

A study on Electronic Properties of Passive Film Formed on Ti

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Electronic properties of passive films formed on Ti at film formation potentials (E_f) V_{SCE} in pH 8.5 buffer solution and in an artificial seawater were examined through the photocurrent measurement and Mott-Schottky analysis.

The passive films formed on Ti in pH 8.5 buffer solution exhibited a n-type semiconductor with a band gap energies (E_g); $E_g^{n^{-2}} = 3.4$ eV for nondirect electron transition, and $E_g^{n^{-0.5}} = 3.7$ eV for direct electron transition. These band gap values were almost same as those for the passive films formed in artificial seawater, indicating that chloride ion (Cl^-) in solution did not affect the electronic structure of the passive film on Ti. E_g for passive films formed on Ti were found to be greater than those ($E_g^{n^{-0.5}} = 3.1$ eV, $E_g^{n^{-2}} = 3.4$ eV) for a thermal oxide film formed on Ti in air at 400 °C. The disorder energy of passive film, determined from the absorption tail of photocurrent spectrum, was much greater than that for the thermal oxide film formed on Ti in air at 400 °C. The greater E_g and the higher disorder energy for the passive film compared with those for the thermal oxide film suggest that the passive film on Ti exhibited more disordered structure than the thermal oxide film. The donor density (about $2.4 \times 10^{20} \text{ cm}^{-3}$) for the passive film formed in artificial seawater was greater than that (about $2.0 \times 10^{20} \text{ cm}^{-3}$) formed in pH 8.5 buffer solution, indicating that Cl^- increased the donor density for the passive film on Ti.

Keywords : photocurrent measurement, mott-schottky analysis, titanium, passive film

1. Introduction

This excellent corrosion resistance of Ti especially in a solution containing chloride ion (Cl^-) is a well known phenomenon.¹⁾ The domain of thermodynamic stability of the passive film on Ti encompasses that of water in the absence of complexants.²⁾ This excellent corrosion resistance of Ti is due largely to the very stable and tenaciously adherent passive film formed on the surface. Elucidating the nature of the passive film is a prerequisite for understanding such a high corrosion resistance of Ti.

Passive film on a metal electrode shows semiconducting or insulating properties depending on the electronic structure of the film. The electronic structure of the semiconducting or insulating passive film as well as its apparent physical structure is an important issue in that ionic movement in the passive film is driven by the electric field, which in turn affected by the electronic structure.^{3,4)} Thus, the electronic structure is closely related to corrosion phenomena involving film breakdown and repassivation processes.⁵⁾ Recently, photocurrent measurement and Mott-Schottky analysis via impedance measurements have been employed to examine the electronic properties of various passive films. The *in-situ* analysis of passive films

on Ti by the photocurrent measurement has been mainly focused on thick anodic oxide films formed in strongly acid solutions at anodic potentials noble to 4 V_{SCE} .⁶⁻¹⁰⁾ A Few papers are concerned with photo-electrochemical analysis of passive films formed at potentials active to 3 V_{SCE} .¹¹⁻¹⁴⁾ Further, there are little works on the effects of Cl^- on the electronic properties of passive film on Ti.

The passive film on Ti was reported to be composed of TiO_2 , but its structure and exact composition is not yet clear. The passive films on Ti at low potentials were often reported to have an amorphous structure¹¹⁾ and a defect of stoichiometry.¹²⁾ However other authors reported that the characteristic peaks of anatase and rutile were observed on Ramam spectra of passive films formed on Ti at low potentials (0-5V).¹³⁾ These anatase peaks were also observed by X-ray diffraction on thick films.¹⁴⁾

The research objective of this work are to characterize the structure of passive films formed on Ti in pH 8.5 buffer solution and in an artificial seawater by examining electronic properties of the passive films through photocurrent analysis and Mott-Schottky analysis, and to investigate the effect of Cl^- on structure and electronic properties of passive film of Ti.

2. Experimental

Specimen or working electrode used in this work was a commercial titanium grade 2 (99.6 wt. % Ti). Electrochemical cell used for the photo-electrochemical tests is a conventional three electrodes cell of 1 L-multineck flask with a quartz window toward photo illumination. The working electrodes were mounted in an epoxy resin with an exposed area of about 1 cm² and polished with SiC paper to no. 2000 grit. A platinum counter electrode and a saturated calomel electrode (SCE) positioned in a salt bridge with a high-silica tip were used in the cell. All electrode potentials in this work are referred to the SCE. The specimens were cathodically pre-polarized at -1.8 V for 5 min to remove the air-formed oxides on the surface, and then anodically polarized to form passive film in deaerated pH 8.5 buffer solution and in an artificial seawater at room temperature. The solution was prepared by mixing 0.2 M boric acid and 0.05 M citric acid with 0.1 M tertiary sodium phosphate solution.

