ) x10^{15} lines/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment</td>
<td>Standard</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.316</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>0.426</td>
<td>4.1954</td>
<td>4.194</td>
<td>20.97</td>
<td>3.43</td>
</tr>
<tr>
<td>0.441</td>
<td>4.1945</td>
<td>4.194</td>
<td>58.60</td>
<td>2.51</td>
</tr>
</tbody>
</table>

Accurate analysis for size and/or strain effects has been precisely accounted by considering the instrumental broadening and lattice strain. Williamson and Hall proposed a method for deconvoluting the size and strain broadening by looking at the peak width as a function of 2θ. The Williamson-Hall relationship was considered for estimation by fitting the peak using Lorentzian function [16, 17].

The Williamson-Hall plot drawn for the optimized film using the diffraction data is as shown in Fig. 4.4. From the linear fit to the data, the crystallite size from the y-intercept and strain from the slope of the fit was estimated. The average grain size and the microstrain obtained from the plot are respectively 55.08 nm and 2.80 x 10^{-3}.
In order to understand the effect of precursor concentration, NiO films were prepared using precursor concentration of 0.3 M. Fig. 4.5 shows the X-ray diffraction pattern of the NiO films prepared for different thicknesses using 0.3 M precursor. XRD patterns reveal the formation of mixed phases of NiO (nickel sequioxide (Ni$_2$O$_3$) phase and bunsenite NiO phase) irrespective of film thickness. Peaks corresponding to Ni$_2$O$_3$ and NiO are present separately in each sample. On increasing the thickness to 0.483 µm, the sequioxide phase begins to reduce and the cubic phase dominates. On further increasing the thickness to 0.513 µm, the overall crystallinity of the film decreases and the film is almost amorphous.
From the observed results, it is concluded that the precursor concentration as well as the film thickness have significant role on the formation of nickel oxide thin films. The microstructural changes in the film may be due to the variations in the droplet formation with precursor concentration [18]. During spray process, diluted precursor would results solute surface precipitation after droplet breakage and solvent evaporation. However, concentrated precursors form solute volume precipitation that favours the production of mixed phases of nickel oxide. From these observations, it is confirmed that 0.2 M precursor pyrolysed at 450 °C is the foremost and sufficient condition for the production of single phase nickel oxide films.
4.1.4 Phase Confirmation

Functional groups present in the starting precursor nickel acetate can be identified from the recorded FTIR spectrum, which is shown in Fig. 4.6. Observed bands at 1030, 963, 908, 820, 750, 678, 624 and 552 cm\(^{-1}\) are the characteristic peaks for the metal acetate salts [19]. The strong absorption bands at 1538 and 1419 cm\(^{-1}\) may be assigned to the asymmetric and symmetric stretching vibrations of the carboxylate group from the acetate anion. The C-O and C-C stretches are normally occurred in the wavenumber range 910 - 970 cm\(^{-1}\). The band at 820 cm\(^{-1}\) is assigned to the out of plane bending of C-O bond. The in-plane bending of C-O bond is assigned to 750 cm\(^{-1}\).

![FTIR spectrum of the starting precursor nickel acetate](image)

**Fig. 4.6 FTIR spectrum of the starting precursor nickel acetate**

For most of the oxides, absorption band are in the low wavenumber fingerprint region and hence the bands occurred at 678, 624 and 552 cm\(^{-1}\) are assigned to the bonding between Ni and O [20]. The broad characteristic absorbance bands at 1700–1500 cm\(^{-1}\) and 2900–3500 cm\(^{-1}\) can be assigned to the bending vibration and the
stretching vibration of O–H which arises due to the coordinated water in the precursor. The sharp band observed at 3475 cm\(^{-1}\) may be assigned to the stretching vibrations of OH groups not involved in hydrogen bonding, whereas the bands at 3138 and 2934 cm\(^{-1}\) may be assigned to vibrations of OH groups involved in significant hydrogen bonding [21].

Fig. 4.7 illustrates the Ni-O phase formation in the deposited films prepared for different thicknesses at the optimized deposition conditions. The broad absorption band in the region of 820 - 400 cm\(^{-1}\) is assigned to Ni-O stretching vibration mode [22]. The broadness of the absorption band indicates that the NiO samples are nanocrystalline in nature as confirmed through the XRD results. In addition, this band is strong in optimized films deposited for the thickness of 0.441\(\mu\)m and also it is shifted to the blue region.

Fig. 4.7 FTIR spectra of the nickel oxide thin films of various film thicknesses
For the bulk NiO material, the main IR absorption maximum corresponds to the long wavelength transverse optical mode and the optical photon frequency lie between 390 and 403 cm\(^{-1}\) [23]. In nanostructures, the wave functions of the electron and the hole are confined to a small region and the energy required for creating an electron/hole pair is higher. This increase in energy shifts the absorption spectra towards shorter wave lengths (blue) [24]. Besides the Ni–O bands, observed overlapped bands in the higher wavenumber region (above 3500 cm\(^{-1}\)) show the O–H stretching vibrations and the band near 1695 cm\(^{-1}\) is assigned to H–O–H bending vibrations due to the molecularly adsorbed water molecules on exposing the films to the air ambient [25-27]. The serrated absorption bands centered at 1520 and 1240 cm\(^{-1}\) are assigned to the O–C=O symmetric and asymmetric stretching vibrations and the C–O stretching vibrations. The absorption band around 2359 cm\(^{-1}\) is assigned to the existence of CO\(_2\), which indicates that the prepared samples have strong tendency for the absorption of water and CO\(_2\).

4.1.5 Elemental Composition Analysis
4.1.5.1 Chemical environment analysis

The surface chemical compositions and states of the NiO thin films prepared using 0.2 M nickel acetate on glass substrate were studied by XPS analysis, which is presented as in Fig. 4.8. The peaks corresponding to Ni 2p, O 1s, C 1s, Ni 3s, Ni 3p and O 2s are obviously observed. The high-resolution spectra corresponding to Ni 2p and O 1s are given in Fig. 4.9 and 4.10.
Fig. 4.8 XPS survey spectrum of NiO thin film prepared using 0.2 M precursor

Fig. 4.9 Ni 2p core level XPS spectrum showing the surface dominated by NiO
Fig. 4.9 shows the nickel 2p core level spectrum consists of two sub levels (2p\textsubscript{1/2} and 2p\textsubscript{3/2}) due to spin–orbit splitting. In addition, a weak peak is also observable at energy value 1.8 eV higher from the main peak in the Ni 2p spectrum. It can be noted that the binding energy of Ni 2p\textsubscript{3/2} located at 854.2 eV and 856.0 eV are the characteristic of Ni\textsuperscript{2+} 2p\textsubscript{3/2} and Ni\textsuperscript{3+} 2p\textsubscript{3/2} peaks respectively. Once again, the observed peaks at the lower binding energy region of the spectrum at 873.3 and 879 eV are due to Ni\textsuperscript{2+} 2p\textsubscript{1/2} and Ni\textsuperscript{3+} 2p\textsubscript{1/2} peaks respectively.

