Temperature and Substrate Effects on the Structural, Morphological, and Optical Properties of Iron Oxide Thin Films Prepared by Spray Pyrolysis Technique

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Abstract

Glass and Fluorine doped Tin Oxide (FTO) coated conducting glass substrates have been chosen for the deposition of Iron Oxide thin films prepared by Spray Pyrolysis Technique. The films were grown at different substrate temperatures (350°C, 400°C, and 450°C) and they were annealed at 300°C for 1 hr. Structural, morphological, optical characterizations of the films have been studied by X-ray diffraction, atomic force micrograph, UV spectroscopy methods. From the XRD studies, films on glass substrates are found to be amorphous in nature with α-hematite phase and crystalline on FTO coated conducting glass substrates. AFM analysis indicates that the films grown on glass substrates are rougher than the films on FTO coated conducting glass substrates. It reveals that the FTO coated conducting glass substrates can be a better choice as a substrate. The transmission spectra have been measured in the wavelength range 200-1200 nm. The transmittance of the films both on glass and FTO coated conducting glass substrates has been observed to be about 40-80% in the wavelength range (500-1100) nm. The optical band gap energy values have been found to be in the range 2.10-2.37 eV.

Keywords: Spray Pyrolysis, Iron Oxide (Fe2O3), Transmittance, Band gap.

I. Introduction

For the past decades various types of films such as composite films, non metallic inorganic films, transition metal oxide films etc. have been studied extensively in the field of materials science. Transition metal oxides (TMO) have emerged to be interesting classes of solids because of their distinguishable electronic properties due to the unique nature of outer d-electrons. TMO materials include wide band gap insulators, semiconductors, metals, or superconductors. They can go through semiconductor to metal transition. Some examples of TMO materials are Titanium dioxide (TiO2), Nickel Oxide (NiO), Manganese oxide (MnO2), Iron oxide (Fe2O3) etc. Materials defects like vacancies, dislocations, stacking faults and grain boundaries are responsible to have remarkable optical and magnetic properties of these materials. Because of their unique properties TMO materials find applications from energy and information technologies to ion conductors through photovoltaics, from thermoelectrics to dielectrics, multiferroics and capacitors. Their uses as electrodes in electrochemical processes, functional components in catalytic processes are also noteworthy applications.

MnO2 is one of the best candidates on account of its electrochemical behaviour, low cost, high theoretical specific capacitance and environmental compatibility.

On the other hand, silver oxide thin films have been proved to be very effective material for dealing with optical near-field and surface plasmons. NiO/Ni thin films have been used as selective solar absorbers. SnO2 has been widely characterized and explored in a variety of applications such as solid state gas sensors, solar cells, transparent electrodes and other optoelectronic devices.

In recent times, large number of improvements has been made using different materials techniques to fabricate solar cells in order to overcome the first generation solar cells based on silicon. CIGS (Copper Indium Gallium Selenide) is one of the thin film based solar cells whose efficiency has been recorded 22.9% which is an improvement over other cell materials. In CIGS, there is a buffer layer which is made of materials which have higher transmittance. Generally transition metal oxide film is used to develop that layer of CIGS. Films can be deposited by using different techniques such as chemical bath deposition, chemical vapor deposition, electrodeposition, molecular beam epitaxy, sol-gel process, spin coating, dip coating, spray pyrolysis etc. Such a wide variety of techniques is very useful of tailoring and engineering of the layers in order to make device performance more efficient.

Over years, attention has been paid on iron oxide materials and its thin films, one of the TMO materials. A.Akl suggested that by varying substrate temperature and deposition time, non crystalline and crystalline iron oxide thin films on glass can be fabricated. Salam Amir Yousif also studied the temperature effect on iron oxide thin films made by spray pyrolysis method. Chemical Bath Deposition Technique has been used by Batin, et.al. to make iron oxide thin films on glass substrate and their work was focused on the optical properties of the films. Most of the works done so far, iron oxide thin films were grown on glass substrates whereas Desai, et.al. fabricated iron oxide films on ITO coated glass substrates and structural, morphological, and optical studies were performed Garcia-Lobato, et. al. obtained the amorphous and polycrystalline iron oxide thin films on glass substrates with the variation of temperature.
Based on the earlier reports, an attempt has been made in our work to prepare iron oxide thin films on glass and FTO coated conducting glass substrates by spray pyrolysis technique. The substrate temperatures were varied keeping the deposition time unchanged and the films were annealed. Our observations were mainly focused on the effects of temperature and substrate type namely glass and Fluorine doped Tin Oxide (FTO) coated conducting glass substrates on the films. Structural, morphological, optical properties of the as-deposited and annealed films have been studied by the X-ray diffraction (XRD), atomic force microscopy (AFM), UV spectroscopy methods.

