

Effects of Edta on the Electronic Properties of Passive Film Formed on Fe-20Cr In pH 8.5 Buffer Solution

EunAe Cho*, HyukSang Kwon**, and Frederic Bernard**

*Fuel Cell Research Center, Korea Institute of Science and Technology, P.O.BOX 131
CheongRyang, Seoul, Korea, 130-650

**Dept. of Materials Science and Engineering, Korea Advanced Institute of Science and Technology
73-1, KuSongDong, YuSongGu, TaeJon, Korea, 305-701

The electronic properties of the passive film formed on Fe-20Cr ferritic stainless steel in pH 8.5 buffer solution containing 0.05 M EDTA (ethylene diammine tetraacetic acid) were examined by the photocurrent measurements and Mott-Schottky analysis for the film. XPS depth profile for the film demonstrated that Cr content in the outermost layer of the passive film was higher in the solution with EDTA than that in the solution without EDTA, due to selective dissolution of Fe by EDTA. In the solution with EDTA, the passive film showed characteristics of an amorphous or highly disordered n-type semiconductor. The band gap energies of the passive film are estimated to be ~ 3.0 eV, irrespective of film formation potential from 0 to 700 mV_{SCE} and of presence of EDTA. However, the donor density of the passive film formed in the solution with EDTA is much higher than that formed in the solution without EDTA, due to an increase in oxygen vacancy resulted from the dissolution of Fe-oxide in the outermost layer of the passive film. These results support the proposed model that the passive film formed on Fe-20Cr in pH 8.5 buffer solution mainly consists of Cr-substituted γ -Fe₂O₃.

Keywords : passive film, electronic properties, EDTA, photocurrent, Mott-Schottky plot

1. Introduction

The excellent corrosion resistance of stainless steels is largely due to the protective passive film formed on the surface. Elucidating the nature of the passive film is a prerequisite for understanding such a high corrosion resistance of stainless steels. Many analytical studies have agreed that the passive film on Fe-Cr stainless steels consists of Cr-enriched (Fe, Cr) oxide/hydroxide,¹⁻⁶⁾ although there is still some controversy as to the detailed structure and composition of the passive film. The extreme complexity of the metal/passive film/electrolyte system of stainless steels makes the clarification of the passive film difficult.

The electronic structure of the passive film is an important issue in that ionic movement in the passive film is driven by the electric field, which is in turn affected by the electronic structure.⁷⁾ In this way, the electronic structure is closely related to corrosion phenomena including film breakdown and pitting initiation.⁸⁾ Recently, photocurrent analysis and Mott-Schottky analysis via impedance measurements for the passive film have been employed to examine the *in situ* electronic properties of

the passive film.

In a previous study using *in situ* photocurrent and Mott-Schottky analysis,⁸⁾ we observed that the passive film formed on Fe-20Cr in pH 8.5 buffer solution was an amorphous or highly disordered n-type semiconductor, in which photocurrent was generated by electron transitions as occurring in γ -Fe₂O₃ with band gap energy of ~ 3.0 eV irrespective of film formation potential. However, it might be questioned that the electronic properties of passive film formed on Fe-20Cr are controlled by γ -Fe₂O₃ in considering the well-known Cr-enrichment in passive film on Fe-Cr alloys.

EDTA (Ethylene Diammine Tetraacetic Acid) is a useful chemical chelating agent for the removal of iron oxide.⁹⁾ Thus it is expected that the iron oxide in passive film on Fe-20Cr be removed by addition of EDTA to a solution. The research objective of present work is to characterize the electronic structure of the passive film formed on Fe-20Cr ferritic stainless steel in a borate buffer solution containing 0.05 M EDTA, and to investigate effects of selective dissolution of iron oxide on the electronic properties of the passive film.

