Synthesis of nanocrystalline α-Fe2O3 by using thermal oxidation of Fe Films

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Abstract. α-Fe2O3 hematite films were prepared by thermal oxidation from Fe films electroplated on silicon. Electrodeposition of Fe thin films was carried out from a sulfate bath containing an ammonium chloride complexing agent. The electrochemical study was performed by cyclic voltammetry. The SEM analysis of the films obtained at a -1.3 V constant polarization shows dendritic grains in the form of islet. The DRX spectra exhibit characteristic iron peaks according to the face centered cubic (Fcc) structure. These samples were annealed. At a temperature of 650 ° C, a single iron oxide phase was well formed, with the hematite structure. The SEM photos show a well-assembled columnar structure with formation of nanowires at the surface of the deposit. The absorbance spectra reveal an absorption features in the ultraviolet range

1. Introduction

Hematite (α-Fe2O3) is a promising material for potential applications in spin electronics [1], catalysis [2], photocatalysis [3], in the fields of biology and biomedical [4], gas sensors and photodetectors energy-related applications. It has attracted a great attention because to its chemical stability in aqueous solutions for water splitting, the abundance in nature, a suitable band gap (Eg) of 2.14 eV and low fabrication cost [5]. In the literature, various α-Fe2O3 morphologies with different shapes have been reported, including α-Fe2O3 nanoparticles [6], nanowires [7], nanorods [8] and nanotubes [9]. Different approaches have been used for the synthesis of α-Fe2O3 nanostructures with higher surface to volume ratios, sol-gel process [10], thermal oxidation of iron foil [11] and solvothermal and hydrothermal [12]. α-Fe2O3 is also produced from electrochemical anodization [13] and electrodeposition [14- 15]. Moreover, it is reported that the films obtained with the electrochemical method possess relatively low band gap [16], which has a great interest in solar cell applications. Recently, Hanedar and co-workers [15] prepared grass-like nanostructured α-Fe2O3 photoelectrodes for the first time through a one-step new electrochemical method from an oxygenated aqueous solution of Fe3+ at room temperature without using surfactants, which are required in most applications, such as sensors and energy conversion and storage. Dalchlie et al. [16] used a different electrochemical approach based on a potential cycling and a potential pulsed electrodeposition procedure to fabricated α-Fe2O3 electrodeposits. Also, Fe2O3 is one of the most promising anode materials for the next generation lithium ion batteries (LIBs) to substitute graphite, demonstrated excellent reversible properties and high theoretical capacity (1007 mAh/g) [17]. The present investigation concerns iron oxide thin films formed by oxidation of iron film. The iron film is firstly deposited directly on the
silicon surface by electrochemical method. This method allows to optimize deposition condition parameters such as bath composition and deposition time to get good iron films. Further thermal oxidation of iron films is performed at temperature 650 °C.

2. Experimental

The electrodeposition of Fe was carried out from an electrolyte bath containing aqueous sulfate solution with Ammonium Fluoride and Saccharin additives. The bath solution was composed of 0.4M H$_3$BO$_3$, 0.4 M NH$_4$Cl, 0.01M Saccharin and 0.1 M FeSO$_4$. The distance between anode and cathode was 0.5 cm. The cathode used was a silicon (n + Si (100)) a with a resistivity $\rho$=0.02-0.04 $\Omega$.cm. The platinum was used an anode electrode. The electrodeposition was performed using Biologic VMP 3 potentiostat with a constant potential at -1.3 V (vs. Ag/AgCl) for different deposition times. The morphologies of the Fe and α-Fe$_2$O$_3$ films were obtained by using scanning electron microscope (SEM). X-ray diffraction (XRD) (X’ Pertro PHILIPS with Cu K$\alpha$ radiation, was used to study the structure of Fe and α-Fe$_2$O$_3$ films. The measurements of magnetic properties were made using a vibrating sample magnetometer (VSM) with the applied field parallel and perpendicular to the surface of sample. The optical properties of the deposits on the ITO-coated quartz plates were studied by recording the absorption spectra using a CARY 500-VARLAN UV-vis-NIR spectrometer at room temperature.

