Preparation and absorption studies of ferric oxide thin films by Spray pyrolysis

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Abstract: Spray pyrolysis method to prepare Fe$_2$O$_3$ thin films on glass substrate has been used. The absorption spectra used in the wavelength range 350 nm to 600 nm to calculate the optical energy gap found to be 2.22 eV. This band gap energy allows efficient utilization of solar spectrum. Fe$_2$O$_3$ thin films which show both direct and indirect allowed transition are present.

Keywords: spray pyrolysis, Fe$_2$O$_3$ thin films

I. Introduction

Ferric oxide is a small band gap (<2.5 eV) semiconductor. It has absorption coefficient of the order of $10^4$ cm$^{-1}$[1]. There has been much interest in the utilization of semiconductor electrodes for liquid junction studies [2-4] and for solar energy conversion [5, 6]. However the problem is to find the semiconducting electrode material which will be stable in electrolyte, easy for preparation utilization of solar spectrum. When the conduction band or the valance band in the semiconductor overlap with the occupied or unoccupied states in the electrolyte then an electron transfer between electrode and electrolyte takes place. Large band gap semiconductor electrodes offer the possibilities for studies of the energy parameter of fundamental charge transfer processes large band gap electrodes such as TiO$_2$[2], ZnO [4], SnO$_2$ [7] have been studied. Small band gap semiconductor such as CdS [8], Si [9] decomposes under anodic polarization. Fe$_2$O$_3$ compound can be prepared by different methods such as electrochemical deposition, vacuum deposition, flash evaporation, sputtering and spray pyrolysis. We have studied selected Fe$_2$O$_3$ which is the most suitable photo anode in photoelectron chemical cell. The aim of this work is to prepare thin films of Fe$_2$O$_3$ by simple, inexpensive method of spray pyrolysis and study their optical properties.

II. Preparation of Sample

Aqueous solution of 1.0 M FeCl$_3$ used for spraying the films. Chemical used was AR grade. The solution was prepared in double distilled water. This solution was stirred by magnetic stirrer for 12 hr. It was observed that the FeCl$_3$ solutions completely dissolve. This solution was spray on preheated glass substrate. The temperature of the substrate was maintained at 450$^\circ$C which was measured by pre-calibrated thermocouple formed by fusing a copper and a constantan wire together. Thin films of Fe$_2$O$_3$ was deposited on this substrate by spraying. Spray rate was maintained at 3.5 ml/min and spraying was done in air at 12 kg/cm$^2$.

The following reaction takes place and a thin film of Fe$_2$O$_3$ is formed on the substrate.

$$4\text{FeCl}_3 + 3\text{O}_2 \xrightarrow{\Delta 450\pm50^\circC} 2\text{Fe}_2\text{O}_3 + 6\text{Cl}_2$$

The thickness of the films was calculated by weighing the glass substrate before and after the deposition of the films by using unipan microbalance by assuming the standard density of Fe$_2$O$_3$ is 5.24. The thin films has brown colour.

III. Absorption Study

Transmittance (T) vs wavelength ($\lambda$) of the films was measured at room temperature using UV-1800 Shimadzu spectrophotometer in the wavelength range from 350 nm to 600 nm. Fig 1 shows transmission (T) vs wavelength ($\lambda$) variation for two different film thickness.

![Graph of Transmittance vs Wavelength](image)

Fig. 1. Transmittance vs Wavelength for two thickness a) $t = 0.198$ $\mu$m, b) $t = 0.182$ $\mu$m
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The absorption coefficient ‘α’ at various wavelengths for a sample of thickness ‘t’ is given by the relation,

\[ \alpha = \frac{1}{t} \log \left( \frac{I_o}{I} \right) \]  

(1)

where, \( I_o \) and \( I \) are the intensities of incident and transmitted radiation respectively. It was observed that interference effects can be neglected for films deposited on a thick non-absorbing substrate [10, 11]. The value of \( \alpha \) at various wavelengths was calculated from the transmission curves using relation (1).

To calculate exact value of band gap, plotting the graph \((\alpha h\nu)^{1/2} vs \ h\nu\) shown in fig.2. The plot gave fairly straight lines. Plots indicate that the transitions are indirect and the band gap energy was 2.4 eV. The other workers reported band gap value was less than 2.50 eV [1, 16].

![Fig. 2. \((\alpha h\nu)^{1/2} vs \ \text{incident photon energy (hν)}\) of Fe\(_2\)O\(_3\) thin films](image1)

![Fig.3. \((\alpha h\nu)^2 vs \ \text{incident photon energy (hν)}\) of Fe\(_2\)O\(_3\) thin films](image2)

Now plot of \((\alpha h\nu)^2 vs h\nu\) (fig.3). The curve is linear. This linear relation indicates that the direct allowed transition, described by the relation [12-15],

\[ \alpha = \frac{A}{\hbar} \nu(\hbar\nu-E_g)^{1/2} \]  

(2)

is probably responsible for the absorption process. The optical band gap \( E_g \) determined from the extrapolated intercept on \( h\nu \) axis was 2.22 eV.

This results are fairly good agreement with the other workers [1, 16]. Pawar et al [1] studied the optical properties of the films of Fe\(_2\)O\(_3\) produced spray pyrolysis. They reported the value of band gap 2.10 eV. While Kennedy and Frewe Karl [2] reported the optical band gap was of 2.07 eV.

IV. Results and Discussion

Ferric oxide films formed which are characteristics by measuring optical absorption in the wavelength range 360 nm – 600 nm. The optical data were analysed to estimate the band gap energy of the films. The plot of \((\alpha h\nu)^{1/2} vs h\nu\) gave fairly good straight lines. The nature of the plots indicates that the transitions are indirect and optical band gap energy is less than 2.5 eV and has absorption coefficient of the order of \(10^4\) cm\(^{-1}\). Hence this semiconductor is interested in the utilization of semiconductor electrodes for liquid junction studies and for solar energy conversion. While \((\alpha h\nu)^2 vs h\nu\) is linear variation in which extrapolated on \( h\nu \) axis shows Fe\(_2\)O\(_3\) thin films is direct allowed transition. Hence this band gap energy allowed efficient utilization of solar spectrum and also used to decompose water by utilizing solar energy under anodic polarization.
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References-

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