2. Experimental

High purity Fe-20 wt.% Cr alloy (Fe-20Cr) was used as a working electrode. A conventional three electrode cell of 1 L-multi neck flask with a quartz window as a photon inlet was used for the photocurrent and impedance measurements. The cell was equipped with a platinum counter electrode and a saturated calomel reference electrode (SCE). The procedures for sample preparation and the experimental arrangement were described in detail previously.⁸⁾ All the experiments were carried out at room temperature in deaerated pH 8.5 buffer solution with or without addition of 0.05 M EDTA. Passive film on Fe-20Cr was prepared by polarization at potentials of 0 to 700 mV_{SCE} for about 24 hrs. The 300 W Xenon arc lamp combined with a scanning digital monochromator was used to impose a monochromatic illumination to the working electrode. The monochromator was controlled at a scanning rate of 1 nm/s by stepping motor, which made it possible to provide monochromatic photons with 200 to 800 nm wavelengths to the working electrode. To increase the photon flux, white light from the Xe lamp was focused to the light inlet using two auxiliary focusing lenses. The capacitance measurements for the Mott-Schottky analysis were conducted on the passive films formed on Fe-20Cr for 1 hr at various potentials ranging from -100 mV_{SCE} to 900 mV_{SCE}, by sweeping the applied potential in negative direction from the film formation potential with excitation voltage of 10 mV (peak-to-peak) using a Frequency Response Analyzer. The imaginary part of the impedance (Z'') was measured as a function of the applied potential, and the corresponding capacitance of space charge layer (C_{SC}) was obtained from $C_{SC} = -1/\omega Z''$, where ω is the angular frequency. Chemical depth profile for the passive film on Fe-20Cr was obtained by XPS analysis using the Al-K α and Mg K α x-ray source (15 kV, 20mA, 300W), and a pass energy of 20 eV. Sputter depth profiles were obtained with argon ions ($P_{Ar} = 5 \times 10^{-7}$ torr, base pressure = 5×10^{-10} torr, energy: 5 kV, current: $3.0 \mu\text{A}/\text{cm}^2$).

3. Experimental results and discussion

3.1 Polarization Responses

Fig. 1 shows effects of EDTA on the polarization responses of Fe-20Cr, Fe and Cr measured in pH 8.5 buffer solution at a potential scan rate of 0.5 mV/s. By addition of 0.05 M EDTA to pH 8.5 buffer solution, 1) the passive region of Fe significantly decreased; in pH 8.5 buffer solution without EDTA a stable passivation occurred from -0.3 V to 1.1 V while in the solution with EDTA from

