Photoelectrochemical Property of Iron (III) Oxide Thin Film Prepared by Sol-Gel Process

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Received August 2, 1989 ; Accepted September 18, 1989

ABSTRACT

Iron(III) oxide (Fe_2O_3) thin film was prepared on ITO-deposited glass substrates by sol-gel method. The starting sols were obtained by the partial hydrolysis of iron(III) tributoxide in the presence and absence of acetylacetone. Dopants (alkoxides of Si(IV) and Mg(II)) were added before hydrolysis. The films were characterized to be amorphous Fe_2O_3 by ultraviolet and visible spectroscopy, X-ray diffraction, differential thermal analysis, and thermal gravimetry. Photoanodic current observed in neutral aqueous solution increased in the following order; (Mg-doped) < (undoped) < (Si-doped). Corrosion of the films by cathodic polarization was observed in the dark. Action spectrum revealed that both direct and indirect band-gap excitation caused the photocurrent.

1 INTRODUCTION

Iron(III) oxide (Fe_2O_3) is a semiconductor being stable in basic or neutral aqueous solution even under photoirradiation. The narrow band gap of ca. 2.2 eV, corresponding to light of wavelength 565 nm, allows the photoexcitation by visible rays sufficiently contained in the solar radiation.¹⁾ The semiconducting property can be modified from n- to p-type by the addition of appropriate dopants.²⁾

Attempts to prepare thin Fe_2O_3 film electrode have been made; for example, thermal³⁾ or anodic oxidation⁴⁾ of iron, chemical vapor deposition,⁵⁾ plasma splay method,⁶⁾ and splay pyrolysis.⁷⁾ However, these methods are unsuitable to the preparation of large-area devices and thin films with controlled amount of dopants. This paper describes the preparation of thin Fe_2O_3 films by sol-gel process,⁸⁾ and discusses the effect of preparation conditions on their photoelectrochemical properties.

2 EXPERIMENTAL

2.1 Materials

Iron(III) tributoxide ($\text{Fe}(\text{O}i\text{Bu})_3$, Hokko Chemicals), magnesium di(2-ethoxyethoxide)

($\text{Mg}(\text{O}i\text{Et})_2$, Hokko), and silicon tetrabutoxide ($\text{Si}(\text{O}i\text{Bu})_4$, Tokyo Chemical Ind.) were used as received. The other chemicals were in best available grades. Indium tin oxide (ITO) deposited glass (60×28×1 mm, 7.5–9 $\Omega/\square$) was supplied from Yoneda Glass Bead Mfg.

2.2 Procedure

Composition of the starting sols was shown in Table 1. Solution B containing water was added dropwise to Solution A containing Fe(III) and dopants, such as Si(IV) and Mg(II). Details of dip-coating and calcination procedures were described elsewhere.⁹⁾ Abbreviation for these Fe_2O_3 films is used in this paper; for example [Fe-Mg/5(773)] denotes the 5-layered film from Sol Fe-Mg calcined at 773K.

Table 1 Molar composition of Fe_2O_3 sols

Soln	Component /mol	Sol			
		Fe	Fe-Si	Fe-Mg	Fe-AA
A	$\text{Fe}(\text{O}i\text{Bu})_3$	0.016	0.016	0.016	0.021
	EtOH	4.9	4.9	4.9	0.51
	AA	—	—	—	0.021
	$\text{Si}(\text{O}i\text{Bu})_4$	—	0.002	—	—
	$\text{Mg}(\text{O}i\text{Et})_2$	—	—	0.002	—
B	EtOH	0.49	0.49	0.49	0.51
	H_2O	0.081	0.081	0.081	0.041
	HCl	0.017	0.017	0.017	—
A+B	Fe/mol dm^{-3}	0.045	0.045	0.045	0.20

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Key Words: Iron(III) oxide, Sol-gel process,
Doping, Photoanodic current, Cathodic corrosion

