The influence of deposition time on optical properties of iron oxide films grown on glass substrate by Chemical Bath Deposition

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This paper deals with the preparation and characterization of iron oxide films using a simple and non-expensive technique that consists in the immersion of the glass substrates in a chemical solution composed of ferrous chloride, urea and distilled water during 1, respectively 3 hours, followed by heat treatment. The optical properties of the iron oxide films were determined using a UV-Vis spectrophotometer. An increase in absorbance was observed with the increasing of deposition time. The estimated optical band gaps of the iron oxide films were found to be 2.57 eV and 2.67 for the sample deposited for 1 hours and 3 hours respectively.

(Received May 29, 2012; accepted July 19, 2012)

Keywords: Iron oxide films, CBD technique, Heat treatment, Optical band gap, Refractive index

1. Introduction

Iron oxide is a cheap and abundant in nature compound, with special properties which makes it a promising material for use in optical devices, sensors, energy conversion and so on. Due to its optical, magnetic, electrical and catalytic properties, iron oxide has attracted attention of researchers from different areas of science. In the last years many efforts have been made in order to obtain iron oxides with different structures and morphologies [1-5], thereby contributing to the improvement of their special optical properties.

Among iron oxides, Fe_2O_3, Fe_3O_4 and FeO are the most known. Bulk hematite (α-Fe_2O_3) has a band gap of 2.1 eV and can absorb a significant amount of sunlight making it a candidate material for photoelectrochemical cells [6,7]. Furthermore α-Fe_2O_3 exhibits optimal properties to be used as gas sensors, as F. Rettig, R. Moos and others authors reported [8-12]. Others important applications of iron oxide are in fields like biomedicine, wastewater treatment or magnetic devices [13-16].

Over the years, a series of chemical, physical or mechanical methods, used to obtain iron oxide, were developed. Iron oxide films were obtained by chemical bath deposition – CBD [17], spray pyrolysis [18,19], atomic layer deposition [20], spin – on sol-gel deposition [21], chemical vapor deposition (CVD) [22], filtered arc deposition [23], ion-beam assisted deposition (IBAD) [24] and so on. It is well known that optical properties are closely related to deposition method and the used reagents. In this paper we report the obtaining of iron oxide thin films using the chemical bath deposition method (CBD) followed by heat treatment. The influence of reaction time on optical properties of iron oxide films is discussed.

2. Experimental

2.1. Preparation of Fe_2O_3 thin films

Iron oxide thin films were grown onto glass substrates by chemical bath deposition method (CBD). The chemical reagents used were iron chloride II as iron source, urea as a complexing agent and distilled water as solvent.

Before deposition, the glass substrates of 75×25×1 mm dimensions were washed with commercial detergent and rinsed with distilled water in abundance. After rinsing, the substrates were treated over night in chromic mixture and then rinsed again with distilled water.

Ferrous chloride solution was prepared in a 100 ml beaker by dissolving required amount of $FeCl_2*4H_2O$ in distilled water to form 1.0 M solution. Then 50 ml of 0.1 M urea solution (NH_2CONH_2) was added, which promotes film formation before precipitation. The substrates were immersed in the solution and suspended vertically. At the end of the deposition process, the films were annealed in a furnace for 4 hours at 500 °C. The experimental conditions for films deposition are given in Table 1.

Table 1. Experimental conditions of iron oxide films (α-Fe_2O_3) deposited by CBD method at 90 $^{\circ}$C.

Parameters	**Sample M2T**	**Sample M6T**
Reaction time	1 hour	3 hours
Thermal treatment: temperature/time/heating rate	500 $^{\circ}$C/4 hours/5 $^{\circ}$C/min	

2.2. Characterization of Fe_2O_3 thin films

Optical characterization of iron oxide films were performed by using UV-Vis spectrophotometer - Lambda 35 (Perkin Elmer). The UV-Vis spectra of the α-Fe_2O_3 films were carried out from 900 to 350 nm spectral range, at room temperature. A blank glass substrate was used as reference. Before the measurements of the optical properties, the layer from one side of the glass substrate was removed.

3. Results and discussions

The optical absorbance of the α-Fe_2O_3 films is represented in Fig. 1. It can be seen that on the NIR region the both films presents almost the same value of the absorption, only from about 640 nm wavelength we can observe a difference on the absorption spectra of the two samples. The film obtained for 3 hours (M6T) presents an increased absorption compared to the film obtained for 1hour (M2T), which has a lower value of the absorption in the visible region.

We can conclude that in the case of iron oxide films obtained by chemical bath deposition, for reaction times of 1, respectively 3 hours, a higher reaction time leads to an increase in absorbance at shorter than 640 nm wavelengths.

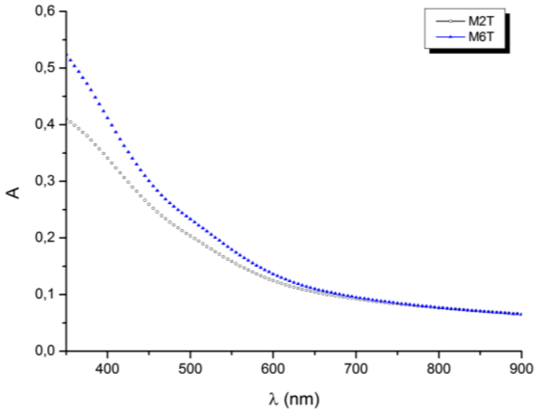

Fig. 1. Optical absorption spectra of α-Fe_2O_3 films obtained by CBD method.