II. Experimental Details

Iron oxide films were deposited on glass and FTO coated conducting glass substrates using spraying pyrolysis technique (SPT). The precursor solution of 0.1 M concentration was prepared by mixing 1.6221 g of anhydrous ferric chloride (FeCl₃) in 100 mL distilled water. The colour of the ferric chloride solution was yellow-orange which was kept in the beaker at 70°C for 10 min. The substrates were preheated at different temperatures 350°C, 400°C, and 450°C. In this process, spray rate and deposition time were kept constant so that the film thickness remains the same. The deposition time was maintained at 12 minutes for all the cases. The spray rate was almost kept constant at 0.08 mL/min. The pressure was maintained at 0.5 bar when the solution was reaching the air blast. The solution formed spray and was sprayed over the preheated substrate. The films thus formed were brownish-red in colour. All the films were annealed at 300°C for 1 hr. The thermal decomposition reaction which occurs in this spraying technique is:

$$2\text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{HCl}$$

The characterization of the film materials have been made using the following instruments: structural characterization of Fe₂O₃ films was made using RIGAKU Ultima IV X-ray diffractometer with CuKα radiation. A range of 2θ (10° to 70°) was scanned to cover all the diffraction peaks of the iron oxide phase. The surface morphological studies were carried out using Atomic Force Microscope (AGILENT N9410A-5500). Optical properties were investigated using a spectrophotometer (Model-OPTIZEN POP) in the wavelength range (200-1200nm).

III. Results and Discussion

XRD studies:

The XRD patterns of Fe₂O₃ thin film deposited by SPT on glass and FTO coated conducting glass substrates at different substrate temperatures (350°C, 400°C, and 450°C) are shown in Fig. 1. Table 1 shows the peak list of Fe₂O₃ films on glass and FTO coated conducting glass substrates.

| Temp (°C) | Planes (h k l) | Phase       |
|----------|----------------|-------------|
|          | Glass          | FTO         | Glass      | FTO         |
| 350      | 220 220        | Maghamite   | Maghamite  |
|          | 104 104        | Hematite    | Hematite   |
|          | 110            | Hematite    | FTO        |
|          | 024            | Hematite    |            |
| 400      | 220 220        | Maghamite   | Maghamite  |
|          | 104 104        | Hematite    | Hematite   |
|          | 110            | Hematite    | FTO        |
|          | 024            | Hematite    |            |
| 450      | 116 220        | Hematite    | Maghamite  |
|          | 104            | Hematite    |            |
|          | 110            | Hematite    | FTO        |
|          | 024            | Hematite    |            |

The films grown on glass substrates are found to be microcrystalline in nature shown in Fig.1(a). A sharp peak is observed at 2Θ=31.66° for the film at substrate temperature 350°C. For 400°C substrate temperature, three peaks are seen at 2Θ=31.72°, 33.16°, and 35.6° which indicate the improvement of the crystalline nature of the films. The reflections are observed for the (220), (104), and (113)
planes accordingly. All the peaks identified here are due to hematite Fe$_2$O$_3$ phase. A broad hump is seen for the film at substrate temperature 450°C. One peak is identified here. The thin film may have lost its crystalline nature in this case. Fig. 1(b) represents Fe$_2$O$_3$ films on FTO coated conducting glass substrates. All the films are found polycrystalline in nature. The reflections are observed for (220), (104), (110), (024) planes indicating the rhombohedral structure. The peaks at 2θ=21.35°,60.34° in Fig.(b) are seen due to FTO. With increasing substrate temperature, the intensities of the films are found to be decreasing. Decrease in intensity can be caused due to the deterioration of crystalline quality. In both figures, the diffraction peaks show the presence of crystalline α-Fe$_2$O$_3$ hematite phase with the rhombohedral structure shown in Table 1. One peak at 2θ = 31.70° has been identified due to 220 plane of maghemite. The values of $a$ and $c$ and $c/a$ ratio are given in Table 2. The lattice constants are comparable to the standard values of $a = 5.0353$ and $c = 13.7495$Å of α-Fe$_2$O$_3$ hematite phase.

### Table 2. Lattice constants of the films at different substrate temperatures (350°C,400°C, and 450°C)

| Substrate Temp. | Lattice constants | $a$ (Å) | $c$ (Å) | $c/a$ |
|-----------------|-------------------|--------|--------|-------|
| 350°C           |                   | 5.06   | 13.69  | 2.70  |
| 400°C           |                   | 5.06   | 13.58  | 2.67  |
| 450°C           |                   | 5.08   | 13.74  | 2.70  |

Crystallite size has been calculated from the stronger peaks of (110) from each XRD patterns using Scherrer’s formula for the films on FTO coated conducting glass substrates shown in Fig. 2.