The splitting of Ni 2p\textsubscript{3/2} spectrum is due to the presence of several oxidation states of Ni, including Ni\textsuperscript{2+} (NiO) and very few amounts of Ni\textsuperscript{3+} (Ni\textsubscript{2}O\textsubscript{3}). Moreover, each oxidation state is accompanied by major and minor peaks, as well as satellite peaks [28, 29]. All these assignments of Ni 2p spectrum components were based on previously reported results [30-33]. The prominent component (854.2 eV) is assigned to NiO which may arise from major, minor, and satellite peaks of NiO [34, 35]. Observed peak at the binding energy 854.2 eV corresponds only to Ni\textsuperscript{2+} 2p\textsubscript{3/2} peak represents the feature of pure NiO. In photoemission spectrum of NiO, the double peak structure in the Ni 2p line of NiO is a result of the presence of both the 2p\textsuperscript{5}3d\textsuperscript{8} and 2p\textsuperscript{5}3d\textsuperscript{9}L configuration, where L denotes a hole in the oxygen valence band. The 2p\textsuperscript{5}3d\textsuperscript{9}L state is produced by a ligand-to-metal charge transfer. The d band of nickel is pulled down by the core hole to below the top of the ligand 2p band. The screening can occur by charge transfer out of the ligand level into the d band. The energy of this final state is smaller than that of another final state. Thus, this final state has a smaller binding energy than another final state. The Ni 2p XPS spectrum will be influenced exclusively by charge transfer processes from the nearest-neighbour oxygen atoms.
From the spectrum of O 1s in Fig. 4.10, two components can be deconvoluted with peaks at 529.9 and 531.6 eV respectively.

These two oxygen species were assigned as the lattice oxygen in NiO, the physical adsorbed oxygen (O$_{2}^-$) for the formation of NiO and the hydroxyl chemical adsorbed oxygen (OH$^-$), respectively. Compared with the previous reports [36], the fitted peaks of O$_{2}^-$ (physical adsorbed oxygen) is much stronger, indicating the formation of pure NiO phase without the Ni$_2$O$_3$ phase and OH$^-$ (chemical adsorbed oxygen) is very weak where the presence of Ni$_2$O$_3$ phase is very minimum in the prepared film.
4.1.5.2 EDS analysis

The composition of NiO thin films were analyzed by energy dispersive X-ray spectral analysis (EDS) is shown in Fig. 4.11.

![EDS spectrum](image)

**Fig. 4.11** EDS spectrum of NiO sample prepared for different film thickness (a) 3.16 (b) 4.26 and (c) 0.441 µm

The EDS results show the presence of Ni and O by the appearance of corresponding peaks with additional peaks that corresponds to the presence of silica and calcium of substrate material as X-rays penetrates deep in to it. Hence, the results are definitive evidence to suggest that the obtained NiO films are dominated only by the presence of nickel and oxygen element.
The amount of elements present in the deposited NiO thin films is listed in Table 4.3. From the obtained quantitative information, the stoichiometry of the optimized film prepared with thickness 4.41 µm has been confirmed with atomic percentages 48.55 and 47.97 respective for the native elements Ni and O. However, the other two samples exhibits nonstoichiometry by with unequal proportions of Ni and O. These results suggest that the prepared NiO thin film for the thickness of 0.441 µm is pure NiO with convincing percentage of Ni and O.

Table 4.3 Elemental composition of NiO thin films

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Elemental Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>Atomic %</td>
</tr>
<tr>
<td>3.16</td>
<td>31.86</td>
</tr>
<tr>
<td>4.26</td>
<td>21.94</td>
</tr>
<tr>
<td>4.41</td>
<td>48.55</td>
</tr>
</tbody>
</table>

4.1.6 Surface Morphological Study

4.1.6.1 Surface topography

The 2-D and 3-D AFM micrographs of the NiO films deposited at 450 °C for different thicknesses are shown in Fig. 4.12. It is evident that the films deposited for thickness 0.441µm have an atomically flat surface.

As the thicker film is crystalline and possesses NiO structure, it has smooth morphology with spherical grains that begins to evolve from the surface. Thus the morphological study proves an additional evidence for the grain growth as visualized from the XRD studies. AFM images can also be used to find out the surface
roughness of the film by noting the height deviations from the least fitted line on the 2-D micrograph. After knowing the height deviations, calculated value of the rms roughness of the films is about 6.21 nm for the film deposited at 450 °C for the thickness of 0.441 µm. In our observations, it is found that the surface roughness decreased with the increase of film thickness.

Fig. 4.12 AFM image of the NiO thin films prepared for different thicknesses using 0.2 M precursor at 450 °C: (a) 0.316 (b) 0.426 and (c) 0.441 µm

The grain size obtained from the 3-D image is about 350 nm. The observed value is somewhat higher than the value obtained through the XRD studies. This is because of the measuring principle involved in the instruments. In XRD, X-rays penetrate deep into the specimen and records the spectrum which gives the average
grain size. However in AFM, data observed is reliable for grains of higher size due to tip convolution artefacts. For smaller grain sizes, the AFM analysis yields higher values, whereas for bigger grains the AFM and XRD data coincides [37]. Moreover, the conductive coating made over the film surface prior to measurements using sputtering technique also alters the grain size.

### 4.1.6.2 Surface measurement

The visualization of the surface of the films shows the inhomogeneity in the smoothness of the films (Fig. 4.13). When the precursor volume is increased from 25 to 75 ml, the thickness of the films also increased from 0.316 to 0.441µm.

![SEM images](image)

**Fig. 4.13** SEM images of the prepared NiO thin films for different thicknesses: (a) 0.316 (b) 0.426 and (c) 0.441 µm
In thinner films, the material deposit is less and therefore the given thermal energy at 450 °C is more and therefore huge amount of fumes generate porous structure on the surface of the film as seen in Fig. 4.13a. On increasing the thickness, most of the energy is utilized for the formation of metal oxide and the release of gaseous products is less. So the surface of the film deposited for the thickness of 0.426 µm has smoother surface compared to the previous one. Finally the thicker film (0.441 µm) has smooth surface without any cracks and the porous structure completely disappears. The presence of macro-agglomerations containing very fine particles (under 0.1 µm) is observed from the synthesized films. The average values of the grain size estimated from SEM statistics measurements are slightly higher than those estimated from XRD measurements: the two techniques are different, the former allows measuring the size of the grain visualized, the latter allows estimating the coherent crystalline thickness.

4.1.7 Electrical Studies

Fig. 4.14 shows the temperature dependent electrical resistivity variations in nickel oxide films prepared for various thicknesses using 0.2 M precursor. As seen, resistivity variations with temperature support the semiconducting behaviour of the prepared material. At RT, the resistivity value of the nickel oxide films deposited for the thickness 0.441 µm is about 99.2 Ωcm and then it decreases with temperature and attains a value of 4.34 Ωcm at 200 °C. Films processed at high temperature usually attain good degree of crystallinity accompanied by increasing the number of crystallites rather than increase of their size. This in turn decreases the resistivity of the sample [38, 39]. In addition, origin of the semiconducting nature may be due to non-stoichiometric NiO that contains many Ni$^{2+}$ vacancies, some of which is oxidized
to Ni$^{3+}$ to preserve the charge neutrality [40]. Every Ni$^{2+}$ ion lost from NiO will result in the production of the 2Ni$^{3+}$ ions. The defect chemistry therefore plays an important role in controlling the electrical properties of this material [41, 42]. Thus the mixed valences of Ni (Ni$^{2+}$ and Ni$^{3+}$) confined to the non-stoichiometry NiO films drastically alters the electrical conductivity of the films.