3. Results and discussion

3.1 Electrochemical study of Fe Films

The electrochemical behavior of Fe$^{2+}$ on Si electrode in solution is further investigated by the cyclic voltammetry in 0.4 M H$_3$BO$_3$, 0.1M FeSO$_4$, as shown in Fig. 2 ((a): solid line)). The pH of solution is adjusted to 1.54

![Figure 1](image_url)

**Figure 1.** A) Cyclic voltammetry of deposit solution: ((a): solid line) without additive; ((b): dash line) with additive NH$_4$Cl (0.4M); ((c): dot line) with additive NH$_4$Cl (0.4M), Saccharin (0.01M) pH=1.54, $v$ = 10 mV/s. B) the zoom of Fig. 2((a): solid line)).

The analysis of the (I-V) curve reveals clearly the oxidation-reduction process of the Fe$^{2+}$/Fe ions (Fig. 1(a) and the zoom of Fig. 1(a)). It can be noted that the reduction reaction of Fe$^{2+}$ ferric cations is predominant in the potential range [-1- -1.2 V (vs. Ag/AgCl)], characterized by a current plateau. Beyond -1.2 V (vs. Ag/AgCl), an increase in the fast cathodic current is observed, traducing the competition between the reduction reaction of the ferric ions and that of hydrogen. From the anodic peak intensity (the zoom of Fig. 1(a)), it can be deduced that a small amount of iron has been deposited on the Si electrode with an important release of hydrogen. Fig. 1((b): dash line) shows cyclic voltammetry of 0.1M FeSO$_4$, 0.4 M H$_3$BO$_3$ and 0.4 M NH$_4$Cl at pH values (1.54). In the presence of 0.4 M NH$_4$Cl in solution, an important cathodic and anodic currents are recorded corresponding to the reduction-oxidation of Fe$^{2+}$/Fe and FeCl$^+$/Fe with a displacement of the cathodic current towards the negative potentials, according to the following reactions.
Fig. 2 illustrates the iron speciation pattern in the presence of the chloride ligand in the aqueous medium.

The total concentration (FeTot) is equal to 0.1 M and the total chlorine concentration is 0.4 M (NH₄Cl). The total concentration of different (Fe (II)) complexed and uncomplexed electro-active species in the chloride medium is given by the iron mass conservation equation as follows:

- \[[\text{Fe(II)}]_{\text{Tot}} = C = [\text{Fe}^{+2}] + [\text{FeCl}^+] + [\text{FeCl}_2(aq)]\]  \hspace{1cm} (3)

On the other hand we have:

- \(\beta_1 = \frac{[\text{FeCl}^+]}{[\text{Fe}^{+2}][\text{Cl}^-]} = 10^{-0.6}\) \hspace{1cm} (4)
- \(\beta_2 = \frac{[\text{FeCl}_2]}{[\text{Fe}^{+2}][\text{Cl}^-]^2} = 10^{-8.17}\) \hspace{1cm} (5)

This is given:

- \([\text{Fe}^{+2}] = \frac{C}{1 + \sum_{i=1}^{2} \beta_i [\text{Cl}^-]^i}\) ; \([\text{FeCl}^+] = \frac{c_i \beta_1 [\text{Cl}^-]}{1 + \sum_{i=1}^{2} \beta_i [\text{Cl}^-]^i}\) ; \([\text{FeCl}_2(aq)] = \frac{c_i \beta_2 [\text{Cl}^-]^2}{1 + \sum_{i=1}^{2} \beta_i [\text{Cl}^-]^i}\) \hspace{1cm} (6)

According to the iron speciation diagram, Fe²⁺ ions are the most predominant species in the solution. The percentage of species present in the deposition bath for 0.39 pCl is given in Table 1. It is found that the presence of the Cl⁻ ions in the electrolytic bath leads to the adsorption of the ion FeCl⁺ on the silicon surface which will subsequently slow down the migration of the protons towards the silicon surface.

| Electro-active specie | Fe²⁺ | FeCl⁺ | FeCl₂ |
|-----------------------|------|-------|-------|
| Molar Percentage %    | 78   | 22    | 0     |

The influence of the simultaneous addition of 0.1 M saccharin and 0.4 M (NH₄Cl) in sulfate bath has been studied, the cyclic voltammetry is given in Fig. 1((c): dot line). In the presence of saccharin, the cathodic current density is increased and the iron dissolution peak increased also. This can be attributed to the adsorption of Fe²⁺ complexed with saccharin and Cl⁻ on the surface of the electrode.
3.2 Morphological observations

Fig. 3(a-b) and (c-d) show the SEM images of the electrodeposited Fe film at -1.3 V (vs. Ag/AgCl) for 1 min and 2 min, respectively. All Fe films reveal dendritic grains in the form of islet, with an average size of 100 nm. By increasing of deposition time, the thickness of Fe layers increases to 350 nm for 2 min.