![Crystallite size](image)

**Fig. 2.** Variation of crystallite size with temperature for the film deposited on FTO coated conducting glass substrate.

### Morphological characterization

Fig. 3 shows the AFM images of the Fe$_2$O$_3$ films on glass and FTO coated conducting glass substrates grown at substrate temperature 400°C. The films were annealed at 300°C for 1 hr. The images shows clearly the difference between the surface morphology and roughness of the films on glass and FTO coated conducting glass substrates. The roughness images for the films on FTO coated conducting glass substrates are shown in Fig.3(c,d) before and after annealing. The roughness values for the films on glass and FTO coated conducting glass substrates are summarized in Table 2.

### Table 2. Roughness values of the films as measured from the AFM images

| Deposition Temp. | Substrate | Roughness average, $Sa$ (nm) | RMS roughness, $Sq$ (nm) |
|------------------|-----------|------------------------------|-------------------------|
|                  | As deposited | Annealed (300°C for 1hr) | As deposited (300°C for 1hr) |
| 400°C            | Glass      | 7.54                         | 16.38                   | 12.82                       | 22.70                       |
|                  | FTO        | 3.11                         | 2.34                    | 4.31                        | 3.00                        |

From the images and the table it is observed that (i) the film adhesion is better on FTO coated conducting glass substrate than the films on glass substrate (ii) the deposition temperature increases the mobility of ad-atoms provides better arrangement of atoms. Also the transparent conduction surface plays an important role for the good crystalline nature of the films because of the nucleation formation. On the other hand the films on the glass substrates are inhomogeneous which may be due to the presence of voids.
As a consequence the films on glass are found to be rough\textsuperscript{14,17}.

Optical Characterizations

Fig. 4 and Fig. 5 show the transmission spectra of the films on glass substrates in the wavelength range 200 -1200 nm. The substrates temperatures were at 350°C, 400°C, and 450°C and the films were annealed at 300°C for 1 hr. Fig. 4 (a) and Fig. 4 (b) represent the transmission spectra of Fe\textsubscript{2}O\textsubscript{3} thin films on glass substrates before and after annealing. The transmission spectra of Fe\textsubscript{2}O\textsubscript{3} films on FTO coated conducting glass substrates before and after annealing are shown in Fig. 5 (a) and Fig. 5 (b). In both cases the transmittance is observed to be about 40-80\% in the wavelength range 500 – 1100 nm.

The transmission spectra of the films can be affected due to (i) roughness of the surface (ii) optical inhomogeneity in the direction normal to the film surface. The broad cut off towards short wavelengths indicates the onset of intrinsic inter-band absorption in the films. The high transparency in the visible region and above results in wide band gap of the films\textsuperscript{18}. No significant changes in the transmittance curves have been observed for the films on both glass and FTO coated conducting glass substrates. When annealed at 300°C for 1 hr, the transmission curves have become smooth. High transmittance of the films in the wavelength range 500-1100 nm suggests that the film can be used as a window or buffer layer in CIGS solar cells.

Fig. 6 and Fig. 7 show the absorptions spectra of the films in the wavelength range 300-1200 nm on glass and FTO coated conducting glass substrates. The substrates were
kept at 350°C, 400°C, and 450°C and the annealing temperature was maintained at 300°C for 1 hr.

A sharp decrease up to 600 nm of the absorbance curves has been observed and the curves became almost stable above 700 nm. The absorption about the band edge is sharp revealing that the Fe$_2$O$_3$ film has a direct band gap$^{18}$. The crystalline quality has been found to be improved upon annealing. No significant change has been observed in the absorption spectra of the films grown on glass and FTO coated conducting glass substrates.

Optical band gap ($E_g$) of Fe$_2$O$_3$ thin films both on glass and FTO coated conducting glass substrates are determined by plotting $(\alpha h \nu)^2$ as a function of band gap energy, $h \nu$ followed by the Lambert law, $\alpha$ is the coefficient of absorption defined by the expression:

$$\alpha = \frac{A_0 (E_g - E_\nu)}{h \nu}$$  \hspace{1cm} (1)

where $n = 0.5$ for direct band gap material or 2 for indirect band gap material or 2, $h \nu$ is the photon energy, $E_g$ is the band gap energy, $A_0$ is a constant related to the effective masses associated with the bands. Since Fe$_2$O$_3$ is a direct band gap material, therefore taking $n = 0.5$, equation (1) takes the form

$$(\alpha h \nu)^2 = A_0^2 (h \nu - E_g)$$  \hspace{1cm} (2)