Moreover, it is noted that the thickness of film has its own consequences in electrical conductivity. Films prepared for the thickness of 0.316 µm has the room temperature resistivity of 306.9 Ωcm, whereas the 0.441 µm thick films have the resistivity of 99.22 Ωcm. The resistivity variations with thickness can be explained with change in mean free path of the carriers. Whenever the specimen becomes thin enough, carriers encounter collision among themselves and susceptible for reflection

**Fig. 4.14** Temperature dependent resistivity of the NiO thin films prepared for various thicknesses using 0.2 M precursor

Moreover, it is noted that the thickness of film has its own consequences in electrical conductivity. Films prepared for the thickness of 0.316 µm has the room temperature resistivity of 306.9 Ωcm, whereas the 0.441 µm thick films have the resistivity of 99.22 Ωcm. The resistivity variations with thickness can be explained with change in mean free path of the carriers. Whenever the specimen becomes thin enough, carriers encounter collision among themselves and susceptible for reflection.
at the surface [43]. In addition, films deposited for lower thickness has drastic variations in electrical resistivity that reveals the non-stoichiometry nature of the film with mixed Ni valences. The p-type conductivity of NiO was confirmed by Hall measurements carried out in Van der Pauw method.

Each cation vacancy in the lattice give rebirth to two holes that leads to p-type conductivity. The carrier concentration of the film is $0.117 \times 10^{24}/m^3$, which is sufficient to have high electrical conduction. But the carrier mobility is very low in the order of $10^{-5} m^2/Vs$, hence the electrical conductivity of the film is moderate.

![Arrhenius plots for the NiO films prepared for different thickness](image)

**Fig. 4.15 Arrhenius plots for the NiO films prepared for different thickness**

From Arrhenius plot (Fig. 4.15), the activation energy of the material is evaluated [44, 45]. The logarithmically scaled resistivity against reciprocal absolute temperature estimates the activation energy values ‘$E_a$’. Obtained value (0.615 eV) is
in full agreement with the values of 0.6 eV reported (Table 4.4) for nano-crystalline nickel oxide films prepared by solution growth and subsequently annealed at 350 °C [46].

Table 4.4 Activation energy ($E_a$) of NiO thin films of different thicknesses

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.316</td>
<td>0.07</td>
</tr>
<tr>
<td>0.426</td>
<td>0.431</td>
</tr>
<tr>
<td>0.441</td>
<td>0.615</td>
</tr>
</tbody>
</table>

Temperature co-efficient of resistance (TCR) is also determined for the films prepared using the precursor of concentrations 0.2 M for various thicknesses. Obtained temperature co-efficient of the resistance values are in the order of $10^{-3}$ K$^{-1}$. Further, the negative values of TCR confirm the semiconducting nature of the prepared NiO films.

4.1.8 Optical Studies

Measurement of optical transmittance provides a satisfactory way to determine the absorption edge and hence the energy band gap, refractive index and porosity. Fig. 4.16 shows the normalized spectral transmittance of the nickel oxide films deposited using the precursor of concentration 0.2 M.

As seen, the optical transmittance increases with wavelength and the optical transmittance is comparatively good in the optimized film. The normalized intensity is less in the visible region and it attains the maximum intensity in the Near Infra-Red (NIR) region. Even though the optimized film is thicker, transmittance is maximum. This may be because of its surface smoothness as evidenced from the AFM and SEM studies. In the UV region, a sudden fall in transmittance is observed, which is mainly
due to the fundamental intrinsic absorption of the title compound. Films deposited for lower thicknesses possess remarkably lower than the value of 0.7 of its normalized transmittance in the visible region claiming higher absorption and scattering due to rough surface.

![Normalized transmittance spectra of NiO thin films deposited for different thicknesses](image)

**Fig. 4.16 Normalized transmittance spectra of NiO thin films deposited for different thicknesses**

The ability of a material to absorb photons of a given wavelength is measured quantitatively by the optical absorption coefficient ($\alpha$), measured in units of reciprocal distance. There are two major types of intrinsic absorption processes involved in determining ‘$\alpha$’, they are the direct and indirect absorption. As a general rule, the larger the band gap, the smaller is the value of ‘$\alpha$’ for a given wavelength but absorption coefficient also depends on the density of states in the conduction and valence bands. Usually the plot of $(\alpha h\nu)^2$ or $(\alpha h\nu)^{1/2}$ against $(h\nu)$ provides the nature and optical band gap value of a particular film [47]. At the absorption edge, ‘$\alpha$’ rises abruptly reaching values of $10^5$ cm$^{-1}$ and beyond the absorption edge, decreases and
the edge shift towards shorter ‘λ’ [48]. The band gap of the films can be deduced from
the extrapolation of the linear part of the graph relative to the function \((\alpha h\nu)^2 = f(h\nu)\) [49]. A typical plot drawn between ‘h\nu’ and ‘(\alpha h\nu)^2’ is presented in Fig. 4.17.

![Graph showing dependence of \((\alpha h\nu)^2\) on incident photon energy h\nu for samples prepared using 0.2 M precursor.]

**Fig. 4.17** Dependence of \((\alpha h\nu)^2\) on the incident photon energy h\nu for the samples prepared using 0.2 M precursor

It can be seen that the plot is linear in the region of strong absorption i.e. near the fundamental intrinsic absorption edge. The linear intercept at the h\nu-axis gives the direct allowed band gap value of the film, which is 3.41 eV for the optimized film. The estimated value is in good agreement with the previously reported value of 3.44 eV [50, 51].

In order to obtain the refractive index of the films practically, the Swanepoel method was used [52]. In the NIR region, the variation in ‘n’ is almost constant and in the UV-visible region, the value drops from the higher value of 2.65. Precursor
pyrolysis at the process temperature yield films with different refractive indices dropped from 2.1 to 1.85 due to the variations in the film density. Obtained values agree well with the previously reported ones [53]. The packing density of bulk material has unit value. Obtained value of packing density is 0.89 at 600 nm. The relationship between the refractive index and the packing density is approximately linear as proposed by Kinosita and Nishibori [54].

4.1.9 Magnetic Studies

Fig. 4.18 shows the magnetization measurements on NiO films prepared for various thicknesses in the applied magnetic field ranging from -15 to +15 KG at room temperature.

![Magnetization versus magnetic field of the NiO samples](image)

Fig. 4.18 Magnetization versus magnetic field of the NiO samples
On increasing the field, the magnetization increases initially and then saturates at higher fields. This variation forms the hysteresis loop that shows the ferromagnetic behaviour of the NiO thin films with saturation magnetization of 0.143 memu. The NiO sample with smaller film thicknesses 0.316 and 0.426 µm shows lower saturation magnetization of 0.057 and 0.123 memu respectively at 15 KG. Thus NiO with higher film thickness possess a higher fraction of surface uncompensated spins as compared to film with lower thicknesses and thus possess higher saturation magnetization values. Measured remanant magnetization ($M_r$) in the optimized film is 0.0836 memu, which is quite different from the bulk sample [55, 56]. It is well known that the thermal fluctuations will significantly reduce the total magnetic moment at a given field when magnetic thin films energy becomes comparable to the thermal energy [57]. In addition to thermal fluctuation, the disordered structure at interfaces provides less magnetic moment per unit mass than that of ferromagnetic core regions, which also leads to a decrease in ‘$M_s$’ [58]. Hence the disordered thin NiO structures have less magnetization values. The magnetic parameters calculated from the ferromagnetic hysteresis loop have been estimated and are listed in Table 4.5.