Figure 3. SEM images of iron deposition on silicon substrate at different deposition times for a potential of -1.3 V (vs. Ag/AgCl); (a and b) 1 min; (c and d) 2 min.

Fig. 4 shows the XRD patterns of the as-prepared Fe at -1.3 V (vs. Ag/AgCl) for 1, 2 and 3 min. It bring out the characteristic diffraction peaks which can be indexed to (110) plane of Fe (fcc) phase (JCPDS, card no.00-001-1267). The presence of weak characteristic diffraction peaks at 2θ= 46.3° (004) and 56.4° (423), corresponding to the formation of FeSi2 phase and a sharp diffraction peak at 2θ= 61.98° (221), corresponding to the FeSi phase were observed. Fig 5. exhibits also the characteristic diffraction peaks, corresponding to Si substrate used as a working electrode which can be identified (JCPDS, card no. 01-080-0018).

Figure 4. X-ray diffraction pattern of iron deposits obtained at -1.3V (vs. Ag/AgCl), for different deposition times.

4. Thermal oxidation of Fe Films

The electrodeposited Fe films were annealed in a furnace at 650 °C for 5 h 30 in air environment. The formation of single oxide α-Fe2O3 nanostructures was confirmed by the XRD pattern displayed in Fig. 5. All new diffraction peaks were attributed to the rhombohedral structure of α-Fe2O3 (JCPDS no. 33-0664).

4.1 Morphological observations of α-Fe2O3

The effect of Fe film electrodeposition time, after annealing at 650 °C for 5h 30 on morphology of the α-Fe2O3 was investigated (Fig. 6). As shown in Fig 6(a), for 1 min of electrodeposition, the formation of well-assembled columnar structure with the growth of nanowires on the hematite surface layer α-Fe2O3 is clear. When the electrodeposition time is increased to 2 min, the SEM image Fig 6(b) reveals that the α-Fe2O3 films have a similar morphology as that to 1 min of electrodeposition. Fig. 6 indicates obviously that the thickness of the α-Fe2O3 depends on the electrodeposition time of Fe film and it is higher of these Fe films as a result to the diffusion of oxygen inside the Fe lattice during thermal oxidation, producing an elongation of lattice.
4.2 Optical properties

Fig. 7 shows the absorbance spectrum of the α-Fe₂O₃ thin layers produced by thermal oxidation at 650°C for 5 h 30 of iron films for deposition time 1 and 2 min. The figure depicts the variation of the absorbance spectrum as a function of the hematite thickness layer obtained. An increase in the absorbance is observed (Fig. 7) when the thickness layer is increased.

The plot of (αhν)² versus photon energy (hν) for iron oxide thin film is presented on Fig 8. The optical band gap energy of the α-Fe₂O₃ is determined by plotting the (αhν)² as a function of (hν). α-Fe₂O₃ film possess a direct band gap transition. The optical band gap energy is found 3.2 eV for α-Fe₂O₃ thickness of 290 nm, which is higher to those reported values for α-Fe₂O₃ nanostructures [16, 17].

Fig. 6.: SEM images in cross-section of thin layer of α-Fe₂O₃ after annealed at 650 °C for 5h 30 of iron films deposit (a and b) 1min; (c and d) 2min.

Fig. 7. Variation of the absorbance spectrum as a function of the thickness α-Fe₂O₃ films

Fig. 8. Estimated band gap of α-Fe₂O₃ films after annealed at 650 °C for 5h 30 of iron films 2min.

