Semiconductor Behavior of Passive Films Formed on Cr with Various Additive Elements

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Photoelectrochemical response and electrochemical impedance behavior was investigated for passive film formed on sputter-deposited Cr alloy in 0.1 kmol $\cdot$ m^{-3}. Photoelectrochemical action spectrum could be separated into two components, which were considered to be derived from Cr$_2$O$_3$ ($E_g \sim 3.6$ eV) and Cr(OH)$_3$ ($E_g \sim 2.5$ eV). The band gap energy, E_g, of each component was almost constant for various applied potentials, polarization periods and alloying additives. The photoelectrochemical response showed negative photo current for most potentials in the passive region. Therefore, the photo current apparently exhibited p-type semiconductor behavior. On the other hand, Mott-Schottky plot of the capacitance showed positive slope, which means that passive film formed on Cr alloy has n-type semiconductor property. These apparently conflicting results are rationally explained assuming that the passive film on Cr alloy formed in the acid solution has n-type semiconductor property with a fairly deep donor level in the band gap and forms an accumulation layer in the most of potential region in the passive state.

Keywords : *passivity, semiconductor property, photoelectrochemical response, impedance, Mott-Schottky plot*

1. Introduction

The wide use of Cr as one of the major alloying elements of Fe and Ni based alloys calls for a thorough understanding of their properties which derive high corrosion resistance. The passive films formed on Fe, Cr and Fe-Cr alloys, such as stainless steel reveal a semiconducting behavior.[1)-4)] Therefore, their electronic properties should play an important role in the corrosion resistance. Since Cr oxide is major components of passive films formed on the high corrosion resistance alloys such as stainless steel, many researches[5)-8)] have been carried out for passive film mainly composed of Cr. However, the electronic properties of the passive film formed on Cr remain controversial and require more clarification.

The aim of the present study is to gain an understanding on the electronic structure of passive films formed on Cr with additive elements, such as Mo, Nb, Zr etc. and its relevance to corrosion resistance. Photoelectrochemical response, AC impedance technique and X-ray photoelectron Spectroscopy(XPS) were used to obtain information on electrochemical properties and on the structure of the passive film.

2. Experimental

Specimen were thin films of pure Cr and Cr with additive elements, such as Mo, Nb, Zr, W, Fe and Ni, deposited on Si wafer using ion beam sputtering technique. The substrates were sputter etched prior to sputter deposition. The process chamber was evacuated to a pressure of 6.0×10^{-8} torr, before each deposition. The total pressure in the chamber during deposition was 4×10-4 torr.

Electrochemical measurements were performed in 0.1 kmol $\cdot$ m^{-3} H$_2$SO$_4$ and 6 kmol $\cdot$ m^{-3} HCl. The solution was prepared from reagent grade chemicals and distilled water and deaerated with N$_2$ gas before and during measurements.

For photoelectrochemical current measurements, the monochromatic light was used, which is obtained by the 500 W Xenon arc lump and a grating monochromator. The light was exposed on the specimen electrode in an electrochemical cell through a quarts window. The intensity of the monochromatic light was calibrated with photo diode optical power meter. The specimen was polarized at 400 mV$_{Ag/AgCl}$ for typically 24 hours, in course of which the photo current transient was occasionally measured for a series of wave length in 250~500 nm.

Then, the applied potential was changed stepwise in the less noble direction. Photo current responses were measured at each applied potential. The photo electrochemical response was measured as the transient of current after the light was exposed and interrupted for typically 12 s, *i.e.* no lock-in amplifier was adopted.

The experimental set-up for AC impedance measurements consisted of potentiostat and frequency response analyzer(FRA). A microcomputer was used to control the FRA and to acquire and analyze the data. AC impedance measurement was conducted at various potentials changed stepwise in less noble direction after polarization for 24 hours.

The corrosion rates of sputter-deposited Cr alloys were estimated from the dissolution of Cr, measured by atomic absorption, after immersion for 168 hours in 6 kmol $\cdot$ m^{-3} HCl solution open to air at 323 K.

3. Results and discussion

3.1 Photoelectrochemical measurements

A typical photocurrent spectrum as a function of wavelength is shown in Fig. 1 for passive film formed on pure Cr polarized at 400 mV$_{Ag/AgCl}$. Assuming that the photo excitation process occurs as an indirect transition usually observed for passive film on Fe-Cr alloys, eq. (1) is adopted to describe the photo spectrum;

$$i_{ph} \cdot hv/I_o = const.(hv - E_g)^2 \qquad (1)$$

therefore,

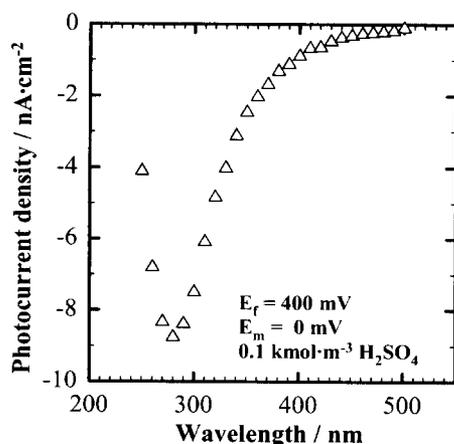$$(i_{ph} \cdot hv/I_o)^{1/2} = S \cdot (hv - E_g) \qquad (2)$$