Table 4.5 Magnetic parameters of NiO thin film prepared for different thicknesses

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Magnetic parameters</th>
<th>Coercivity ($H_c$) (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Magnetization ($M_s$) (memu)</td>
<td>Retentivity ($M_r$) (memu)</td>
</tr>
<tr>
<td>3.16</td>
<td>0.057</td>
<td>0.039</td>
</tr>
<tr>
<td>4.26</td>
<td>0.123</td>
<td>0.078</td>
</tr>
<tr>
<td>4.41</td>
<td>0.143</td>
<td>0.084</td>
</tr>
</tbody>
</table>

The coercive field ($H_c$) and the saturation magnetization ($M_s$) of well crystallized NiO samples are about 575.71 G and 0.143 memu, respectively. The
origin of the ferromagnetic property variations may be attributed to the size confinement effect of the NiO samples [59, 60]. Nickel oxide thin films are made of small magnetic domains. Each magnetic domain is characterized by its own magnetic moment oriented randomly. The total magnetic moment of the sample is the sum of these magnetic domains coupled by dipolar interactions.

4.2 FERRITE THIN FILMS

Nano sized iron oxide particulates have emerged as versatile materials for different applications due to their, magnetic, electronic, photonic and optical properties. The structure-function relationship of these nano particles have been intensively studied because of the applications in magnetic storage, gas sensing, biomedical, and catalysis applications [61-65]. The iron oxide compounds like zinc-containing ferrites have contributed greatly to the development of telecommunication and computer systems. Moreover, ferromagnetic films have many applications for microwave devices as well as high-density recording media [66–68]. However, only yttrium iron garnet-based films have been investigated and practically used as magnetostatic wave components. It is well known that the ferrites have a strong chemical stability [69–71], and furthermore, Co-ferrite thin films also exhibit an excellent magneto-optical property. Therefore, these films are expected to be advantageous materials for magneto-optical memory and their recording applications. There are as many as 15 phases formed by Fe and O as oxides of iron [72]. They are abundant in earth’s crust. They can be synthesized in pure, mixed oxides as well as doped structures. Iron oxide is used as an electrode in non-aqueous and alkaline batteries [73, 74] and as a cathode in brine electrolysis [75].
Iron oxides are widely abundant and are therefore low-cost materials. These oxides have been widely used in several industrial processes such as dehydration, oxidation and Fischer–Tropsch synthesis [76]. Amongst the oxides of iron, haematite (α-Fe$_2$O$_3$) is a numerous investigated material because of its chemical stability in a broad pH range, optical band gap around 2 eV, utilizing quite significant (about 40 %) amount of the incident solar radiation and position of the valence band which is appropriate for oxygen evolution [77]. Hematite is used as a red pigment, an anticorrosive agent, and in electrochromic devices and gas sensors [78]. Fe$_2$O$_3$ is found to have large third-order non-linear optical susceptibility and faster response time showing potential applications in optical computing [79]. It appears to have catalytic properties useful for N$_2$ fixation [20]. These oxides have been widely used in several industrial processes, such as dehydration and oxidation synthesis [81-83]. The electrochemical supercapacitor (ES) can be used as a reliable energy storage and delivery device due to its high power density and high durability. This ES has prominent applications such as electric vehicles, electric hybrid vehicles, digital communication devices, digital cameras, mobile phones, electric tools, pulse laser techniques, and uninterruptable power supplies as well as energy storage generated by solar cells [84-86]. According to recent literature, the iron oxide is a low-cost, easily available, environmentally friendly material exhibiting pseudocapacitive behavior.

The present work is focused on fabricating Fe$_2$O$_3$ thin films by spray pyrolysis system and to check its purity. The effects of the process variables on structural, surface and magnetic properties of the Fe$_2$O$_3$ films have been investigated and are discussed below.
4.2.1 Preparation of Fe$_2$O$_3$ Thin Films

Iron oxide thin films have been prepared using 0.15 M ferric chloride dissolved in 100 % ethanol for different temperatures 350, 400 and 450 °C. This solution was then sprayed on to the heated substrates, which were chemically and ultrasonically cleaned before coating. The flow rate of the solution was fixed at 3.5 ml/min. and the carrier air flow rate was maintained at 0.4 kg/cm$^2$. The substrate to nozzle distance was maintained at 30 cm during all depositions. Prior to thin film depositions, the decomposition behavior of the precursor has been carried out using Perkin Elmer. Favorable deposition conditions for well adherent iron oxide films are listed in Table 4.6.

Table 4.6 Optimized deposition parameters for the preparation of Fe$_2$O$_3$ thin films

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>Ferric Chloride</td>
</tr>
<tr>
<td>Solvent</td>
<td>100 % ethanol</td>
</tr>
<tr>
<td>Precursor concentration</td>
<td>0.15 M</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>350, 400, 450 °C</td>
</tr>
<tr>
<td>Precursor volume</td>
<td>50 ml.</td>
</tr>
<tr>
<td>Precursor flow rate</td>
<td>3.5 ml/min.</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Air</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>0.4 kg/m$^2$</td>
</tr>
<tr>
<td>Substrate-Nozzle distance</td>
<td>30 cm.</td>
</tr>
</tbody>
</table>

Thickness of the prepared samples was measured using the Mitutoya surftest SJ-301, a stylus type surface roughness and thickness-measuring instrument. For measuring film thickness, the stylus was placed over the uncoated surface and made to move towards the coating. The vertical displacement on reaching the coated film
surface gave a vertical tilt that measures the thickness of the coating with an estimated error of ±10%. The thickness of the prepared thin film samples was in the order of 1.63 to 3.18 µm.

4.2.2 Structural Characterization

Fig. 4.19 shows the XRD pattern of Fe₂O₃ thin films prepared for different temperature 350, 400 and 450 °C respectively. These samples show the formation of hematite polycrystalline structures without any additional secondary phases. Obtained peaks at specified 2θ locations match for the hematite phase (R3̅(148) group), which crystallizes in a rhombohedral crystal structure with lattice parameters a = b = 5.03 Å and c = 13.73 Å in the hexagonal settings. A strong preferential orientation is observed in the (110) direction.

Fig. 4.19 XRD pattern of Fe₂O₃ films for various concentration
From the observed patterns, it is clear that all the films are of \( \alpha\)-Fe\(_2\)O\(_3\) without any impurity phase. Moreover, two main peaks are along (104) and (110), and two tiny peaks are indexed for its (116) and (214) lattice planes, respectively. Also, it is noticed that the optimised film prepared at 450 °C has its preferential orientation along the (110) direction. It was reported that \( \alpha\)-Fe\(_2\)O\(_3\) had a strong anisotropic conductivity, which is 4 orders of magnitude higher along the (110) than in the orthogonal direction [87].