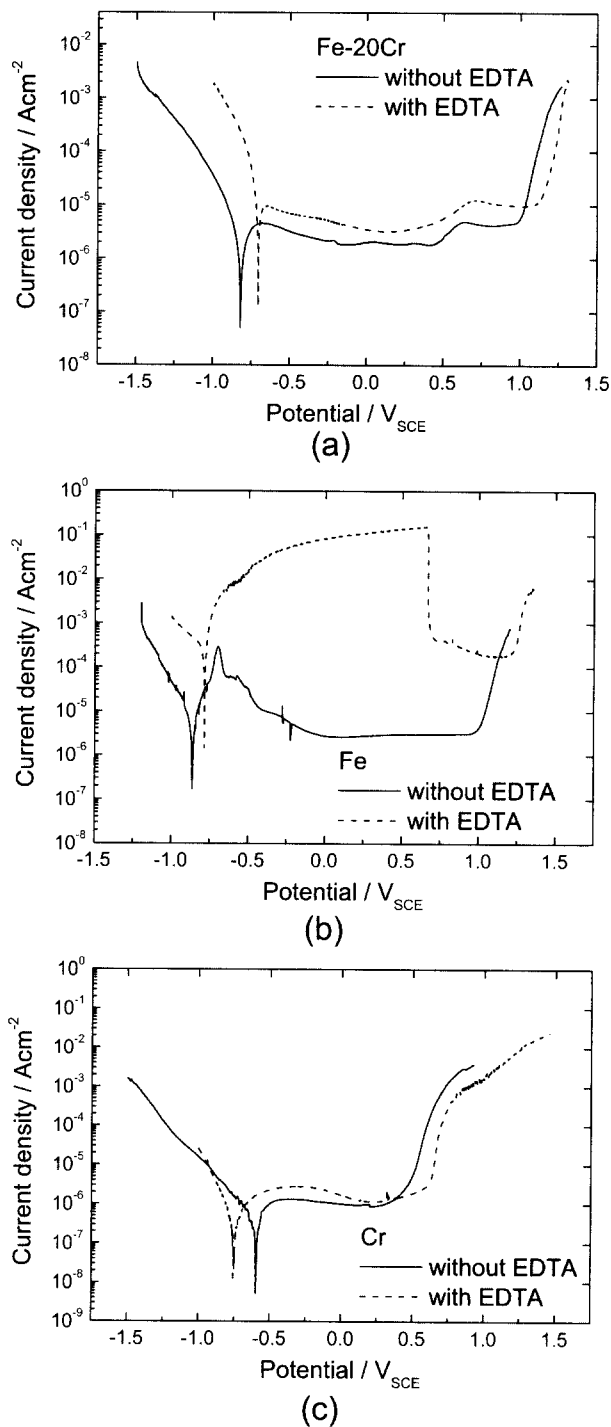


Fig. 1. Effects of EDTA on potentiodynamic polarization responses of (a) Fe-20Cr, (b) Fe, and (c) Cr measured at a scan rate of 0.5 mV/s in deaerated pH 8.5 buffer solution with and without 0.05 M EDTA.

0.7 to 1.1 V; 2) the passive current density of Fe-20Cr increased more than 2 times; 3) the passive current density of Cr increased slightly or remained similar. These results

reveals that in the solution with 0.05 M EDTA the stable passivation of Fe-20Cr over a wide range of potential is caused by chromium present in the alloy and that EDTA prohibits iron from passivation whenever iron exists as a pure metal or in an alloy, in accordance with previous results that EDTA is an effective chelating agent to dissolve iron ions.⁹⁾

3.2 XPS depth profiles

In order to investigate chemical composition of passive film on Fe-20Cr and to examine the effects of EDTA on the chemical composition, XPS depth analysis was performed for the passive film formed on Fe-20Cr at 0.2 V in pH 8.5 buffer solution with and without EDTA, which is a stable passive potential as revealed in Fig. 1(a). Fig. 2 presents the results as Cr/(Fe+Cr) ratios in-depth. Film thickness was estimated from sputter rate calibrated with SiO₂. In pH 8.5 buffer solution, at the beginning of sputtering Cr ratio increased with depth of the film, exhibited the maximum at the estimated thickness of about 1 nm, and then decreased, which is well corresponded with the previous results reported by Haupt et al.⁴⁾ Kirchheim et al.³⁾ also observed that the Cr concentration in the passive film on Fe-Cr alloys slowly decreased towards film/alloy interface after forming the strongly Cr-enriched outermost layer. These results show that the outer part of the passive film is more enriched in Cr than the inner part, and the Cr content decreases towards the film/alloy interface whenever the maximum appears just below the surface⁴⁾ or at the surface.³⁾ Thus, passive film with these characteristics can be considered to have a heterogeneous single-layered structure. On the other hand, the Cr content in the outermost part of the passive film formed on Fe-20Cr in pH 8.5 buffer solution with 0.05 M EDTA was significantly increased, accompanying by a selective dissolution of Fe from the film. For the film formed in the solution containing EDTA, the Cr concentration of the film exhibits a maximum at the surface and subsequently decreases towards the film/alloy interface. In addition, chromium content in the passive film slightly increased all over the film thickness, compared with that formed in the solution without EDTA. These results confirm that EDTA removes, even not completely, iron from the passive film.

3.3 Photoelectrochemical response

EDTA is a useful chemical chelating agent for removing iron oxide by forming stable complexes with Fe²⁺ ions.⁹⁾ Anodic polarization responses (Fig. 1) and XPS concentration depth profiles (Fig. 2) showed that EDTA impeded passivation of iron and dissolved iron from the passive film. Thus, in pH 8.5 buffer solution with 0.05

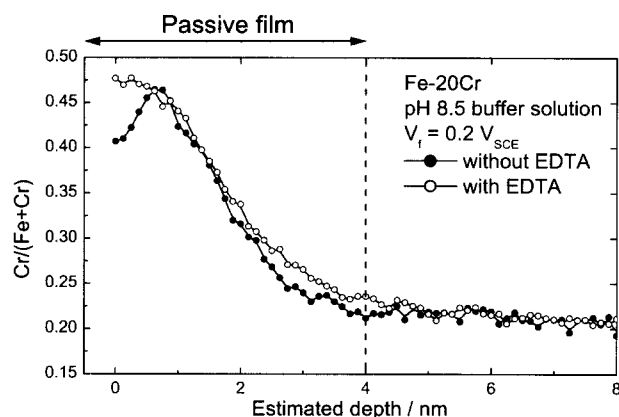


Fig. 2. XPS depth concentration profile of passive film formed on Fe-20Cr at 0.2 V SCE in deaerated pH 8.5 buffer solution with and without 0.05 M EDTA.