Photoelectrochemical property of the Fe_2O_3 film coated on ITO electrodes was measured in 0.1 mol dm^{-3} aqueous Na_2SO_4 solution under Ar atmosphere. Pt plate and Ag/AgCl electrode were employed as counter and reference electrodes, respectively. The cell constitution followed that reported by Baba.¹⁰⁾ The apparent surface area of Fe_2O_3 electrode was 3.5 cm^2 . The Fe_2O_3 electrode was irradiated by focused light beam from a 1-kW Xe lamp through the electrolyte solution. The action spectrum was measured with a JASCO CT-25N grating monochromator and a Philips 500-W ultra-high-pressure Hg arc. The absolute intensity of the monochromatic light was measured by a multichannel photodiode array detector (Ohtsuka MCPD-100) correlated by ferric oxalate chemical actinometry.¹¹⁾

3 RESULTS AND DISCUSSION

3.1 Physical properties

3.1.1 Preparation of sols and films

Table 1 shows the molar composition of sol containing Fe(III). These red-yellow solutions were clear and transparent without appreciable precipitation. In the absence of acetylacetone (AA), further increase in Fe(III) concentration led to the precipitation, and the film obtained from thus precipitated suspension was heterogeneous and opaque. Addition of AA prevented the precipitation of Fe(III) hydroxide, so that the clear sol of higher Fe(III) concentration (Sol Fe-AA) could be obtained. This stabilization is attributable to the complexation of AA with Fe(III) cation, as observed in an aluminum(III) oxide sol.¹²⁾ Red-brown Fe_2O_3 films prepared from these sols in Table 1 were homogeneous and transparent.

The thickness of film was measured by multiple beam interferometry¹³⁾ with a Nikon Optiphot microscope to obtain average value of 51 nm for one layer of film ([Fe-Mg/1(473)]).

3.1.2 Optical absorption

Electronic absorption spectra of iron oxide films coated on ITO-deposited glass substrates were shown in Fig. 1. Difference in spectra among these doped and undoped films prepared under similar conditions was small; broad absorption with tailing up to 700 nm was observed. However, detailed inspection showed that Si-doping [Fe-Si/10(773)] caused a slight increase in absorption at around 400 nm and at $> 500 \text{ nm}$, compared with the undoped and Mg-doped films. Thicker film [Fe-AA/5(773)] showed larger absorption in the wavelength region $< 700 \text{ nm}$.

3.1.3 X-ray diffraction (XRD)

XRD analysis (Fig. 2, Rigaku Geigerflex

2013) revealed that the film calcined at $< 873 \text{ K}$ is amorphous exhibiting no appreciable peaks in 2θ region $< 70 \text{ deg}$. For the film calcined at $\geq 973 \text{ K}$, small diffraction peaks corresponding to $\alpha\text{-Fe}_2\text{O}_3$ (hematite) appeared. Also, the bulk gel prepared by evaporation and calcination (1273 K) of starting sol exhibited XRD peaks consistent with the hematite crystal structure. Consequently, the thin Fe_2O_3 films used in the photoelectrochemical measurements (calcination at $< 873 \text{ K}$) consisted of amorphous Fe_2O_3 .

Fig. 1 Electronic absorption spectra of Fe_2O_3 thin films on ITO glass substrates, as prepared and after anodic polarization (open symbols), and after cathodic polarization (closed symbols) of [Fe/10(773)] (○, ●), [Fe-Mg/10(773)] (□, ■), [Fe-Si/10(773)] (△, ▲), and [Fe-AA/5(773)] (◎). The absorption of a base ITO glass is also shown (▽).

Fig. 2 XRD patterns of Fe_2O_3 thin films [Fe-AA/5] on (a) glass and (b) quartz, and (c) powder obtained by evaporation and calcination (1273 K) of Sol Fe-AA. Calcination temperature; A: 873, B: 773, C: 573, D: 1073, and E: 973 K. Marked peaks in (c) were assigned to hematite Fe_2O_3 .

Crystalline Fe_2O_3 electrodes were not prepared, since ITO-glass substrate was softened and degraded at such higher temperature to crystallize Fe_2O_3 .