Fig. 1. Photocurrent spectra of passive film on Cr at 0 mV after 86.4 ks at 400 mV.
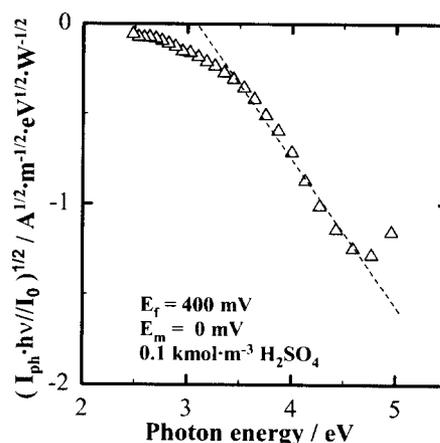

Fig. 2. Photoelectrochemical spectra of the photo current shown in Fig. 1.

where i_{ph} is photocurrent, hv the energy of the incident photon, E_g an optical band gap energy of passive film, I_o the power of the incident light flux, and S constant. E_g is determined from $(i_{ph} \cdot hv /I_o)$ vs. hv plot at the photon energy where the line of $(i_{ph} \cdot hv /I_o)$ equals to 0. As shown in Fig. 2, photo current action spectra plotted following eq.(2) could be fit with a straight line with E_g about 3.1 eV. The spectrum, however, was attained with a tail in the low photon energy region. In the most literature, spectra in this low energy region, which is sometime called "Urbach tail", might be ignored because of uncertainty of mobility gap of thin amorphous semi-conductor. As usually known, the passive film is not uniform, but consists of multi components. In this study, we separated this spectrum, assuming that passive films formed on Cr are composed of multi layers. Therefore, the observed photo current is assumed to be sum of n components. The photo current spectrum is described as following,

$$\left(\frac{i_{ph} \cdot hv}{I_o} \right)^{1/2} = \left\{ \sum_{k=1}^{n} S_k \cdot (hv - E_{gk})^2 \right\}^{1/2} \qquad (3)$$

The procedure of separation was described elsewhere.[9] Most of spectrum observed in this work was divided into two components. E_g of approximately at 2.5 eV and 3.5-3.7 eV are recognized and are almost constant for any applied potentials and passivation periods tested. Furthermore, as shown in Fig. 3, E_g is independent of the species and amount of additive elements. Referring E_g for Cr reported by Sunseri *et al.*[10] and XPS, these films may be composed of an external more hydrated Cr(OH)$_3$ layer with a band gap energy of 2.5 eV and an internal Cr$_2$O$_3$ layer with 3.5-3.7 eV. Fig. 4 shows the separated slopes
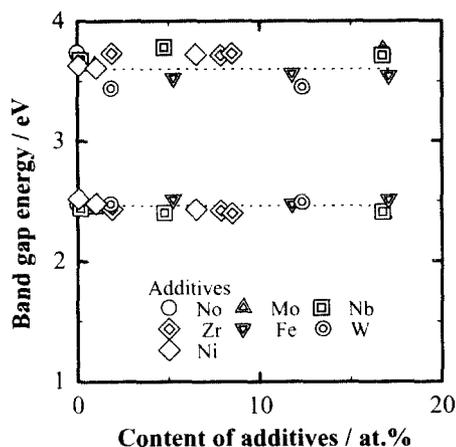
Fig. 3. Band gap energies of passive films formed on sputter-deposited Cr with various additives passivated at 400 mV for 86.4 ks.
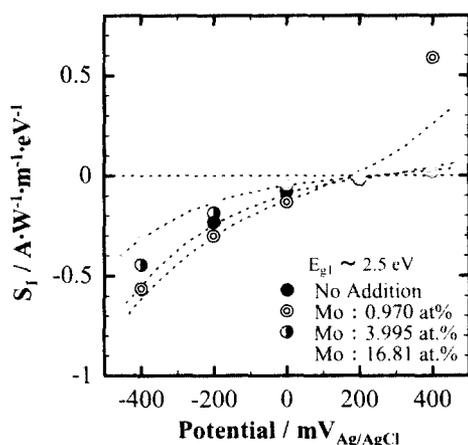
Fig. 4(a). Changes in the slope of photoelectrochemical spectrum, S1, passive films on Cr-Mo as a function of potential at which the photocurrent was measured.
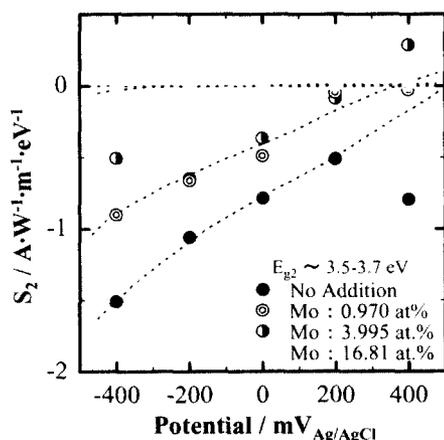
Fig. 4(b). Changes in the slope of photoelectrochemical spectrum, S2, passive films on Cr-Mo as a function of potential at which the photocurrent was measured.