M EDTA, the maximum chromium concentration appeared at film/electrolyte interface while in the solution without EDTA at about 1 nm below the surface.

Fig. 3 presents photocurrent spectrum for passive film formed on Fe-20Cr at 0.7 V in pH 8.5 buffer solution without and with 0.05 M EDTA. In the solution without EDTA, as shown in Fig. 3(a), photocurrent began to increase at approximately 3.0 eV, exhibiting a shoulder at 3.8 eV with the peak current density at 4.5 eV. On the other hand, in the solution with EDTA (Fig. 3(b)) photocurrent begins to increase at approximately 3.0 eV, and passes through a maximum at 4.4 eV without a shoulder at 3.8 eV that was observed on the photocurrent spectra for passive film formed on Fe-20Cr in pH 8.5 buffer solution. According to Cho et al.⁸⁾ the peak at 4.5 eV and the shoulder at 3.8 eV were generated by the d-d transition from Fe³⁺ band to Fe²⁺ band and the p-d transition from O-2p to Fe²⁺ band in γ -Fe₂O₃, respectively. Thus, the disappearance of the shoulder at 3.8 eV, compared to the photocurrent spectra obtained in pH 8.5 buffer solution, could be associated with dissolution of Fe in the outermost part of the passive film by addition of EDTA. The anodic photocurrent indicates that the passive film is an n-type semiconductor. The absence of sharp features on the spectra, which are referred to as the "Urbach tail", is a characteristic of amorphous or highly disordered (or defective) semiconductor.¹⁰⁾ Passive films formed on Fe-20Cr at 0 ~ 0.6 V in the solution with 0.05 M EDTA also showed the same photocurrent response as that depicted in Fig. 3(b).

Band gap energy of the passive film can be obtained from Eq. (1) derived based on the assumption that the measured photocurrent is proportional to the optical absorption coefficient.

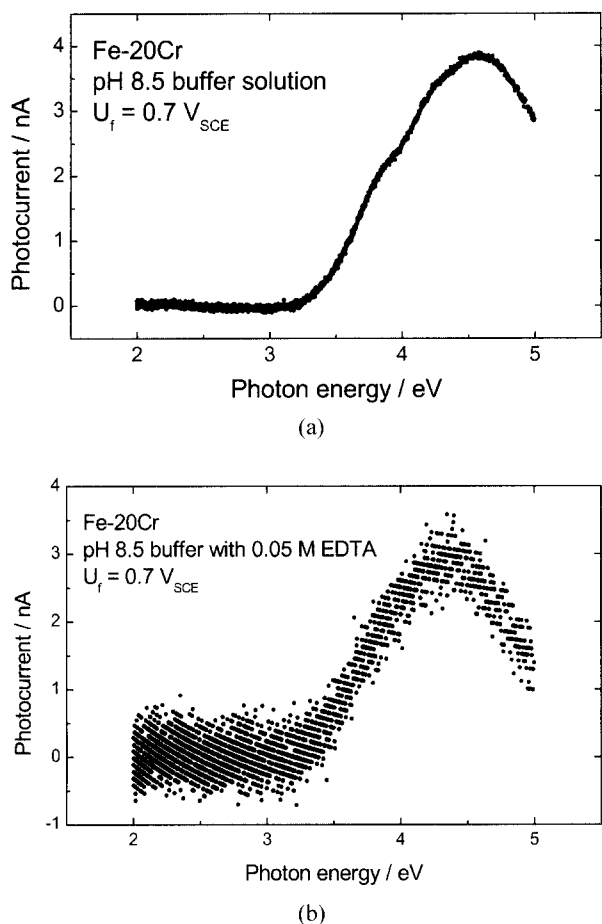


Fig. 3. i_{ph} vs. $h\nu$ plot for the passive film formed on Fe-20Cr at $0.7 V_{SCE}$ in deaerated pH 8.5 buffer solution (a) without and (b) with 0.05 M EDTA

$$i_{ph} = A(h\nu - E_g)^n/h\nu \quad (1)$$

where A is a constant, $h\nu$ is energy of incident photon, E_g is the band gap energy, and n describes the type of transition between the valence and the conduction band in a crystalline material. In amorphous material, the same equation has been found as an empirical relation with n having different values, but predominantly 2.¹¹⁾ The band gap energy for the film was determined by extrapolating the $(i_{ph} \cdot h\nu)^{1/2}$ vs. $h\nu$ plots with $n = 2$ to the axis of photon energy. The band gap energies for the passive film formed on Fe-20Cr in pH 8.5 buffer solution containing 0.05 M EDTA were estimated to be 2.9~3.09 eV and almost independent of film formation potential (0 to $0.7 V_{SCE}$), as in the solution without EDTA.