Prepared nanocrystalline films are polycrystalline and are rhombohedral in crystal structure having space group \( R\bar{3}(148) \). These films of \( \alpha\)-Fe\(_2\)O\(_3\) are comparable with 24-0072 in a powder diffraction file (PDF) collected by the Joint Committee on Powder Diffraction Standards (JCPDS). Peaks with lesser intensities are due to film thickness that initiates amorphous character in thin films. A slight hump in the XRD pattern around 32.19 is the evidence for this. As the substrate temperature is increased to 450 °C, the diffraction angle of the (110) peak is almost in agreement with the Fe\(_2\)O\(_3\) thin film, implying that no evident residual stress or inclusion-induced lattice distortion has developed in the Fe\(_2\)O\(_3\) film due to increase in substrate temperature. The lattice parameters ‘a’ and ‘c’ of the prepared \( \alpha\)-Fe\(_2\)O\(_3\) films are determined from the analysis of the X-ray diffraction patterns. The calculated values of ‘a’ and ‘c’ for the \( \alpha\)-Fe\(_2\)O\(_3\) films are \( a = 5.037 \, \text{Å} \) and \( c = 13.77 \, \text{Å} \), which are close to the values which are in agreement with the mentioned JCPDS standards, \( a = 5.038 \, \text{Å} \) and \( c = 13.77 \, \text{Å} \). The calculated grain size for (110) peak are listed in Table 4.7.
Table 4.7 Structural parameters of \( \text{Fe}_2\text{O}_3 \) thin Films

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Lattice Parameters (Å)</th>
<th>Grain size (D) nm</th>
<th>Dislocation density (( \bar{\rho} )) x10^{15} lines/m²</th>
<th>Micro strain (( \varepsilon )) x10⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment</td>
<td>Standard</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.63</td>
<td>5.036</td>
<td>13.81</td>
<td>14.20</td>
<td>1.85</td>
</tr>
<tr>
<td>1.73</td>
<td>5.037</td>
<td>13.77</td>
<td>32.25</td>
<td>1.05</td>
</tr>
<tr>
<td>3.18</td>
<td>5.037</td>
<td>13.77</td>
<td>32.54</td>
<td>1.04</td>
</tr>
</tbody>
</table>

It is observed that the crystallite size of \( \alpha\text{-Fe}_2\text{O}_3 \) is 14.2 nm for the film deposited for the thickness 1.63 µm and it increases with increasing substrate temperature (Table 4.7). It is also found that the dislocation density increases with decrease in grain size. For films with small grains have much amount of grain boundaries that increases the dislocation intensity. It is very natural that, for smaller crystallites the numbers of interfaces in a given volume are more, giving maximum dislocation density. The microstrain provides the information about the defects present in the lattice.

4.2.3 Phase Confirmation

Fourier transform infrared measurements were carried out and it is an easy way to identify the presence of certain functional groups in the prepared thin film. In the present study, the information about the functional group in \( \alpha\text{-Fe}_2\text{O}_3 \) is investigated from the FTIR spectra within the wavelength range 400–3500 cm⁻¹, which is shown in Fig. 4.20. Obtained spectra shows the absorption in the region 1645, 1146, 603 and 466 cm⁻¹. The absorption peaks around 1645 cm⁻¹ is attributed to the O–H bending vibrations combined with Fe atoms and also another flat peak at around 1146 cm⁻¹ represents C - O - C vibration peak [88]. The peaks at 603 and 466 cm⁻¹ correspond to the metal–oxygen (Fe-O) stretching and bending vibrational modes of the \( \alpha\text{-Fe}_2\text{O}_3 \) respectively and these two peaks are characteristics of spinel.
compounds. Out of these two bands, the band at 466 cm$^{-1}$ is sharp and another band at 603 cm$^{-1}$ is low intense that represents the Fe-O bonding. Obtained results are in good agreement with the reported literature [89] and each Fe$^{3+}$ ion is octahedral oxygen coordinated for the film prepared for the thickness of 3.18 µm. When the film thickness decreases to 1.63 µm, the sharp peak obtained at 466 cm$^{-1}$ disappears gradually and it may be due to the amorphous nature of the film as revealed by XRD.

![Fig. 4.20 FTIR spectra of α-Fe$_2$O$_3$ thin films prepared for different temperatures](image)

The Fe-Fe distance in α-Fe$_2$O$_3$ is larger than the critical length which is equal to 0.289 nm in metal iron. However, the transport properties depend on the deviation from the stoichiometry. The defect structure has been the subject of numerous investigations [90] and discussion of the transfer in oxides is based on the model of thermally activated hopping through local electron states. The outer 3d electrons in Fe$_2$O$_3$ can be considered as localized and the variation in structural properties occurs predominantly by electron hopping between mixed states Fe$^{2+}$/Fe$^{3+}$ located in
crystallographically equivalent sites and the ionic radii of Fe$^{2+}$ and Fe$^{3+}$ are close to each other in six fold coordination. Result thus confirmed the presence of Fe-O bonds, and the coordinated –OH groups in Fe$_2$O$_3$ thin films and there is no evidence for any contamination in the form of foreign materials in the prepared thin film.

4.2.4 Elemental Composition Analysis
4.2.4.1 Chemical environment analysis

The XPS survey spectrum was recorded in the BE range from 0 to 1400 eV is shown in Fig. 4.21. Elements assigned for various peaks confirmed the presence of Fe and O elemental signatures. Absence of elemental signals other than Fe and O in the XPS spectra shows the purity of the prepared sample. The Fe 3s, 3p peaks are less prominent as compared to Fe 2p. The peak positions corresponding to Fe 2p and O 1s are in the BE range 705 - 730 and 528 - 540 eV, respectively.

Fig. 4.21 XPS survey spectrum of $\alpha$-Fe$_2$O$_3$ thin film
The Fe 2p core level spectrum is shown in Fig. 4.22. Observed peaks at 710.9 and 724.4 eV are the characteristic doublets of Fe 2p$_{3/2}$ and 2p$_{1/2}$, which are very close to the previously reported values [91]. Out of these two peaks, Fe 2p$_{3/2}$ peak is narrower and stronger than Fe 2p$_{1/2}$ and the area of Fe 2p$_{3/2}$ peak is greater than that of Fe 2p$_{1/2}$ because of spin–orbit (j–j) coupling; Fe 2p$_{3/2}$ has degeneracy of four states whilst Fe 2p$_{1/2}$ has only two. The peak position of Fe 2p$_{3/2}$ has been investigated by many researchers and the values of between 710.6 and 711.2 eV have been reported [92-95].

![Fig. 4.22 Fe 2p core level spectrum of α-Fe$_2$O$_3$ thin film](image)

The binding energies of Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ obtained from the present study are 710.9 (standard deviation (S.D.) = 0.01) and 724.4 eV (S.D. = 0.17) respectively. There is also distinctive shake up satellite around 719 eV [96], approximately 8.1 eV higher than the main Fe 2p$_{3/2}$ peak of α-Fe$_2$O$_3$ is clearly distinguishable and does not overlap either the Fe 2p$_{3/2}$ or Fe 2p$_{1/2}$ peaks. In addition, there appears to be another satellite peak at 732.1 eV, this may be the satellite peak for Fe 2p$_{1/2}$. All the above
observations clearly informed the presence of Fe$^{3+}$ ions of α-Fe$_2$O$_3$, as the binding energy values are too high comparable to other oxide species of iron [97]. All the observed findings are analogues to XRD results that confirmed the formation of α-Fe$_2$O$_3$ without any impurities.

