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AC Potential Modulation Reflectance of Iron Electrode Covered by Thin Passive Oxide

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ABSTRACT

AC potential imposed to the iron electrode with the thin passive oxide induces modulation of both charge and reflectance. The modulated reflectance, i.e., potential modulation reflectance (PMR) was measured to characterize the passive oxide on iron in pH 8.4 borate buffer solution. The dependence of PMR signal on anodic potential exhibited similar behaviour of modulated charge, i.e., film capacitance. The both reciprocals of PMR signal and the capacitance proportionally increased with the thickness which linearly grew with increase of anodic potential. The Mott-Schottky type plot held for the PMR during the decreasing potential as well as the film capacitance. The spectroscopic measurement of the PMR, the light absorption edge of the passive oxide was estimated to be 2.4-2.5 eV.

1. Introduction

The passive oxide on iron in neutral solution was most investigated among the surface thin oxides inducing the passive state of metals. It was found from ellipsometry that the oxide film was several nm thick, linearly growing with increase of potential [1–4]. During the step-wise increase of potential the reciprocal capacitance (C_f^{-1}) was also increased linearly [5,6]. When one applied the Mott-Schottky plot to the capacitance data during the step-wise or continuously decrease of potential, n-type semiconducting character appeared for the passive oxide, *i.e.*, C_f^{-2} was linearly decreased with decreasing potential [5,6]. The application of ex-situ X-ray photo-electron spectroscopy (XPS) analysis indicated that the passive film was mainly composed of Fe(III) oxide of oxy-hydroxide [7]. Extended X-ray absorption fine structure (EXAFS) measurement found a cubic structure of Fe_3O_4-γ-Fe_2O_3 [8]. Application of in-situ Raman spectroscopy also indicated the existence of Fe_3O_4-γ-Fe_2O_3. [9,10]

In this paper, we applied AC potential modulation reflectance (PMR) to the passive oxide film on pure iron. Simultaneously the thickness of the passive oxide was precisely measured by three-parameter ellipsometry [11]. From the comparison with the data of AC impedance spectroscopy, we examined the PMR signal to characterize the passive oxide.

In the PMR the reflectance modulated by AC potential imposed was measured as a function of DC potential, frequency, and wavelength of light incident and the technique has been also called electrolyte electrorefletance (EER). Since the PMR technique is sensitive to the change of electrode surface modified by adsorption of elecroactive species [12–14] or covered with thin layer containing redox species [15,16], it has been used for investigation of kinetics and mechanism of charge transfer reaction on metallic electrodes. When the PMR is applied to the semiconductor electrode or the electrode covered by semiconducting oxide film, the AC potential induces change of charge distribution in the semiconductor and at the semiconductor- electrolyte interface, thus bringing about the modulation reflectance. The AC potential added to the semiconducting electrode is impressed on both the electrolytic side including electric double layer (EDL) and solid semiconductor side with a ratio of AC potential applied to one side and the ratio may depend on the frequency. When the frequency is higher, the larger ratio of AC potential appears at the electrolyte side. For investigation of the semiconducting passive oxide under the depletion state of electrons, relatively low frequency may be suitable, because most of the AC potential can be impressed on the space charge layer under the depletion state. Many authors have reported complicated PMR spectra for passivated iron, nickel, and their alloys with frequencies higher than a hundred Hz [17–21]. The complicated spectra may be originated in the high frequency modulation

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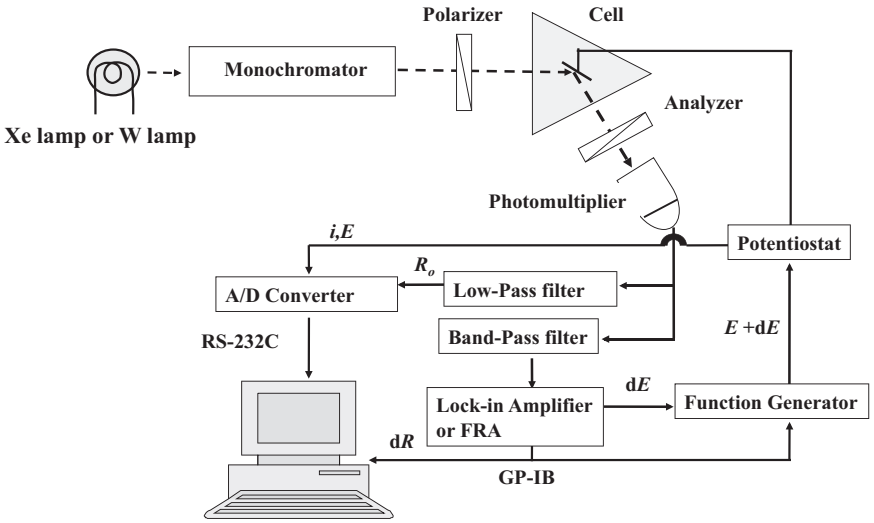

Fig. 1. Schematic model of apparatus of potential modulation reflectance and ellipsometry.

that induces the reflection modulation in both the semiconducting oxide film and the electrolyte side including the EDL. To preferentially focus the semiconducting passive oxide on the metal, the frequency for the PMR measurement should be selected from a comparison with the AC impedance. In this paper we adopted a frequency at 13 Hz at which the most of the AC potential imposed is responded for the space charge capacitance, which is discussed later.