Consequently, passive film on Fe-20Cr in borate buffer solutions used in this study was an amorphous (or highly defective) n-type semiconductor although chromium was

highly enriched in the passive film and particularly even if chromium exhibited maximum concentration at the film/solution interface. Photocurrent responses with respect to incident photon energy revealed that photo-excitation processes was controlled by Fe species in the passive film. This is in accordance with the previous result that iron diffused into chromium oxide changed the semiconducting properties of the chromium oxide similar to those of iron oxide.⁶⁴ It was assumed that passive film on Fe-20Cr had a spinel structure,¹³⁾ represented as $(Fe_{2-x}^{3+}Cr_x^{3+}Fe^{2+})O_4^{2-}$ with $1 \leq x \leq 2$.¹⁴⁾ Based on the modified electronic band structure for passive film on Fe,¹⁵⁾ photo-assisted generation of electron-hole pairs in the passive film on Fe-20Cr was attributed to d-d transition from Fe^{3+} band to Fe^{2+} band and the p-d transition from the valence band (O-2p) to the conduction band (Fe-3d). A significantly reduced photocurrent intensity for passive film on Fe-20Cr, compared with that for passive Fe, could be ascribed to the presence of Cr^{3+} ions in the passive film. This was supported by the change in photocurrent intensity with respect to applied potential. Thus, the passive film formed on Fe-20Cr in pH 8.5 buffer solution is composed of Cr-substituted γ - Fe_2O_3 in which conduction of photo-generated electrons and holes, generated by the d-d and p-d electron transition and coupled with ionic movements in passive film, might be impeded by the Cr^{3+} ions. Formation of Cr^{6+} ions at transpassive potential could increase electronic conductivity and hence photocurrent intensity by donating electrons to the conduction band.

3.4 Mott-schottky analysis

To examine the electronic properties of passive film with the maximum chromium concentration at surface, capacitance was measured for the passive film formed in pH 8.5 buffer solution containing EDTA. Fig. 4 compares Mott-Schottky plots for the passive film formed at $0.6 V$ in pH 8.5 buffer solution with and without 0.05 M EDTA. As can be seen, by adding EDTA to pH 8.5 buffer solution, the Mott-Schottky plots shifted in high-potential direction and the slope was lowered, resulting in higher flat band potential, higher donor density for the film formed in the solution with EDTA. The Mott-Schottky plot has a positive slope, indicating that the passive film is still an n-type semiconductor. The deviation from linearity at high potential region exhibits that the passive film has amorphous or highly disordered structure.¹⁶⁾ Similar behaviors were observed for all the passive film formed at formation potentials from -0.1 to 0.9 V.

Fig. 5 presents the Mott-Schottky plots for the passive film formed at -0.1 to 0.9 V_{SCE} in pH 8.5 buffer solution

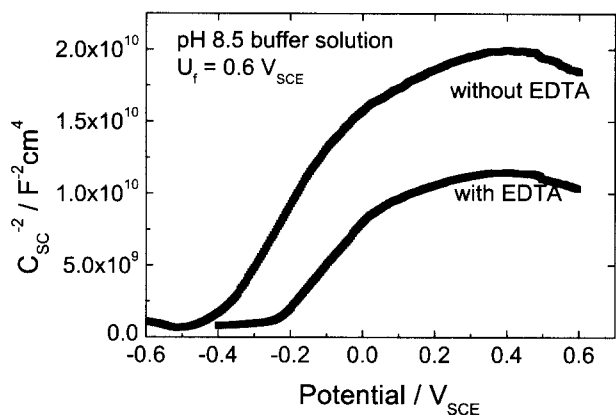


Fig. 4. Effects of EDTA on Mott-Schottky plots for the passive film formed on Fe-20Cr formed at 0.6 VSCE in deaerated pH 8.5 buffer solution with and without 0.05 M EDTA. Capacitance was measured at 1000 Hz with a scan rate of 1 mV/s.