Fig. 4.23 is the core level spectrum of O 1s peak that shows a single peak positioned at 530.9 eV accompanied with a shoulder at 531.8 eV. The shoulder peak, which is about 0.9 eV on higher BE side of main peak represents the presence surface coordinated OH$^-$ from air or non-stoichiometric surface oxygen. Oxygen can take two chemical states due to O$^{2-}$ and O$_2^-$ having lower and higher BE respectively. The presence of peak at 530.9 eV can be assigned to the surface O$^{2-}$ possessed in the oxides [98-99]. Therefore the XPS studies indicate iron in Fe$^{3+}$ and oxygen in O$^{2-}$ chemical states confirms the formation of Fe$_2$O$_3$. The XRD studies have already identified the crystalline phase formed as α-Fe$_2$O$_3$ [100].

![Deconvoluted profile for O 1s core level spectrum of Fe$_2$O$_3$ thin film sample](image)
4.2.4.2 Elemental analysis

Energy dispersive spectra of $\alpha$-Fe$_2$O$_3$ thin films prepared for various film thickness is shown in Fig. 4.24. Emitted energy of the X-rays corresponding to various elements show only the electron transfer among the various energy levels of Fe and O implies that the prepared films are Fe$_2$O$_3$ without any addition of impurities during spray deposition.

Fig. 4.24 EDS spectra of Fe$_2$O$_3$ thin films prepared for different thicknesses: (a) 1.63 (b) 1.73 and (c) 3.18 $\mu$m
Usually, when a precursor is heated along with the solvent ethanol, the following reaction may be initiated.

\[
\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + \text{H}_2\text{O} + \text{heat} \quad (4.3)
\]

\[
\text{4FeCl}_3 + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 6\text{Cl}_2 \quad (4.4)
\]

The chlorine liberated may get chemisorbed on the Fe$_2$O$_3$ film during film deposition as formation of film is taking place layer by layer. Such inclusion of chlorine is attributed to the difference in relative rates of transport of aerosol precursor reactants to the substrate and chemical reactions on it at a given substrate temperature [101]. Even then, the absence of chlorine on the surface of the film clearly shows the purity of the sample.

Observed elements of the films both in atomic and mass percentage are shown in Table 4.8. From the table, it is evident that the prepared films are nonstoichiometric as the atomic and mass percentage of both Fe and O are not equal. As the thickness of the film is increased, the atomic and mass percentage of Fe decreases and O increases.

**Table 4.8 Elemental composition of Fe$_2$O$_3$ thin films**

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Elemental Compositions</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Atomic %</td>
<td>Mass %</td>
</tr>
<tr>
<td>1.63</td>
<td></td>
<td>13.02</td>
<td>34.32</td>
</tr>
<tr>
<td>1.73</td>
<td></td>
<td>8.22</td>
<td>23.82</td>
</tr>
<tr>
<td>3.18</td>
<td></td>
<td>6.55</td>
<td>19.65</td>
</tr>
</tbody>
</table>
Non-stoichiometry Fe$_2$O$_3$ films are useful in many applications such as tunneling magneto-resistance based device applications [102]. Magnetic thin films of iron oxide have significant attention for their applications in various fields of medical care such as drug delivery system, cancer therapy, and magnetic resonance imaging [103] and these iron oxide films are of technological importance due to their application in many fields including high density magnetic storage devices, ferro-fluids, magnetic refrigeration systems, catalysis and chemical/biological sensors [104].

4.2.5 Surface Analysis

4.2.5.1 Surface morphology

The surface morphology of the thin films was studied using atomic force microscope are shown in Fig. 4.25.

Fig. 4.25  AFM image of $\alpha$-Fe$_2$O$_3$ thin films prepared for different thicknesses: (a) 1.63 (b) 1.73 and (c) 3.18 $\mu$m
The morphology of the iron oxide films can be characterized by irregular grains visualized on the surface of the films. Fig. 4.25a shows the representative AFM image of Fe$_2$O$_3$ thin film. It can be seen that the film have vertically aligned nano rods that shows the rounded edge view of the sphere like grains. Besides, all spherical grains are strongly elongated in one direction, and highly textured Fe$_2$O$_3$ film is grown on a face almost vertical to the substrate, which results in a great pore-solid ratio. The conversion into vertical growth may be attributed to the increase in substrate temperature.

Similar behaviour is also observed in aluminum-doped zinc oxide thin films [105]. Besides these, in all of our experiments, it is demonstrated that the surface roughness increases with the increase of film thickness. The average surface roughness was also calculated from AFM micrographs and found to be 28.99, 79.69 and 158.56 nm for the films deposited for the film thickness of 1.63, 1.73 and 3.18 µm, respectively. Also, the films grown with film thicknesses 1.73 and 3.18 µm almost have similar morphologies but with different porosity. The dependence of the porosity on prepared film thickness can be attributed to the fact that the number of nuclei changes with the flow rate. In the initial stage of deposition, the nucleation and the growth of nuclei compete with each other. In the case of the higher film thickness, the generation reaction rate is high, and the rate of nuclei exceeds that of growth of nucleation; while in the case of the low film thickness, the rate of nucleation predominates. Thus, the porosity in films deposited at high film thickness is smaller than that in the films deposited at low film thickness.
4.2.5.2 Nature of the surface

The SEM micrographs of the Fe\textsubscript{2}O\textsubscript{3} films deposited for different film thickness from ethanolic solution have been depicted in Fig. 4.26. It is seen that the Fe\textsubscript{2}O\textsubscript{3} film (Fig. 4.26c) surface is porous and well covered with smooth, irregular shaped grains of random size. It clearly observed the grains which are interconnected with each other.

![SEM images of the prepared α-Fe\textsubscript{2}O\textsubscript{3} thin films](image)

**Fig. 4.26** SEM images of the prepared α-Fe\textsubscript{2}O\textsubscript{3} thin films prepared for different thicknesses: (a) 1.63 (b) 1.73 and (c) 3.18 µm

The average grain size for the film prepared for the thickness 3.18 µm is about 150 nm. This value is higher than that calculated by XRD measurements. The values of the grains sizes obtained by XRD and SEM analysis are in contradiction, because SEM gives the grains size on the surface of the films and XRD gives it in the bulk.
The higher value of the grains size observed by SEM may be explained by the tendency of the small grains to aggregate to the big grains on the surface of the films. This phenomenon is also observed in ZnO [106], WO$_3$ [107] and CeO$_2$ [108] thin films elaborated by spray pyrolysis.

4.2.6 Electrical Studies

Electrical resistivity measurements were measured on the prepared $\alpha$-Fe$_2$O$_3$ thin film samples at various temperatures using the two-point probe technique. Two aluminium electrodes coated on the surface of the test sample served as electrical contact to connect precision electrometers.