of photo current spectrum, S, for passive film on Cr-Mo alloy measured at the formation potentials, 400 mV, and at a series of the less noble potentials. The constant, S, implies both direction and amplitude of photocurrent. The response of oxide, which is negative value at the most of measuring potential, decreases with increasing potential. The response of hydroxide is small compared with that of oxide, and slightly shifts in a positive direction with increasing potential. Since negative photocurrent is generated in most of polarization conditions, passive films of Cr alloys in the acid solution have p-type semiconductive property for the most of potential range in the passive region. The semiconducting behavior of Cr has been reported as p- and/or n-type depending on the condition examined.[5)-6),10)] In this work, such variation was clearly shown as a function of applied potential. The flatband potential, E_{fb}, at which the photo current changes from negative to positive with increasing potential, was apparently shown in Fig. 4. As described previously, the photoelectrochemical response was divided into two components, which are attributed to oxide and hydroxide. The detailed analysis of photo current response reveals flatband potentials of each component. As shown in Fig. 4, E_{fb} of $Cr(OH)_3$ is about 200 mV$_{Ag/AgCl}$, whereas E_{fb} derived from Cr_2O_3 is around 400 mV$_{Ag/AgCl}$. Passive films formed on other Cr alloys show similar behavior. Therefore, passive film formed on Cr alloys show p and n type semiconductor properties in the potential region between 200 mV and 400 mV$_{Ag/AgCl}$. In another word, photo current response might be positive and negative simultaneously, depending on the incident photon energy which is actually observed.

3.2 Capacitance measurements

Assuming that additional capacitive elements such as Helmholtz layer can be neglected, the capacitance measured by impedance is derived from space charge layer in the passive film. When the semiconductor layer is biased to form depletion layer, the relation between capacitance, C, and potential, E, follows the next equation, which is known as Mott-Schottky plot.

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_o qN}(E - E_{fb} - \frac{kT}{q}) \tag{4}$$

where N represents the carrier concentration, ε the dielectric constant of the passive film, ε_0 the vacuum permittivity, q the elementary charge, k the Boltzman constant, T the absolute temperature and E_{fb} the flatband potential. Fig. 5 depicts the Mott-Schottky plots for passive films formed on Cr-Mo alloy at 400 mV. The
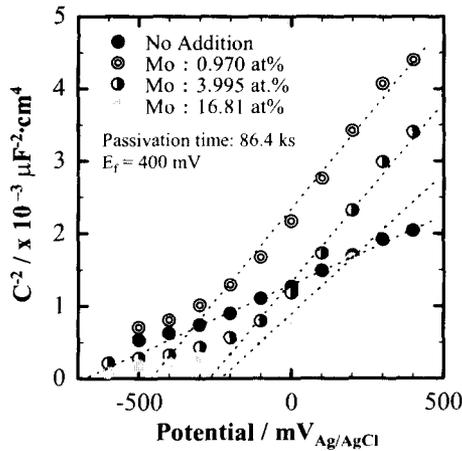
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Fig. 5. Mott-Schottky plots for passive films formed on Cr-Mo in 0.1 kmol·m⁻³ H₂SO₄.
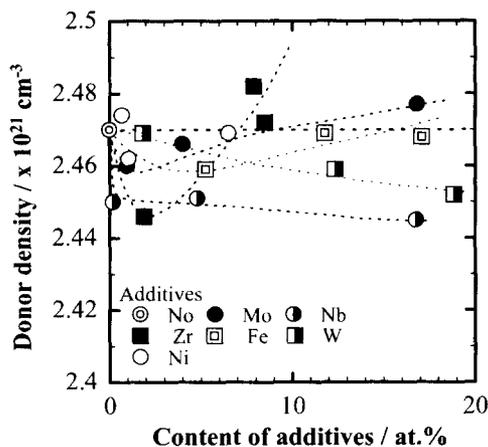

Fig. 6. Donor densities of passive films formed on sputter-deposited Cr with various additives passivated at 400 mV for 86.4 ks.

