Structural and optical properties of spray pyrolytically prepared Fe_2O_3 thin films

Y D TEMBHURKAR

Department of Physics, S K Porwal College, Kamptee Distt., Nagpur 441 002, India

MS received 24 April 1995; revised 7 August 1995

Abstract. Fe_2O_3 thin film was prepared using aqueous solution of FeCl_3 by spray pyrolysis. The substrate temperature was 450°C . The lattice parameters a and c for different concentrations were calculated from X-ray diffraction study. Hexagonal structure of the Fe_2O_3 thin film was confirmed. Band gap values of Fe_2O_3 prepared from different concentrations were determined from optical transmission data.

Keywords. Spray pyrolysis; Fe_2O_3 .

1. Introduction

Ferric oxide is a small band gap (< 2.5 eV) semiconductor. It has absorption coefficient of the order 10^4 cm^{-1} (Pawar *et al* 1989). There has been much interest in the utilization of semiconductor electrodes for liquid junction studies (Gerischer 1969; Gleria and Memming 1975; Kennedy and Frewe 1978) and for solar energy conversion (Frank and Bard 1975; Fuji *et al* 1975). However the problem is to find the semiconductor electrode material which will be stable in electrolyte, easy for preparation and of the proper band gap energy to allow efficient utilization of solar spectrum. The large band gap semiconductor electrodes such as TiO_2 , ZnO etc offer the possibilities for studies of the energy parameters of fundamental charge transfer processes.

An attempt has been made to discuss the optical and structural properties of Fe_2O_3 polycrystalline thin films prepared by spray pyrolysis method. This method of preparing thin film is simple and inexpensive. Absorption edge analysis was carried out on spectronic-20 spectrophotometer using transmittance data. The structural parameters a and c were determined using X-ray diffraction pattern.

2. Film preparation

Aqueous solution of ferric chloride was used for spraying the films on hot glass substrates. Different concentrations used were 0.25, 0.50, 0.65, 0.75 and 0.85 M and were prepared in double distilled water. The chemical used was of AR grade. Biological glass slides 1.3 mm thick were used as substrates. The temperature of the substrate measured by precalibrated thermocouple was maintained at $450 \pm 10^\circ\text{C}$, which was the most suitable for the production of Fe_2O_3 thin films. The distance between the sprayer and substrate was kept at 30 cm. The sprayer was mechanically moved to and fro during spraying to avoid the formation of droplets on the hot glass substrate and to ensure instant evaporation. The solution was sprayed at a pressure of 12 kg/cm^2 . The rate of flow was maintained at 3.5 ml/min .

3. Optical absorption study

Transmittance T of the film was measured at room temperature using spectronic-20 spectrophotometer. The spectrophotometer is generally used to study the transmittance of solutions. In our experiment we used this spectrophotometer for measuring the transmittance of the film deposited on glass substrate. Identical glass plate without film was used as a standard for adjusting 100% transmittance. Having adjusted 100% transmittance the standard plate was replaced by thin film on the substrate and transmittance noted. The transmittance for different wavelengths in the range 700–350 nm were recorded. Figure 1 shows variation of transmittance T against wavelength λ for the films deposited using different concentrations. It was observed that transmittance was constant for higher wavelength and then suddenly decreased. The onset of decrease of transmittance depends on concentration and represents the fundamental absorption edge (Tembhurkar and Hirde 1992a, b, 1993). The onset of decrease of transmittance is shown by an arrow on each transmittance curve. It was observed that the arrow shifted slightly towards the lower wavelength sides as the concentration increased up to 0.65 M and as the concentration increased above 0.65 M, the arrow slightly shifted towards higher wavelength sides.

The absorption coefficient (α) at various wavelengths for thickness (t) is given by the relation,

$$\alpha t = \ln(I_0/I), \quad (1)$$

where I_0 and I are the intensities of incident and transmitted radiation respectively. The value of α at various wavelengths for all concentrations of the films was calculated from the transmittance curve (figure 1) using (1). This showed that the absorption coefficient of the same order of 10^4 cm^{-1} was obtained for all prepared concentration films. To

Figure 1. Transmission T as a function of the wavelength for the concentration (a) 0.25 M, (b) 0.50 M, (c) 0.65 M, (d) 0.75 M and (e) 0.85 M.