All iron oxide films investigated were of n-type semiconductors in the measured temperature range from 40 to 200 °C and this was proved by the hot probe method. The variation of the resistivity ($\rho$) of iron oxide films with temperature is shown in Fig. 4.27. It is observed that the electrical resistivity of $\alpha$-Fe$_2$O$_3$ tends to decrease with increasing the temperature showing that the conduction processes of the films are thermally activated and also indicating its semiconducting behaviour. The room temperature electrical resistivity of $\alpha$-Fe$_2$O$_3$ film prepared for the thickness of 1.63 µm is 8.32 x 10$^2$ Ω cm and it decreases to 5.46 x 10$^2$ Ω cm as film thickness increases to 3.18 µm. The increase in resistivity for lower film thickness is due to the decrease in mean free path of the charge carriers in addition to the inclusion of small amounts of sub-oxides that could have a large effect on the electrical properties [109].

It is of common practice to compare the obtained data with the Fuchs-Sondheimer (F–S) theory. It is well known that F-S theory can be applied on metals based on the free-electron model, however, the applicability of F-S theory to
semiconductors was also reported [110]. Our obtained data indicates a linear relation. This is expected, even though the preparative conditions (substrate temperature, deposition time and film thickness) are diverse. Moreover, the electrical conduction of the prepared ferrite film is due to hopping conduction mechanism, where the electrons jump from an occupied level to empty level. For this type of conduction, both donor and acceptor levels are required. There are two types of hopping conduction mechanisms viz. Nearest-Neighbor Hopping (NNH) and Variable Range Hopping (VRH), which can play significant role in conduction process of $\alpha$-Fe$_2$O$_3$.

**Fig. 4.27 Variation of resistivity of the Fe$_2$O$_3$ thin films with temperature**

The obtained value of ‘$\rho$’ for the crystalline films of $\alpha$-Fe$_2$O$_3$ is in full agreement with the previously reported value ($5.46 \times 10^2 \ \Omega \text{cm}$) for the similar film of thickness 3 $\mu$m [111]. Also, similar values were reported for RF sputtered $\alpha$-Fe$_2$O$_3$.
films of thickness 150 nm deposited onto alumina substrates [112]. The typical Arrhenius plot for the prepared films is shown in Fig. 4.28, where the conductivity of the prepared films increases with film thickness.

![Fig. 4.28 Arrhenius plot for the prepared Fe$_2$O$_3$ thin films prepared for different film thicknesses](image)

Obtained activation energy also increases with film thickness and are reported in Table 4.9. It is observed that the high activation energy for the prepared film with thickness 3.18 µm is due to the formation of conduction barriers at grain boundaries which is caused by the complete stoichiometric oxidation of Fe at grain boundaries. In certain films, re-oxidation is required at the boundaries that resulted lower activation energies as evidenced for the film prepared for the film thickness of 1.63 µm.
Table 4.9 Activation energy of prepared Fe$_2$O$_3$ thin films

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.63</td>
<td>0.465</td>
</tr>
<tr>
<td>1.73</td>
<td>0.493</td>
</tr>
<tr>
<td>3.18</td>
<td>0.588</td>
</tr>
</tbody>
</table>

4.2.7 Optical Studies

In addition to optical absorption, optical band gap energy of Fe$_2$O$_3$ thin films are determined from the optical transmittance recorded in the wavelength range of 300 - 1100 nm. Optical properties of the α-Fe$_2$O$_3$ thin films can change or affect the characteristics of light passing through it by modifying its propagation intensity. The optical absorption studies reveal more information regarding the existence of electronic states of materials. Theoretically, optical absorption bands in the optical spectra of many of the compounds are attributed to either crystal field or charge transfer electronic processes.

Fig. 4.29 shows the UV-visible absorbance spectra of α-Fe$_2$O$_3$ thin films prepared for different thicknesses in the wavelength range 250 - 1000 nm. It shows a clear absorption band at 600 nm for the sample prepared for the thickness of 3.18 µm and the intensity of the absorption spectra decreases as the thickness of the films decreases. Again a strong absorption occurred in the lower wavelength region that reveals transition of charges between the band edges.

The α-Fe$_2$O$_3$ shows high absorbance in the visible region, indicating its applicability as an absorbing material. The absorption of incident radiation depends on the factors such as Bohr radius of the given semiconductor, the effective masses of the electron and hole, and the shape of the grains/crystallites. When the dimension of
these grains/crystallites becomes smaller than the exciton Bohr radius, the exciton is physically confined and as a result the energetic spectrum of the semiconductor changes. However, in the present investigation it is observed that the optical absorption at the band edge increases with increasing film thickness.

![Optical absorption spectra of α-Fe₂O₃ thin films prepared for various thicknesses](image)

**Fig. 4.29** Optical absorption spectra of α-Fe₂O₃ thin films prepared for various thicknesses

It is well established that three types of electronic transitions occur in the optical absorption spectra of Fe³⁺ substances that is, the Fe³⁺ ligand field transitions or the d-d transitions, the ligand to metal charge-transfer transitions and the pair excitations resulting from the simultaneous excitation of two neighbouring Fe³⁺ cations that are magnetically coupled [113]. The band edge of inorganic solid is located at the low energy end of the continuum band above the valence band. It is difficult to determine the band edge for transition metal oxides because there are a lot of narrow d–d bands in the gap, and some even extend into infrared region with a
definite probability. It is widely accepted that the band edge of Fe$_2$O$_3$ is located in the range of 580 - 620 nm [114]. Clearly the transitions in this energy region include the d-d transition, pair excitation and less charge transfer, and the former two transitions mainly come from the narrow d bands, so the optical properties of the Fe$_2$O$_3$ band edge cannot be accounted for intrinsic semiconductor.

The spectral distribution of transmission $T(\lambda)$ for the three $\alpha$-Fe$_2$O$_3$ thin film samples deposited on glass substrate for various thicknesses are shown in Fig. 4.30. It is seen that the entire wavelength region can be divided into three special regions: (i) the strong-absorption region (lowering of about 45 % in transmittance), where ‘$\lambda$’ is typically smaller than 450 nm; (ii) the transparent region, where ‘$\lambda$’ is typically higher than 700 nm and (iii) the absorption region between the two said regions.
The films of $\alpha$-Fe$_2$O$_3$ produced for the film thickness of 3.18 µm are found to be highly transparent of about 80% in the visible and near infrared region. The transmittance is expected to depend on several factors, such as oxygen deficiency, surface roughness, and impurity centers. Usually, films that are sprayed at higher temperature show a relatively high transmittance. In the other two samples average value of transmittance is less in the visible range of electromagnetic radiation. The lower value of transmittance could be due to light scattering as these films are having rough surface and defect states as evidenced from AFM and SEM surface analysis.

High transparency in $\alpha$-Fe$_2$O$_3$ films prepared using the chemical vapour deposition was already reported by Maruyama et al. [115]. According to the solid band theory, the direct and indirect optical band gap can be calculated using the Tauc’s relationship by substituting the power value $n$ as 1/2 for direct transition and 2 for indirect transition [116, 117]. An extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ on the y-axis versus photon energy ($h\nu$) on the x-axis gives the value of the optical band gap $E_g$ (Fig. 4.31).