2. Experimental

Iron sheet 1 mm thick and 99.99% pure was used for the working electrode. The sheet was cut to 10 × 20 mm with a small tub for electric connection. The iron electrode was mechanically polished by alumina abrasive at 0.05 μm diameter immediately before the passivation treatment. Electrolyte was prepared from analytical grade reagents and Mili-Q pure water. A 1:1 mixture buffer solution of 0.075 mol dm^{-3} (M) sodium borate ($Na_4B_4O_7$) and 0.30 M boric acid (H_3BO_3) was used for passivation of iron electrode. The pH value of the solution was pH 8.4. Before use, the solution was deaerated by bubbling of pure nitrogen gas at least for 0.5 h.

The apparatus for potential modulation reflectance (PMR) and ellipsometry is schematically drawn in Fig. 1. Light sources used were Xe lamp for PMR and W lamp for ellipsometry. Output of the W lamp was kept constant by a feed-back circuit. The light was then monochromated by a spectrometer. Two polarizers were fixed before and after the reflection surface, named as polarizer and analyzer, respectively. The angle of incidence was fixed at 60.0 deg. The reflection light intensity was converted to current by a photo-multiplier.

For PMR measurement, both azimuths of the polarizer and analyzer were fixed at 0 deg. respective to the incidence plane, *i.e.*, PMR was measured by the parallel (p)-polarized light. The AC potential (dE) at 0.1 V_{rms} amplitude at frequencies from 20 kHz to 0.01 Hz was superimposed on DC potential. The AC signal of reflectance dR was detected by a band-pass filter, NF Electronic Instruments E-3210A Decade Filter and a lock-in amplifier, EG & G Instruments 7260 or a frequency response analyzer (FRA), NF Eletronic Instruments 5020. The DC signal of reflectance, R_0 was measured through a low-pass filter, NF Electronic Instruments E-3210A Decade Filter. The PMR signal was calculated in a personal computer to be following.

$$PMR = (dR/dE)(1/R_0) \quad (1)$$

For PMR measurement as a function of wavelength of light and potential, AC potential at a constant frequency of 13 Hz was imposed.

For ellipsometric measurement, the reflectance was measured at constant azimuth of the polarizer (P) as a function of the azimuth of analyzer (A) which was controlled by a stepping motor. The ellipsometric parameter, tan Ψ (relative amplitude ratio) and Δ (relative phase retardation) were calculated by the following equations as well as the average reflectance, R_{av}.

$$\tan \Psi = (\tan P)(R_{A=0}/R_{A=90}) \quad (2)$$

$$\cos \Delta = (R_{A=45} - R_{av})/[R_{av}^2 - (R_{A=0} - R_{av})^2]^{0.5} \quad (3)$$

$$\cos \Delta = -(R_{A=135} - R_{av})/[R_{av}^2 - (R_{A=0} - R_{av})^2]^{0.5} \quad (3')$$

$$R_{av} = (1/2)((R_{A=0} + R_{A=90}) \quad (4)$$

where P is a fixed azimuth of the polarizer and $R_{A=i}$ is intensity of reflection light at $A = i$ deg. Exact measurement was performed by detection of R_A at A = 0, 45, 90, 135, 180, 225, 270, and 315 deg. with constant P, and then Ψ, Δ, and R_{av} were calculated. The thickness and complex refractive index of the oxide film grown on the iron electrode was simulated by a Basic program coded by the authors with assumption of a homogeneous and flat oxide film from the changes of Ψ, Δ, and R_{av}.

Electrochemical impedance spectroscopy (EIS) of the passivated iron electrode was also measured by the FRA at frequencies from 20 kHz to 10 mHz with AC potential of 0.01 V_{rms}. A potentiostat specially designed by our laboratory was used for the impedance as well as the PMR and ellipsometry.

The potential of iron electrode was measured against a reference electrode of Ag/AgCl/saturated KCl (SSC) which is 0.197 V vs. SHE and the potential in this paper is plotted against SSC.

3. Results and discussion

3.1. Film thickness from ellipsometry

The passive oxide film formed for 1 h at individual potentials in the passive region was measured by ellipsometry. Fig. 2 sows the changes of Ψ, Δ, and reflectance, $\delta\Psi$, $\delta\Delta$, and $\Delta R/R_0$, from the iron surface reduced at constant current of 10 μA cm^{-2} before the passivation. The changes were taken after 1 h oxidation at