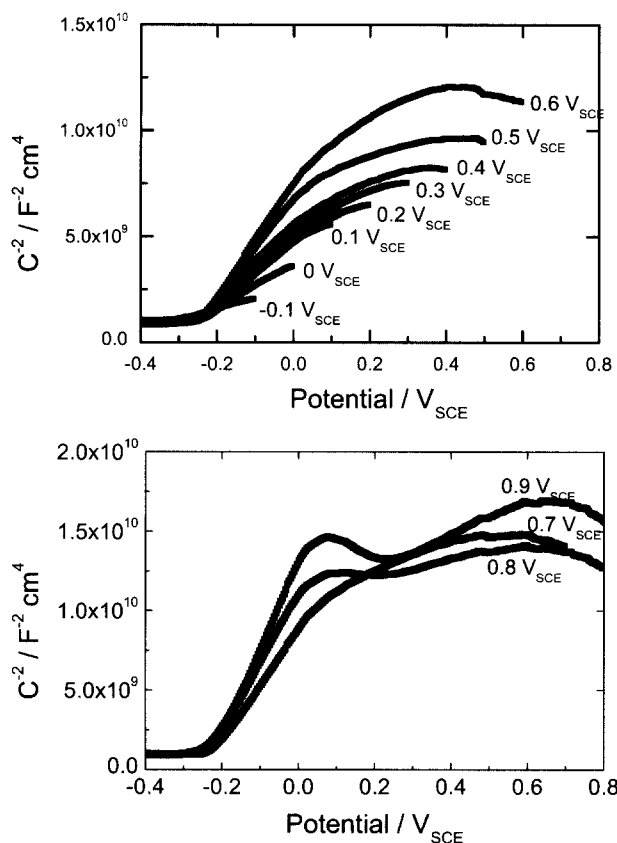


Fig. 5. Mott-Schottky plots for the passive film formed on Fe-20Cr at different potentials in deaerated pH 8.5 buffer solution containing 0.05 M EDTA. Capacitance was measured at 1000 Hz with a scan rate of 1 mV/s.

with 0.05 M EDTA. As in pH 8.5 buffer solution without EDTA, for the passive film formed at potentials in transpassive region two (0.7 to 0.9 VSCE) linear regions

appeared, while for the passive film formed at potentials in passive region (-0.1 to 0.6 VSCE) one single straight linear section was observed. Donor density and flat band potential can be calculated from the data shown in Fig. 5 and the Mott-Schottky relation;¹⁷⁾

$$\frac{1}{C_{SC}^2} = \left(\frac{2}{\epsilon_0 e N_D} \right) \left(U - U_{FB} - \frac{kT}{e} \right) \tag{2}$$

where C_{SC} is capacitance of space charge layer, N_D is donor density, U is applied potential, U_{FB} is flat band potential, ϵ is the dielectric constant, ϵ_0 is the permittivity of the vacuum, k is Boltzmann constant, T is temperature, and e is the electronic charge. The concentration of the donors can be determined from the two slopes S_1 and S_2 of Mott-Schottky plots by using the following equations;

$$S_1 = \frac{2}{\epsilon \epsilon_0 e N_{D1}} \quad \text{at lower potential region} \tag{3a}$$

$$S_2 = \frac{2}{\epsilon \epsilon_0 e (N_{D1} + N_{D2})} \quad \text{at higher potential region} \tag{3b}$$

where N_{D1} and N_{D2} are the densities of the donors at shallow and deep donor levels, respectively. Using Eq. (2) and (3), donor densities and flat band potential were calculated and presented with those obtained in the solution without EDTA in Fig. 6 and 7, respectively. With increasing film formation potential, the donor densities were decreased and the thickness of space charge layer and the flat band potential increased. Addition of EDTA to pH 8.5 solution increased the donor densities and the flat band potentials of the passive film and decreased the thickness of space charge layer. These results imply that the exposed layer has a more defective structure containing higher concentration of probably oxygen vacancies due to the removal of iron by addition of EDTA.