Based on the measured optical properties, we determined the optical band gap (Eg) of the α-Fe_2O_3 films.

There are many different methods for determining the optical band gap. Yadav et al. [1], Dghoughi et al. [19], Pejova and coworkers [25], Ismail et al. [26] determined the band gap from the relation between the absorption coefficient α and the energy of incident light hν [19]:

$$(\alpha h\nu)^n = B(h\nu - Eg) \tag{1}$$

where α is the absorption coefficient, hν is the photon energy, B is a constant, Eg is the energy band gap and n represents the transition type (n=2 for direct transition, n=1/2 for indirect transition).

The optical band gap of the iron oxide films was estimated from the plot of $(\alpha h\nu)^2$ versus hν, by extrapolation of the linear part of the curve (see Fig. 2). Band gap energy of 2.57 eV was obtained for the film synthesized after 1 hour, respectively 2.67 eV for the film obtained after 3 hours. It can be seen that the value of Eg slightly increase (0.1 eV) with the increasing of the deposition time of the iron oxide films.

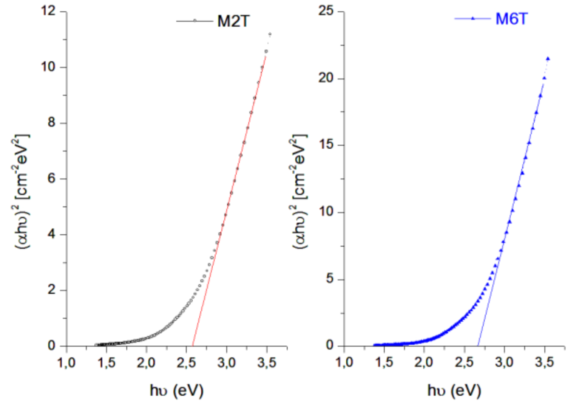

Fig. 2. Determination of Eg from $(\alpha h\nu)^2$ vs hν plot of α-Fe_2O_3 films elaborated at 1 hour (M2T) and 3 hours (M6T).

The values of the optical band gap for the iron oxide films obtained by CBD (2.57 eV for sample M2T and 2.67 eV for sample M6T) are in good agreement with the data reported in the literature [17,19,26]. Fe_2O_3 films are sensitive to visible light. The difference between the value of the Eg obtained for the films and the value corresponding to bulk Fe_2O_3 can be explained by the quantum size effect.

Optical properties of the materials give us considerable informations related to the type of applications for which they can be employed. As Akl mentioned, the refractive index is an important optical constant for the semiconductors and for photoelectronics applications [18]. The refractive index of iron oxide films was calculated according to the formula proposed by P. A. Ilenikhena [27]:

$$n = (1 + R^{1/2}) / (1 - R^{1/2}) \tag{2}$$

where n is the refractive index and R is the reflectance obtained from the expression [28]:

$$A + T + R = 1 \tag{3}$$

A is the absorbance and T is the transmittance.

The variation of refractive index, n, as a function of wavelength for the iron oxide films obtained by CBD at different deposition time is shown in Fig. 3. The both samples have a similar behavior. An increase of the refractive index value with the decrease of the wavelength in the visible region was observed. The maximum for the refractive index of the iron oxide film obtained for 1 hour is about 2.54 and 2.63 for the film obtained at 3 hours, at short wavelengths (450 nm). Similar values for the refractive index of iron oxide films obtained by different methods were reported in the literature. The refractive index for the multilayer sol-gel Fe_2O_3 films obtained by Gartner et al [29] varies from 1.8 to 2.4.

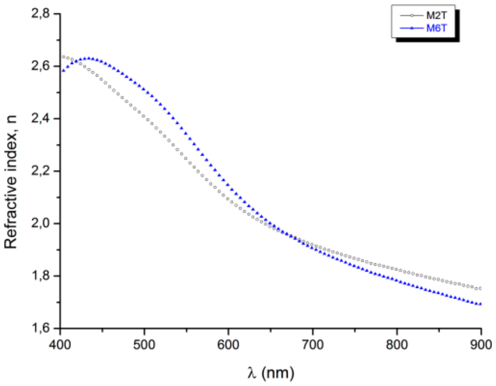

Fig. 3. The refractive index of α-Fe_2O_3 films as a function of wavelength.

Close values of the refractive index (1.84-2.12) were obtained for the sprayed iron oxide films prepared by Akl [18]. We noticed that at higher wavelengths, there is an obvious decrease of the refractive index value, behavior which was described by Akl too, for the iron oxide films obtained by spray pyrolysis [18].

4. Conclusions

- Iron oxide films were obtained by chemical bath deposition technique, followed by heat treatment at 500 °C for 4 hours.
- A higher reaction time leads to an increase in absorbance at short wavelengths.
- The optical band gap, Eg, obtained for the iron oxide films varies from 2.57 eV to 2.67 eV.
- An increase of the refractive index was found to take place at low wavelengths.

Acknowledgment

Paper developed within Project "Doctoral studies in engineering science for the development society based on knowledge - SIDOC"; Contract POSDRU /88/1.5/S/60078.

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