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Size Dependent Physical Properties of Nanostructured α-Fe_2O_3 Thin Films Grown by Successive Ionic Layer Adsorption and Reaction Method for Antibacterial Application

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Thin films of nanostructured α-Fe_2O_3 with thickness of 156, 203 and 251 nm were deposited by successive ionic layer adsorption and reaction (SILAR) method onto glass substrates using $FeCl_3 \cdot 6H_2O$ and NaOH as cationic and anionic precursors. The X-ray diffraction studies revealed that, α-Fe_2O_3 thin films are nanocrystalline in nature with rhombohedral structure. The morphological properties were investigated by field emission scanning electron and atomic force microscopy. The optical studies showed that α-Fe_2O_3 exhibits direct as well as indirect optical band gap energy. The electrical resistivity of α-Fe_2O_3 at 305 K decreases from 11.76×10^2 to 9.46×10^2 Ω cm as film thickness increases from 156 to 251 nm. The thermo-emf measurements confirmed that α-Fe_2O_3 exhibits n-type conductivity. The nanocrystalline α-Fe_2O_3 exhibits antibacterial character against *Staphylococcus aureus* and its efficiency increases from 37.50% to 87.50% depending on crystallite size.

KEY WORDS: Thin films; Nanostructures; AFM (atomic force microscopy); Physical properties; Antibacterial efficiency

1. Introduction

Nanomaterial exhibits unusual structural, optical, electronic, magnetic and chemical properties and can be tailored by controlling their size during the growth process. It is an exciting issue in nanoscience to understand the simple and economic chemical growth process by which tailoring of materials at nanoscale can lead to novel and enhanced functionalities. Therefore, the interest in preparation, characterization, and applications of nanomaterial continues unabated. In this regard, the synthesis of nanocrystalline binary metal oxide semiconductors has been a rapidly growing area of research due to their important applications in semiconductor optoelectronic devices[1].

Thin films of iron oxide have showed great scientific attention due to its novel structural, optical, electrical and magnetic properties. It has different crystalline phases depending on stoichiometry, such as wustite (FeO), magnetite (Fe_3O_4), hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3). Among these, several researchers have studied α-Fe_2O_3 and γ-Fe_2O_3 phases of iron oxide and studied their related applications[2−4]. The synthesis of high quality maghemite is difficult as it shows phase transition from ferrimagnetic γ-Fe_2O_3 to antiferromagnetic hematite (α-Fe_2O_3) at higher temperature[5]. However, n-type hematite (α-Fe_2O_3) is an attractive environmental friendly semiconductor material for photoelectrochemical and photocatalytic purposes due to its stability, benign nature and abundance. Also because of its low cost, high resistance to corrosion, good chemical stability, high refractive index and non-toxicity, it has been traditionally used as catalysts, pigments, gas and humidity sensors, solar filters, supercapacitors, as an electrode material, in water treatment, in magnetic storage devices and in solid state lithium batteries, etc[6−17]. In addition to this, α-Fe_2O_3 shows biomedical applications such as drug delivery system, hyperthermia and magnetic resonance imaging[18,19].

Numerous methods have been used to deposit α-Fe_2O_3 thin films such as ultrasonic spray pyrolysis[20,21], atomic layer deposition[22,23], electrodeposition[24], thermal decomposition[25], metal organic chemical vapor deposition (MOCVD)[26,27], spray pyrolysis[28,29], atmospheric pressure chemical vapor deposition (APCVD)[30], chemical vapor deposition (CVD)[31], plasma-enhanced chemical vapor deposition (PECVD)[32], electrochemical methods[33,34], aqueous

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combustion method[35], radio frequency magnetron sputtering[36], sol gel[37] and successive ionic layer adsorption and reaction method[38] etc. The utmost research until the present time has focused on the growth of α-Fe_2O_3 thin films by physical methods. However, very little research has been performed on chemical methods to synthesize nanocrystalline α-Fe_2O_3 thin films. As compared to physical methods, successive ionic layer adsorption and reaction (SILAR) is one of the simple, nonhazardous and economic chemical solution method[39,40]. The growth process in successive ionic layer adsorption and reaction (SILAR) technique was carried out at room temperature and under ambient pressure utilizing aqueous solutions. The substrate was immersed in separately placed cationic and anionic precursors alternately. The substrate is rinsed after each immersion to isolates the individual steps. In SILAR method film thickness can be easily controlled directly by adjusting the number of the deposition cycles[41,42].

In the present work, low cost chemical SILAR method has been successfully utilized to grow nanostructured α-Fe_2O_3 thin films. The main goal of the paper is to investigate the effect of film thickness on structural, morphological, electrical and optical properties of α-Fe_2O_3. Also the thickness dependent antibacterial character of α-Fe_2O_3 against *Staphylococcus aureus* by spread plate technique is discussed.