Figure 2. Plot of $(\alpha h\nu)^2$ against incident photon energy ($h\nu$) for the concentration (a) 0.25 M, (b) 0.50 M, (c) 0.65 M, (d) 0.75 M and (e) 0.85 M.

calculate the exact value of band gap (E_g), a graph $(\alpha h\nu)^2$ against $h\nu$ was plotted for the region above and below the absorption edge (figure 2). Each graph had some linear portion above the fundamental absorption edge, the extrapolated intercept on $h\nu$ axis gave the value of band gap.

The linearity of the graph indicated that the directly allowed transition described by the relation (Tembhurkar and Hirde 1992a, b, 1993),

$$\alpha = (A/h\nu)(h\nu - E_g)^{1/2}, \quad (2)$$

was probably responsible for the absorption process. The band gap values obtained were 2.01, 2.06, 2.24, 2.22 and 2.14 eV for the concentration of the films 0.25, 0.50, 0.65, 0.75 and 0.85 M respectively (figure 2). The nature of the plot indicated that the transition was direct. This agreed well with the results obtained by other workers (Quin *et al* 1976; Shinnar and Kennedy 1981). Pawar *et al* (1989) studied the optical properties of thin Fe_2O_3 films produced by spray pyrolysis method. They found that the band gap varied between 1.95 and 2.10 eV for 0.25, 0.5 and 0.75 M concentrations. Kennedy and Frewe Karl (1978) reported the optical band gap of $\alpha\text{-Fe}_2\text{O}_3$ thin films (2.07 eV) requiring photon support.

4. Lattice constant a and c by X-ray diffraction

An XRD study was carried out on a Phillips X-ray diffractometer using CuK_α radiation with wavelength 1.542 Å. Figures 3a and b show the typical X-ray pattern of as-deposited

Figure 3. X-ray diffraction pattern of as-deposited Fe_2O_3 thin film for the concentration: (a) 0.50 M and (b) 0.75 M.

Table 1. Lattice parameters of as-deposited Fe_2O_3 thin films.

Concentration of FeCl_3	a (Å)	c (Å)
0.25 M	5.031	13.761
0.50 M	5.037	13.769
0.75 M	5.055	13.776
0.85 M	5.044	13.770

film of Fe_2O_3 prepared at 0.50 M and 0.75 M concentrations respectively. X-ray diffraction studies confirmed the hexagonal structure of the film. The lattice parameters a and c for different concentrations calculated from XRD patterns are listed in table 1. Our value of a and c agreed well with ASTM data. The presence of sharp peaks showed that the film was well oriented polycrystalline in nature. It was observed from figures 3a and b that increase in the concentration of FeCl_3 increased the height of the prominent peaks. This indicated that the grain size of the film improved with concentrations. This may be due to presence of larger number of ferric ions in a droplet which evaporates instantly on the substrates. As the concentration increases above 0.75 M, the lattice parameter decreases (table 1), probably due to overlapping of the grain boundaries. The high intensity of reflection from the (104)

plane indicates the preferred orientation along the (104) direction. A similar preferred orientation along the (104) direction has also been reported for single crystal (ASTM data).

5. Conclusion

Spray pyrolysis is a successful method for growing Fe_2O_3 thin film using ferric chloride solution ($< 1 \text{ M}$). X-ray results indicate that the film of Fe_2O_3 is a hexagonal structure. The structural parameter and optical band gap were found to be concentration dependent.

References

- Gerischer H 1969 *Surf. Sci.* **18** 97
Gleria M and Memming R 1975 *J. Electrochem. Soc.* **65** 163
Fuji Shime A, Kenayakawa K and Honda K 1975 *Bull. Chem. Soc. Jap.* **48** 1041
Frank S N and Bard A J 1975 *Am. Chem. Soc.* **97** 339
Kennedy John H and Frewe Karl W 1978 *J. Electrochem. Soc.* **125** 709
Pawar S H, Patil P S, Madhale R D and Lokhande C D 1989 *Indian J. Pure & Appl. Phys.* **27** 227
Quin R K, Nasby R D and Baughman R J 1976 *Mater. Res. Bull.* **11** 1011
Shinnar R and Kennedy J H 1981 *J. Electrochem. Soc.* **128** 2371
Tembhurkar Y D and Hirde J P 1992a *Bull. Mater. Sci.* **15** 143
Tembhurkar Y D and Hirde J P 1992b *Thin Solid Films* **215** 65
Tembhurkar Y D and Hirde J P 1993 *Bull. Mater. Sci.* **16** 177