As the results of Mott-Schottky analysis, the passive films on Fe-20Cr in pH 8.5 buffer solution with or without EDTA is an amorphous (or highly defective) n-type semiconductor. For passive film formed at transpassive potentials, both the shallow and the deep levels of donor states in the space charge layer would be ionized at potentials higher than 0.2 VSCE to contribute to the space charge. With lowering the applied potential, effects of the deep donors, which could be identified as Cr^{6+} ions, disappeared due to the reduction of Cr^{6+} ions to Cr^{3+} . For passive film formed at passive potentials, only the shallow donors are ionized, which is detected by single linear region on Mott-Schottky plots. According to the point defect model

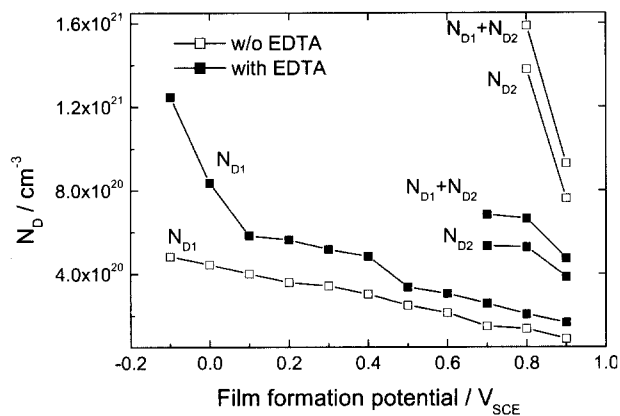


Fig. 6. Effects of donor densities of shallow level (N_{D1}), deep level (N_{D2}), and total $N_{D1}+N_{D2}$ on film formation potential in deaerated pH 8.5 buffer solution with and without 0.05 M EDTA.

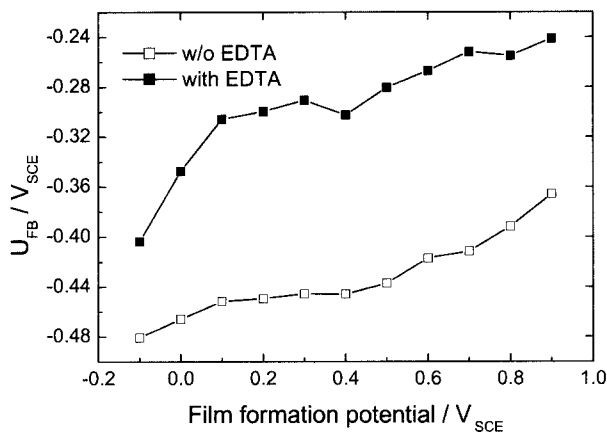


Fig. 7. Effects of flat band potential (U_{FB}) of the passive film on film formation potential in deaerated pH 8.5 buffer solution with and without 0.05 M EDTA.

(PDM)¹⁸⁾ and the electronic structure model by Bojinov et al.,¹³⁾ the shallow donor can be oxygen vacancies generated at metal/film interface. With increasing film formation potential, the donor densities decreased and the thickness of space charge layer and the flat band potential increased, which could result in a more stable structure. The increase in the flat band potential with higher donor density is probably related to the change in electrolyte. Generally flat band potential increases as donor density decreases. It was found that flat band potential of a chromium oxide was shifted approximately -60 mV/pH without any change in electronic properties of the chromium oxide.¹⁹⁾

4. Conclusions

Electronic properties of the passive film formed on Fe-20Cr in pH 8.5 buffer solution containing 0.05 M EDTA were examined by photocurrent measurement and Mott-Schottky analysis. Conclusions drawn from this study are as follows:

(1) The passive film formed on Fe-20Cr in pH 8.5 buffer solution with 0.05 M EDTA is an amorphous or highly disordered n-type semiconductor, which was characterized by photocurrent spectra; anodic photocurrent, absence of sharp increase in the photocurrent spectra, and capacitance measurement; positive slope of Mott-Schottky plots and curved lines of Mott-Schottky plots.

(2) The photocurrent spectrum for the passive films formed on Fe-20Cr in pH 8.5 buffer solution containing 0.05 M EDTA was almost same in shape to that for the passive film formed in pH 8.5 buffer solution, which demonstrated that the passive film on Fe-20Cr is composed of Cr-substituted γ -Fe₂O₃ involving the d-d and p-d electron transitions.

(3) The band gap energy of the passive film was measured to be ~ 3.0 eV, almost independent of film formation potential ranging from 0 to 0.7 V_{SCE} .

(4) The addition of EDTA to pH 8.5 buffer solution significantly increased donor densities and flat band potential, which could be related to the dissolution of iron as revealed by XPS depth concentration profile.

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