3.1.4 Differential thermal analysis (DTA) and thermal gravimetry (TG)

Fig. 3 shows DTA and TG patterns (ULVAC HPC-5000, rate of temperature elevation: 5 deg min^{-1}) of bulk gel prepared from Sol Fe-AA. A broad endothermic peak at $< 400 \text{ K}$ and a sharp exothermic peak at ca. 455 K are attributed to the evaporation of solvents (ethanol and/or water) and combustion of acetylacetone, respectively. This was proved by the fact that the former peak appeared for all sols in Table 1, while the latter was not observed for the bulk gel without acetylacetone. From the TG pattern, the molar ratio of acetylacetone to Fe(III) in the bulk gel was calculated to be 0.94, on the assumptions that the final residue consists of pure Fe_2O_3 and that weight decrease at around 455 K is attributed to the detachment of acetylacetone. This ratio is close to that in feed (1.0). Therefore, the residual acetylacetone in the film calcined at $> 500 \text{ K}$ could be neglected.

The weight decrease up to ca. 700 K was assigned to the inter-particular detachment of butanol and/or water in the course of sintering of porous Fe_2O_3 particles. Small exothermic peak at ca. 550 K may correspond to this process.

At $> 873 \text{ K}$, weight loss was negligible in the TG pattern. It is also noted that a small exothermic peak at 873 K and exothermic drift at higher temperature up to 1273 K in DTA was observed. These were accounted for by the crystallization of amorphous Fe_2O_3 , which was also observed in the above XRD analyses.

3.2 Electrochemical properties

3.2.1 Photoinduced current

Fig. 4 shows steady-state anodic current of doped and undoped Fe_2O_3 electrodes. Dark anodic current (i_d) was observed at the potential $> 0.6 \text{ V}$ regardless of dopants. This i_d was attributed to the oxidation of water, probably at bare ITO surface. Although we have no structural evidence, cracks or detached part in the surface Fe_2O_3 layer caused such leak current due to the oxidation of water.

Photoirradiation enhanced the current of all electrodes used in this study, showing the n-type semiconducting property of Fe_2O_3 films. The current increment from i_d is represented as photocurrent (i_p). Except for Mg-doped film for which i_p decreased above 0.8 V , i_p was saturated at $> 0.8 \text{ V}$. The maximum i_p increased in the following order;

Mg doped $<$ undoped $<$ Si doped. This doping effect is discussed in the following section.

No appreciable change in optical absorption was observed by the above-described anodic polarization, indicating no photocorrosion of these Fe_2O_3 films. Therefore, the photoinduced current arises from the following reaction processes.

Fig. 4 also shows steady-state cathodic current of the Fe_2O_3 electrodes. Relatively larger cathodic current was observed in the dark at the potential $< \text{ca. } -0.2\text{V}$, and Fe_2O_3

Fig. 3 (a) DTA and (b) TG patterns of bulk gel obtained from Sol Fe-AA by evaporation at room temperature.

Fig. 4 Plots of i_d (closed symbols) and i_p (open symbols) of $[\text{Fe}/10(773)]$ (○, ●), $[\text{Fe-Mg}/10(773)]$ (□, ■), and $[\text{Fe-Si}/10(773)]$ (△, ▲).

films were dissolved; the optical absorption was markedly decreased by the cathodic polarization (Fig. 1). Since the Fe_2O_3 layers were prepared on both sides of glass substrates and the corrosion occurs on the ITO-deposited side which faces to electrolyte solution, the absorption was not completely reduced by cathodic polarization. This cathodic corrosion was also observed even in an alkaline solution ($0.1 \text{ mol dm}^{-3} \text{ NaOH}$). At present, the mechanism of this corrosion was not clear. The p-type character of Fe_2O_3 electrode could not be confirmed.

3.2.2 Action spectrum

Figure 5 shows the quantum yield (ϕ) for the anodic i_p (at 1.0 V) of Fe_2O_3 electrode [Fe-AA/18(773)] as a function of irradiation light wavelength. The quantum yield was defined as a ratio of number of electrons passed through the electrode-electrolyte interface to that of incident photons to the cell. The yield rose up at ca. 560 nm and increased with the decrease of wavelength to attain its maximum at ca. 350 nm. The decrease at $< 350 \text{ nm}$ may be due to the light absorption by the glass cell window. This action spectrum quite resembled the absorption spectrum (Fig. 1).