Fig. 8 and Fig. 9 show the plots $(\alpha h \nu)^2$ as a function of band gap energy, $h \nu$ for the films on glass and on FTO coated conducting glass substrates. From these figures the extrapolation of the linear region of the curves on the energy axis $h \nu$ has been used to find out the direct band gap $E_g$ of Fe$_2$O$_3$ thin films. Fig. 8 (a,b) represents Fe$_2$O$_3$ films on glass before and after annealing whereas Fig. 9 (c, d) shows Fe$_2$O$_3$ films on FTO coated conducting glass substrates before and after annealing. The direct band gap values of Fe$_2$O$_3$ thin films on glass and FTO coated conducting glass substrates as obtained from the figures are summarized in Table 3.
Fig. 8. Plots of $(\alpha h \nu)^2$ vs. $\nu$ for Fe$_2$O$_3$ thin films on glass substrates at substrate temperature 450°C (a) before (b) after annealing at 300°C for 1 hr.

Fig. 9. Plots of $(\alpha h \nu)^2$ vs. $\nu$ for Fe$_2$O$_3$ thin films on FTO coated conducting substrates at substrate temperature 450°C (c) before (d) after annealing at 300°C for 1 hr.

Table 3. Direct band gap values of Fe$_2$O$_3$ thin films on glass and FTO coated conducting glass substrates before and after annealing

| Substrate Type | Temp.  | Band Gap, $E_g$ (eV) | Standard Values |
|----------------|--------|----------------------|-----------------|
|                | As deposited | Annealed |                  |
| Glass          | 350°C  | 2.37                 | 2.30            | 2.2-3.3          |
|                | 400°C  | 2.125                | 2.10            |                  |
|                | 450°C  | 2.33                 | 2.25            |                  |
| FTO            | 350°C  | 2.24                 | 2.20            |                  |
|                | 400°C  | 2.25                 | 2.13            |                  |
|                | 450°C  | 2.21                 | 2.20            |                  |

Table 3 shows that the band gap energy values of the annealed samples are less than the values obtained for the as-deposited films. Band gap energy values $E_g$ have been reported between 2.2 and 3.3 eV for single crystal Fe$_2$O$_3$. The band gap values $E_g$ values in our work are found to be between 2.10 and 2.37 eV, the results obtained are in good agreement with those obtained for single crystal Fe$_2$O$_3$. It can be inferred that (i) the band gap energy values are affected by the substrate temperature and film thickness (ii) the annealing temperature can reduce the energy gap of the film (iii) There may be other phases like Maghemite, Fe$_3$O$_4$ etc. present in the films (iv) The large value of the band gap energy may be due to quantum size effect (v) low value of band gap is due to disorder at the grain boundary.

IV Conclusion

Fe$_2$O$_3$ thin films have been synthesized successfully by spray pyrolysis technique on glass and FTO coated conducting glass substrates. The substrates were preheated at different substrate temperatures (350°C, 400°C, and 450°C). The substrate type and the temperature effects on the structural, morphological, and optical properties of the films were analysed. XRD pictures reveal that the films on FTO coated conducting glass substrate are more crystalline than the films grown on glass substrate. Most
of the diffraction peaks are identified as crystalline $\alpha$-$\text{Fe}_2\text{O}_3$ hematite phase. Moreover, using FTO coated conducting glass substrate, polycrystalline films were possible to grow even at temperature 350°C and the low deposition time. Because of the good adhesion of the films on the FTO coated conducting glass substrate before and after annealing as can be seen from the AFM images, the films were found crystalline and smooth. The structure of $\text{Fe}_2\text{O}_3$ thin films on glass substrates remained amorphous with $\alpha$-$\text{Fe}_2\text{O}_3$ phases present. At low substrate temperature 350°C poor adhesion of the films to the substrate was observed but at higher temperatures agglomeration of particles as well as voids were observed in the AFM studies. As a result the surface of the films became rough. The high transmittance and the low absorbance of the crystalline $\text{Fe}_2\text{O}_3$ films on FTO coated conducting glass substrates in the wavelength range (500-1100 nm) have been observed that can be used as a window layer in the CIGS cell. A small band gap of about 2.10-2.37 eV makes iron oxide films to be used as photocathodes. Also because of the small band gap values, $\text{Fe}_2\text{O}_3$ films can absorb a significant amount of sunlight and can be used as a material for PEC cells. The amorphous $\text{Fe}_2\text{O}_3$ thin films on glass substrates with high transmittance can be used to make thin film solar filters.

In conclusion, it can be inferred that the structural, morphological, and optical properties of $\text{Fe}_2\text{O}_3$ thin films are influenced by the temperature and the substrate type. Our studies suggest that FTO coated conducting glass substrates can be a better choice as a substrate for the deposition of $\text{Fe}_2\text{O}_3$ thin films.

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