existence of a straight line with positive slope reveals n-type semiconductivity. The flatband potential, E_{fb}, derived from the intercept of the straight line, slightly shifts in a positive direction with increasing the amount of Mo. For the photoelectrochemical response, negative photo current is mainly observed, that is, passive films on Cr alloys in the acid solution reveal p-type semiconductivity, although electrochemical impedance spectroscopy, Mott-Schottky plot, shows positive slope, that is, n-type semiconductivity. Therefore, E_{fb} is different largely between the result of the photoelectrochemical response and that of the capacitance measurement. In the case of the n-type semiconductor, Mott-Schottky relation is applied when space charge layer appears as a depletion layer. Therefore, in this work, the inner oxide of the passive film on Cr formed in the acid solution has n-type semiconductor property with a fairly deep donor level in band gap,

assuming that the capacitance is generated in the inner oxide layer of the passive film. And at the less noble potential than the flatband potential, the inner oxide film forms an accumulation layer. Since the flatband potential of the inner layer is located in the high potential, around 400 mV$_{Ag/AgCl}$, the space charge layer becomes an accumulation layer in the most of potential region in the passive state. Therefore, the Mott-Schottky plot is not applicable. In the case that space charge region forms an accumulation layer, the space charge capacitance of a semiconductor is given by following equation;[11]

$$C_{sc} = q\left(\frac{N\varepsilon\varepsilon_0}{2k_BT}\right)^{1/2} exp\left\{\frac{-q(E - E_{fb})}{2k_BT}\right\}$$ (5)

The carrier densities of these oxides can be estimated from the intercept of lnC$_{sc}$ vs. E plot, using a value of 12[12]-[14] for the dielectric constant of chromium oxide. Fig. 6 shows influence of alloying elements on donor densities of passive films formed on Cr alloys. It is found that alloying Nb and W increase donor densities with amounts of additives, whereas that of passive films on Cr alloys with Fe, Zr and Ni decrease once in little additives, but increase beyond some amounts of additives.

3.3 Corrosion rates of sputter-deposited Cr alloys

In order to consider a detailed relationship between the semiconducting properties of passive films on Cr alloys and the corrosion rates, the corrosion rates of sputter-deposited Cr alloys were measured after 168h immersion in 6M HCl at 323K. Fig. 7 shows corrosion rates of Cr

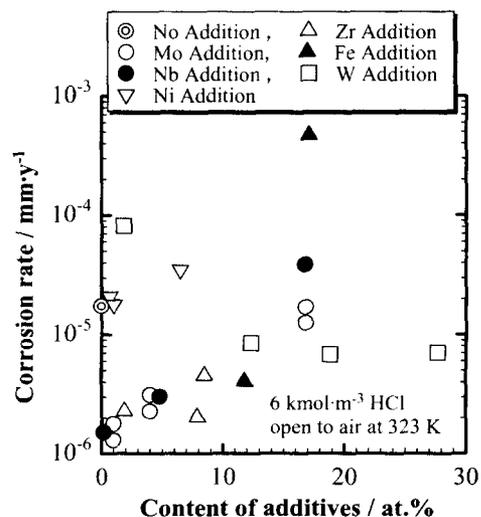**Fig. 7.** Changes in Cr dissolution rate in 6 kmol·m⁻³ HCl at 323 K with content of additives after immersion for 168 hours open to air.

alloys as a function of the additive contents. The corrosion rates are very low and vary with additive elements in different ways. In case of Mo, Nb, Zr and Fe, the trace amounts of them decrease abruptly the corrosion rates of sputter-deposited Cr and further contents gradually increase it. On the other hand, the trace amounts of W increase the corrosion rates, but increasing W contents decrease it by degrees. Furthermore, addition of Ni increases the corrosion rates with increasing contents of additives. As compared with donor densities of passive films as shown in Fig. 5, the corrosion rates is considered to be independent of them. That is to say, the general corrosion could be predominant in the corrosion rate measurements, whereas the donor densities are seemed to relate to the localized corrosion, like a pitting corrosion.

4. Conclusion

The electronic properties of passive films on Cr and Cr with additive elements were investigated using photoelectrochemical response and AC impedance technique. The photoelectrochemical response showed negative current for most potentials in the passive region. Therefore, passive films of Cr alloy were showed apparently p-type semiconductive behavior. On the other hand, Mott-Schottky plot exhibited positive slope, which suggest n-type semiconductive property. These discrepancies are reasonably explained presuming that the passive film of Cr alloys formed in the acid solution is n-type semiconductor with a fairly deep donor level in the band gap and forms an accumulation layer in the most condition examined in this work.

In this paper, the band state model, which is derived from the results of photoelectrochemical response and AC impedance technique, is presented and discussed. However, since other models might be also considered from these results, more discussion is required to understand the electronic structure of passive films on Cr alloys.

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