2. Experimental Procedure

2.1. Preparation of iron oxide thin films

The nanocrystalline α-Fe_2O_3 thin films were deposited by successive ionic layer adsorption and reaction method onto glass substrates. For the deposition of thin films, 0.05 mol/L $FeCl_3 \cdot 6H_2O$ of pH 1 and 0.001 mol/L NaOH of pH 11 were used as cationic and anionic precursors, respectively. In the deposition mechanism the nature of the substrate surface is very important to grow uniform film over the entire substrate surface. Extreme cleaning of the substrate is required for the deposition, since the contaminated substrate surface provides nucleation sites facilitating the growth, which results in non-uniform growth. Hence cleaning of the substrate prior to the actual deposition is important in the deposition of the thin films. Commercially available glass micro slides of dimension 26 mm × 76 mm × 2 mm were boiled in chromic acid for 30 min, then washed with liquid detergent and rinsed in acetone. Finally slides were ultrasonically cleaned with double distilled water for 15 min prior to the actual deposition. The film growth in the SILAR method consists of four steps: in the first step cations are adsorbed on the substrate surface, in the second step all cations not adsorbed are rinsed away with purified water. The solvated anions enter the diffusion layer in the next reaction step and they react with the adsorbed cations. The ions, which have not reacted, are again washed away with purified rinsing water in the fourth step.

For the deposition the well cleaned glass substrate was immersed in cationic precursor for 20 s, where Fe^{3+} iron species were adsorbed on the surface. This substrate was then rinsed in deionized water for 20 s to remove loosely bound species of Fe^{3+} ions from surface. After removal of loosely bound species of Fe^{3+} the substrate was then immersed in an anionic precursor for 20 s to form a layer of iron oxide material. To remove unreacted or excess species from substrate, it was again rinsed in deionized water for 20 s. This completes one SILAR deposition cycle. By taking several trials the deposition parameters were optimized to get good quality films. The optimized preparative parameters for the synthesis of α-Fe_2O_3 thin films are tabulated in Table 1. The α-Fe_2O_3 thin films with thickness of 156, 203 and 251 nm were deposited by repeating 40, 50 and 60 SILAR cycles, respectively. The as-deposited thin films were annealed at 573 K for 2 h to convert iron hydroxide into FeO(OH). These films were further annealed at 773 K for 3 h to get α-Fe_2O_3 phase.

2.2. Antibacterial test

The antibacterial behavior of α-Fe_2O_3 thin films were studied against *S. aureus* using spread plate technique. The culture of *S. aureus* bacteria was prepared in nutrient broth. The loopful culture of *S. aureus* organisms was inoculated into 20-mL sterilized nutrient broth and incubated at 310 K for 24 h. Then 20-μL culture of *S. aureus* was inoculated on iron oxide deposited and undeposited glass substrates of area 1 cm^2 with the help of inoculating needle. These glass slides were then placed in previously sterilized petri dishes and incubated at 310 K for 24 h. After this incubated slides were transferred to 3 mL of buffer peptone solution in a test tube and ultrasonicated to detach bacteria thoroughly from the substrate. From this, 20-μL washed buffer peptone solution was then inoculated on nutrient agar plates by spread plate technique and incubated at 310 K for 24 h to obtain viable bacteria. After successful incubation the viable bacteria colonies were counted and antibacterial efficiency was calculated using the relation[43].

$$E(\%) = \frac{(A-B)}{A} \times 100\% \quad (1)$$

where E is the antibacterial efficiency, A is the number of viable bacteria with undeposited film (standard) in the petri dish and B is the number of viable bacteria with α-Fe_2O_3 deposited films in the petri dish.

2.3. Characterization techniques

In the present work, thickness of the film was measured by gravimetric weight difference method using the relation,

$$t = \frac{m}{\rho \times A} \quad (2)$$

where m is the mass of the film deposited on the substrate in g, A is the area of the deposited film in cm^2 and ρ is the density of α-Fe_2O_3 in bulk form (5.242 g/cm^3)[16]. The mass of the deposited film was measured by using a sensitive micro balance. The

Table 1 Optimized preparative parameters for the deposition of α-Fe_2O_3 thin films

Deposition conditions	Cationic precursor	Anionic precursor
Precursors	$FeCl_3 \cdot 4H_2O$	NaOH
Concentrations (mol/L)	0.05	0.001
pH	1	11
Immersion time (s)	20	20
Temperature (K)	303	303
No. of SILAR Cycles	60	60
Volume of precursor (ml)	50	50