Replots of this action spectrum, ϕ^2 vs. $h\nu$, are shown in Fig. 6. A bent line with flexion at 2.7 eV was observed. Such bent plots have been reported for undoped Fe_2O_3 thin film prepared by spray pyrolysis.⁷⁾ The extrapolation of the linear part at higher energy region gave the transition energy of 2.7 eV (corresponding to 464 nm). This suggests the direct band-gap excitation leading to the photoanodic current. On the other hand, replots of $(\phi h\nu)^{1/2}$ vs $h\nu$ in lower energy region intersect at ca. 2.0 eV, exhibiting the indirect transition. In the absorption spectrum (Fig. 1, [Fe-AA/5(773)]), a shoulder peak at ca. 520 nm could be observed. Therefore, the photoresponse of undoped Fe_2O_3 film is caused by the direct band-gap excitation with the partial participation of indirect excitation.⁷⁾

3.2.3 Effect of doping

The photocurrent, i_p , was affected by the dopants (Fig. 4). The order of anodic i_p agreed with the previous observation⁶⁾ on the Fe_2O_3 electrode prepared by plasma spray method; Si(IV) and Mg(II) dopings increased and decreased the i_p of undoped film, respectively. It is known that the addition of tetravalent cation, Si(IV), as an electron donor enhances the n-type character, while divalent cation, Mg(II), as an electron acceptor modifies to p-type character. Therefore, the observed order of anodic i_p seems to be reasonable. In this study, however, the p-type character could not be confirmed because of the cathodic dissolution.

Fig. 5 Action spectrum of i_p of [Fe-AA/18(773)].

Fig. 6 Correlation of ϕ^2 (O) and $(\phi h\nu)^{1/2}$ (●) with $h\nu$.

Fig. 7 Anodic i_d (closed symbols) and i_p (open symbols) of [Fe-AA/5] films calcined at 873 K (O, ●), 773 K (□, ■), and 573 K (△, ▲).

3.2.4 Effect of calcination temperature

Fig. 7 shows steady-state current-potential curves for Fe_2O_3 electrodes ([Fe-AA/5]) calcined at various temperature. Photocurrent, i_p , increased with increased calcination temperature; drastic change in i_p was observed at > 773 K. On the contrary, dark anodic current, i_d , was reduced by the elevating calcination temperature. These phenomena are attributed to the decrease in porosity of the as-prepared gel by calcination; not only the leak current (i_d) due to the direct contact of electrolyte solution with ITO surface but also the photocurrent flowing through the porous Fe_2O_3 layer was improved by high-temperature calcination. The change in weight of bulk gel in TG analysis (Fig. 3) at > 673 K is less significant than that between 473–673 K, suggesting that the heat-induced sintering occurs predominantly at < 673 K. This finding reasonably interprets the drastic changes in i_p and i_d at > 673 K.

Comparison of data for [Fe-AA/5(773)] with that for [Fe/10(773)] in Fig. 4 clearly indicates that the Fe_2O_3 electrode from the acetylacetone-containing sol exhibited higher photoresponsibility in the anodic potential region. This is mainly due to the increased photoabsorption by the thicker Fe_2O_3 films, as was observed in Fig. 1.

3.2.5 Effect of number of dip-coatings

Fig. 8 shows the variations of i_p as a function of number of applications of dip-coating. With the increase in number of Fe_2O_3 layers, i_p increased, especially at higher anodic potential, and showed the maximum at 18 layers. This is also attributable to the increased photoabsorption by Fe_2O_3 film. Further application rather decreased i_p , probably due to the increase in the bulk resistance.

4 CONCLUSION

In conclusion, the thin film electrodes of amorphous Fe_2O_3 prepared by sol-gel process exhibited photoresponse as an n-type semiconductor. The electrochemical properties could be modified by the composition of starting sol, the calcination temperature, and the number of applications in dip-coating.

5 ACKNOWLEDGMENT

The supply of metal alkoxides by Hokko Chemical is gratefully acknowledged. The authors express our thanks to Professor K. Tanaka and Dr. T. Iyoda (Kyoto University) for their valuable advice on the

measurements of film thickness and monochromatic light intensity, respectively. Dr. M. Ye (Kyoto University) is acknowledged for his assistance in chemical actinometry.

Fig. 8 Variation in i_p of [Fe-AA(773)] with number of coatings. Applied potential was 1.0 V (○), 0.8 V (□), 0.6 V (△), and 0.4 V (▽).

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