α-Fe₂O₃ photoanodes has been extensively studied by several groups for use in solar water splitting [17, 19]. The photoelectrochemical current densities of the α-Fe₂O₃ nanostructures electrodeposited onto ITO electrode were carried out by linearly sweeping the potential from 0.0 to 1.8 V (vs. Ag/AgCl) with a scan rate of 10 mV/s in 0.1 M KOH aqueous solution, in the dark and under illumination. The (J-V) curves under illumination shows a significant increase in the photocurrent at low bias due to the photogeneration of electrons and holes, Fig. 10.
The photocurrent density of the columnar α-Fe₂O₃ was 0.5 mA/cm² at 1 V (vs. Ag/AgCl) and it reaches to approximately 3.5 mA/cm² at 1.8 V (vs. Ag/AgCl). By comparison with other works, the characteristic in the dark (I-V) demonstrates a high current density at less positive potential with respect to that obtained by Y. Hanedar et al [17] of grass-like nanostructured hematite and by R. Lui et al [19] of Au nanoparticles incorporated into α-Fe₂O₃ platelets by plasmonic. Under light illumination, the α-Fe₂O₃ columnar structure shows a remarkable photocurrent improvement, this result is comparable to that R. Lui et al [19]. It was found that a various design of morphology can be affected an enhancement of hematite photoelectrodes by exploiting a plasmonic [19].

4.3 Magnetic properties

Fig. 10 shows the magnetic hysteresis curves recorded at room temperature for α-Fe₂O₃ film, after annealing at 650 °C for 5h 30, of iron film deposit 1min. The magnetic hysteresis loops, (Fig. 10) shows the ferrimagnetic behavior of the α-Fe₂O₃ film, as also observed in the previous studies [19].

5. Conclusion

Columnar structure α-Fe₂O₃ thin films have been fabricated onto silicon substrate using a two-step electrochemical method and thermal oxidation of iron films. Optimized preparative parameters using cyclic voltammetry leads to iron films with dendritic grains in the form of islet. After thermal oxidation, the DRX result demonstrated that a single phase has been formed with the hematite structure. The UV-Visible characterization showed that the thin hematite film has been a direct gap of Eg = 3.2 eV for thickness 290 nm. Annealed film exhibits soft magnetic properties with a small ratio Mr/Ms of 0.06. The columnar structure α-Fe₂O₃ photoanode showed significantly photocatalytic performance.

References

[1] Janisch R, Gopal P, Spaldin 2005 J. Phys. Condens Matter 17 657
[2] Li C, Shen Y, Jia M, Sheng S, Adebajo M O, Zhu 2008 J. Catal. Commun 9 355
[3] Huang M C, Chang W S, Lin J C, Chang Y H, Wu C C 2015 J. Alloys. Comp 636 176-182
[4] Kim J S, Yoon T J, Kim B G, Park S J, Kim H W, Lee K H, Park S B, Lee J K, Cho 2006. J. Tox Sci, 89 338
[5] Sivula K, Formal F L, Grätzel M 2011 J. Chem Sus Chem 4 432-49
[6] Zhang H, Wang W W, Li H F, Meng S L, Li D Q 2008 *J. Mater Lett* 62 1230–3
[7] Pascal C, Pascal J L, Favier F, Moubtassim M L, Payen C. 1999 *J. Mater Chem* 11 141–7.
[8] Lian S, Wang E, Kang Z, Bai Y, Gao L, Jiang M, Hu C and Xu L 2004 *J. Solid State Commun* 129 485–90
[9] Wen X G, Wang S H, Ding Y, Wang Z L, Yang S H. 2005 *J. Phys Chem* 109 B 215–20
[10] Watanabe A, Kozuka H 2003 *J. Phys Chem* 107 B 12713-12720
[11] Liao L, Zheng Z, Yan B, Zhang J X, Gong H, Li J C, Liu C, Shen Z X, Yu T 2008 *J. Phys Chem* 112 C 10784-10788
[12] Du M, Xu C, Sun J, Gao L 2012 *J. Electrochim Acta* 80 302-307
[13] Wang L, Fei T, Lou Z., Zhang T 2011 *J.ACS Appl. Mater Interfaces* 3 4689-4694
[14] Kulkarni S S, Lokhande C D 2003 *Mater Chem and Phys* 82 151-156
[15] Hanedar Y, Demir U, Oznuluer T 2016 *J. Superlattices Microstruct* 98 371-378
[16] Schrebler R S, Altamirano H, Grez P, Herrera F V, Munoz E C, Ballesteros L A, Cordova R A, Gomez H, Dalchiele EA 2010 *J. Thin Solid Films* 518:6844–6852
[17] Park Y, Oh M, Park J S, Baek S H., Kim M, Kim S, Kim J H 2015 *J. Carbon* 94 9-17
[18] Skoog D, Analisis Instrumental 1989 McGraw Hill México
[19] Liu R, Yang X, Anfuso C L, Huang Z and Han L 2001 *J. Rev. Adv Sci Eng* 4 1-9

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