The Fe$_2$O$_3$ film deposited for the thickness of 3.18 µm exhibit higher band gap as compared to the other film deposited for the thickness of 1.79 µm, which could be due to (i) the enhancement in crystallinity with increase in film thickness that leads to lesser defects and better crystal structure and (ii) the presence of hematite phase in case of the films deposited for 3.18 µm, which exhibit higher band gap as compared to magnetite phase. The calculated band gap for the Fe$_2$O$_3$ thin films is found to be near 2.38 eV as reported earlier [118]. The obtained film has multiple band gaps, the band gaps obtained for the thin film prepared for the thickness 3.18 µm are 2.46 and
2.38 eV respectively. The band gap 2.38 eV is obtained due to as mentioned above when the band edge of this band gap (2.38 eV) is located in the range of 600 nm and the transitions in this energy region include the d-d transition, pair excitation, and less charge transfer.

Fig. 4.31  Tauc plot of \((\alpha h\nu)^2\) vs. \(h\nu\) for Fe\(_2\)O\(_3\) thin films prepared for different thicknesses

In fact, the films of Fe\(_2\)O\(_3\) present a good crystallinity for the film thickness of 3.18 µm as it is shown by XRD and SEM analysis. Moreover, it has been shown that the band gap of crystalline material is greater than that of the corresponding amorphous materials. On the other hand, the obtained band gap values are comparable to those obtained by Zotti et al. [119] and Miller et al. [120] for \(\alpha\)-Fe\(_2\)O\(_3\) thin films prepared by electrodeposition and R.F. sputtering methods, respectively. The
following mechanisms may account for the possible causes of the observed band gap shift from amorphous to crystalline phase.

(i) Defect-induced absorption caused by incomplete transformation of non-crystalline to crystalline phase.

(ii) Presence of quantum size effect originated by the microstructure nature of the films.

4.2.8 Magnetic Studies

Magnetic properties associated with magnetization of the samples were investigated by VSM at room temperature and its variation with applied field is shown in Fig. 4.32.

![Graph showing variation of magnetisation with field in ferrite thin films prepared for different thicknesses](image)

Fig. 4.32 Variation of magnetisation with field in ferrite thin films prepared for different thicknesses
As evidenced, the hysteresis curve exhibits property variation that depends on thickness. The Fe$_2$O$_3$ films deposited for a thickness of 1.63 µm has low value of saturation magnetization ($M_s$) and remanence ($M_r$) which may be due to low degree of crystallinity and spin disordered on surfaces. In addition to this, the lower values of magnetization as compared to bulk ferrites could be due to a large grain boundary volume present in the nanocrystalline thin films [121]. On thicker films (3.18 µm), it has larger value of remanence, $M_r = 0.958 \times 10^{-3}$ memu and saturation magnetization, $M_s = 1.80 \times 10^{-3}$ memu. Enormous variations in magnetization and their related parameters with film thickness may be due to greater degree of crystallinity as confirmed through XRD studies.

Obtained magnetic parameter values for the prepared Fe$_2$O$_3$ thin films with various thicknesses are listed in Table 4.10. From the above table, α-Fe$_2$O$_3$ thin films synthesized with higher thickness have higher value of coercivity ($H_c = 589.68$ G), which could be called ferromagnetic at room temperature [122].

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Magnetic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Magnetization ($M_s$) $10^{-3}$ (memu)</td>
</tr>
<tr>
<td>1.63</td>
<td>0.62</td>
</tr>
<tr>
<td>1.73</td>
<td>1.62</td>
</tr>
<tr>
<td>3.18</td>
<td>1.80</td>
</tr>
</tbody>
</table>

The observed higher values of coercivity as compared to those for bulk ferrites are due to the formation of nanocrystalline grains resulting in large number of grain boundaries, which act as pinning sites for domain walls usually considered responsible for higher coercivity values for ferrite films [123] prepared with higher
thickness (3.18 µm). This observation shows that ferrous oxide nanostructures with high coercivity and high saturation magnetization value could be used as suitable semiconductor materials to act as photoanodes for Photoelectrochemical (PEC) water splitting.

4.3 CONCLUSION

Nickel oxide films have been prepared onto glass substrates from nickel acetate solution using spray pyrolysis technique. Deposition temperature was judged from the decomposition behavior of the starting precursor and accordingly nickel oxide has been prepared for various thicknesses by maintaining the substrate temperature at 450 °C. XRD results revealed the thickness dependent structural property variations that vary from amorphous to crystalline phase as the thickness is increased. Moreover, Ni rich precursor (0.3 M) modifies single phase NiO films (bunsenite) to mixed phase Ni₂O₃ (nickel sequioxide) in addition to NiO. IR bands at the fingerprint region 678, 624 and 552 cm⁻¹ confirmed the bonding between Ni and O. The chemical environment was further confirmed through XPS by locating Ni 2p₃/₂ at the binding energy 854.2 eV that corresponds only to Ni²⁺ 2p₃/₂ peak, which was the characteristic for the formation of pure NiO. The thickness related structural changes affect the refractive index of the material slightly. However its influence on direct optical energy gaps was remarkable. Electrical resistivity variation was found to alter with film thickness. NiO films prepared for the thickness of 0.316 µm has the room temperature resistivity of 306.9 Ω cm, whereas the 0.441 µm thick films have the resistivity of 99.22 Ω cm. Hall measurement dictated the presence of p-type carriers with carrier concentration of 0.117x10²⁴/m³. Negative value of temperature co-efficient of resistance further confirmed the semiconducting nature of the prepared
NiO films. NiO samples with small film thickness possess higher saturation magnetization compared to film with higher thickness and all the films exhibited ferromagnetic behavior irrespective of film thickness. Smooth surface with excellent structural stability, optical, electrical and magnetic properties make the NiO films suitable for fabrication of electrochromic display devices.

$\alpha$-Fe$_2$O$_3$ (hematite) films were spray pyrolytically prepared for various thicknesses onto glass substrates using ferric chloride solution. On increasing film thickness, the diffraction angle of two representative peaks (110) and (104) planes is almost in agreement with the Fe$_2$O$_3$ iron oxide thin film. XPS peaks observed at 710.9 and 724.4 eV are the characteristic doublets of Fe 2p$_{3/2}$ and 2p$_{1/2}$ which confirmed the presence of Fe$^{3+}$ ions in $\alpha$-Fe$_2$O$_3$. The IR peaks at 603 and 466 cm$^{-1}$ correspond to the metal-oxygen (Fe-O) bending confirmed the formation of pure $\alpha$-Fe$_2$O$_3$ thin film. It is observed that for $\alpha$-Fe$_2$O$_3$, the electrical resistivity tends to decrease with increasing the substrate temperature and reaches a nearly constant value of $5.46 \times 10^5 \, \Omega \text{cm}$ for the film thickness of 3.18 $\mu$m. The surface of the prepared films are smooth with no visible cracks or holes and the film prepared for the thickness of 3.18 $\mu$m shows surface with crystallites distributed in the form of interconnected spheres. The direct optical bandgap for the film prepared for the thickness 3.18 $\mu$m is 2.38 eV. VSM analysis confirmed the ferromagnetic behaviour of prepared $\alpha$-Fe$_2$O$_3$ thin film. By varying the film thickness, the morphology and the crystallinity of the films can be tuned.
REFERENCES


