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Preparation and characterization of iron oxide thin films by spray pyrolysis using methanolic and ethanolic solutions

J.D. Desai, H.M. Pathan, Sun-Ki Min, Kwang-Deog Jung, Oh-Shim Joo *

Eco-Nano Research Centre, Korea Institute of Science and Technology, P.O. Box No. 131, Chongryang, Seoul 130-650, Republic of Korea

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Abstract

Iron oxide thin films have been obtained by spray pyrolysis using 100% methanolic and ethanolic solutions of iron trichloride. The films were deposited onto ITO-coated glass substrates. The preparative conditions have been optimized to obtain compact, pin-hole-free and smooth thin films which are adherent to the substrate. The structural, morphological and compositional characterizations have been carried out by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis. The films deposited using ethanolic solution results into pure hematite; α-Fe_2O_3 thin films, however, films deposited using methanolic solution consists of hematite and maghemite-c phases of iron oxide. The films are nanocrystalline with particle size of 30–40 nm. The optical absorbance of the film was of the order of 10^5 cm^{-1}. The optical band gap of films was found to be 2.26 and 2.20 eV for the films deposited using methanolic and ethanolic solutions, respectively.

Keywords: Iron oxide; Thin Film; Spray pyrolysis; Preparation and characterization

1. Introduction

There are as many as 15 phases formed by Fe and O, as oxides of iron [1]. 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 [2,3] and as a cathode in brine electrolysis [4]. Recently, Fe_2O_3 is found to have large third-order non-linear optical susceptibility and faster response time showing potential applications in optical computing [5]. It appears to have catalytic properties useful for N_2 fixation [6]. These oxides have been widely used in several industrial processes, such as dehydration, oxidation and Fischer–Tropsch synthesis [7–9]. Maghemite (γ-Fe_2O_3) is used in high-density magnetic recording devices [10]. Magnetite (Fe_3O_4) in different forms is well understood for its giant magneto-resistance. Hematite is well known for its property of parasitic or canted magnetism. It is used in red pigments

* Corresponding author. Tel.: +82 2 958 5217;
fax: +82 2 958 5219.
E-mail address: joocat@kist.re.kr (O.-S. Joo).

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[11], anticorrosive agents [12], gas sensors to detect combustible gases, such as CH_4, C_3H_8, and *i*-C_4H_8 [13,14] and electrochromic devices [15]. Due to the wide range of spectrum of applications, these oxides can be prepared in the form of powder, thin film and colloidal particles [16]. The most common oxides are hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4). These have different electrical, magnetic, electro-optical and chemical properties. Amongst these three common iron oxides hematite and maghemite have applications in gas sensors. The sensing mechanism in both cases is not the same. In γ-Fe_2O_3, it is from electron exchange between Fe^{3+} and Fe^{2+} and in α-Fe_2O_3 it is due to surface conductivity changes caused by the catalytic oxidation of reducing gases with chemisorbed oxygen-related species, such as O^- or O^{2-} [17]. Hematite, α-Fe_2O_3 has optical band gap around 2 eV, good chemical stability and appropriate valence band edges (i.e. +1.6 V/SCE at pH 14) for photo-induced oxygen evolution from water [18]. It has been tested as an electrode in photoelectrochemical (PEC) cell for energy conversion due to proper band gap [19]. Actual applications in devices require iron oxide in thin film forms. The thin film preparation can be broadly divided into physical and chemical methods. The physical methods result into excellent quality of thin films but lack flexibility and cost effectiveness. The chemical methods like spin coating, deep coating, chemical solution deposition and spray pyrolysis are more flexible and economic. Preparations of spray pyrolytic thin films of α-Fe_2O_3 have been reported by various groups [20–25].

The present study deals with the spray pyrolytic deposition of iron oxide thin films from methanolic and ethanolic solutions of iron tri-chloride. The oxygen was used as a carrier gas. The structural, morphological, compositional and optical properties of iron oxide thin films deposited by spray pyrolysis using methanolic and ethanolic solutions have been reported.

2. Experimental

2.1. Solution preparation and substrate cleaning

All the chemicals and reagents used were AR grade. Iron tri-chloride ($FeCl_3{\cdot}6H_2O$) of proper amount was dissolved in 100% methyl and ethyl alcohol, separately. The color of the solution was yellow-orange. The solution concentrations used varied from 0.1 to 0.2 M. Commercially available tin-doped indium oxide (ITO)-coated glass (Samsung Corning Co. Ltd., Gumi Korea) were used as substrates. They were sputter coated with thickness of 1650 ± 200 Å, transmittance of 80–92% and resistance of $8.5 \pm 1.5\ \Omega\ cm^{-1}$. They were cut into 5 cm × 1 cm. Substrate cleaning is an important step in preparation of thin films. ITO was ultrasonically cleaned in acetone and then in isopropyl alcohol, and finally washed with triple distilled water and stored in it. Substrates were dried in argon gas before using for film deposition.

2.2. Spray pyrolysis set-up

There are varieties of the spray pyrolysis set-up as regards the atomization techniques, such as ultrasonic nebulized, corona, electrostatic spray, etc. The simple form of spray pyrolysis set-up was used, which was designed and fabricated in our laboratory. It uses pressurized oxygen gas to atomize the solution mixture without ultrasonic nebulizaton. Fig. 1 shows the schematic diagram of the spray pyrolysis set-up. It consists of substrate heater. The substrate temperature was controlled using substrate heater with thermocouple feedback. The circular area of 50 cm^2 over the heater gave constant temperature without gradient. The ITO substrates were kept on it. The automatic spray gun (Lumina STA-6R Fuso Seiki Co., Ltd Tokyo, Japan) of orifice-size 1.0 mm was used for solution spray. It has provision to control the spray rate by setting the position of piston. The solution feed was under gravity from calibrated container. Oxygen was used a carrier gas with pressure controlling device, and measurement of pressure by use of gauge. The position of the nozzle of spray gun was adjusted such that ITO glass substrates were well covered by the spray-cone formed. The pressure of the carrier gas was chosen such that fine droplets of the solutions are distributed uniformly over the substrate. Powerful exhaust fan was utilized to escape exhaust gases and volatile byproducts through spray chamber.

2.3. Thin film preparation

Aerosol droplets of the solution were spread onto preheated ITO-coated glass substrates. Temperature of