Passive films on samples had been formed potentiostatically for about 20 h until a steady state was reached, and then illuminated monochromatically at the film formation potential. Xenon arc lamp of 300 W was used as a light source, and a monochromatic illumination was provided by a scanning digital monochromator controlled by stepping motor, which allowed to produce automatically the monochromatic photon in a range of wavelengths 200 to 800 nm at a scanning rate of 1nm/sec. In order to investigate the effects of applied potential on the electrical and optical properties of passive film, photocurrent spectra for the passive films on Ti were measured at applied potentials of -0.5 to 5 V. Auxiliary focusing lenses were used to raise the intensity of photons toward the monochromator. Mott-Schottky plots were obtained from impedance measured to the scan rate of 0.05 V/sec from the film formation potential to -0.5 V.

3. Results and discussion

3.1 Polarization response of Ti

Fig. 1 shows polarization curves of Ti measured in pH 8.5 buffer solution and also in an artificial seawater at a scan rate of 0.5 mV/sec. The corrosion potential(-0.64 V) of Ti in pH 8.5 buffer solution was about 90 mV active to that (-0.55 V) in artificial seawater. However, Ti exhibited almost same passive current density in passive range in both solutions, implying that protectiveness of the passive film formed on Ti was not affected by Cl⁻. Electronic properties of passive films formed on Ti at potentials of -0.5, 0, and 0.5 V in pH 8.5 buffer solution

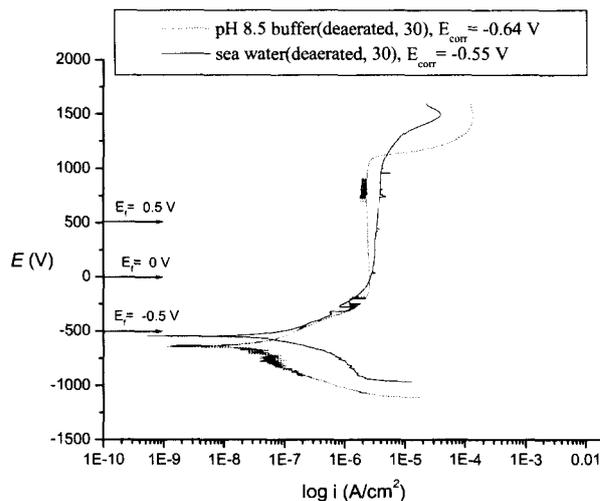


Fig. 1. Anodic polarization curve of Ti in deaerated 30°C pH 8.5 borate buffer solution and in artificial seawater.

and in an artificial seawater were examined through the photocurrent measurement and the Mott-Schottky analysis.

3.2 Effect of E_f on photocurrent spectra

Fig. 2 and 3 shows the effects of E_f on the photocurrent spectra for the passive film formed on Ti in pH 8.5 buffer solution and also in an artificial seawater, respectively. The overall feature of photocurrent spectra for passive films formed in both solutions is almost same irrespective of the E_f , although there are large differences in photocurrent depending on the E_f . The photocurrent began to increase at a photon energy of 3.5 eV, and showed a peak at approximately 4.2 eV with the peak current being proportional to E_f .

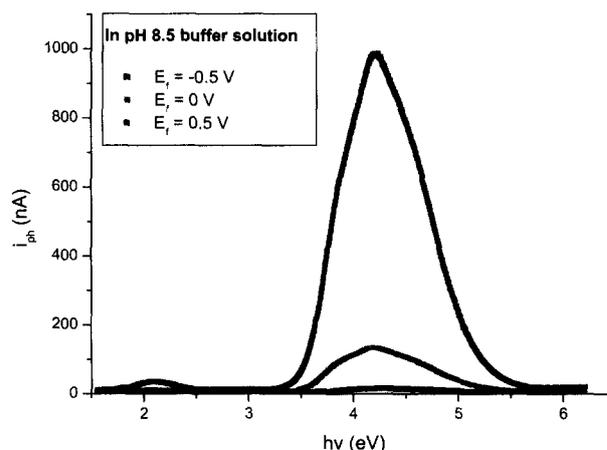


Fig. 2. Effect of E_f on the photocurrent spectra for the passive film formed on Ti grade 2 at various potentials (-0.5V~0.5V) in deaerated pH 8.5 buffer solution.

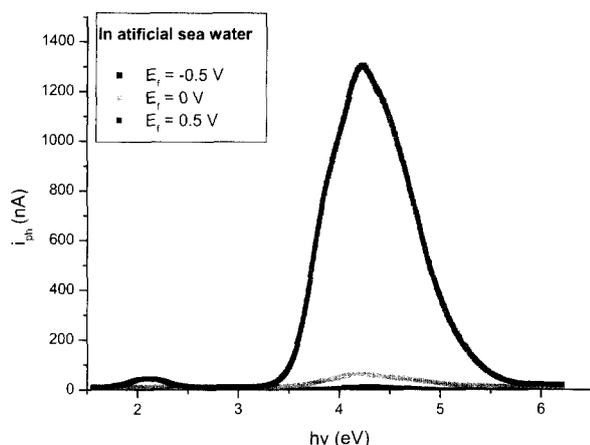


Fig. 3. Effect of E_f on the photocurrent spectra for the passive film formed on Ti grade 2 at various potentials (-0.5V~0.5V) in deaerated artificial seawater

3.3 Band gap energy

The absorption coefficient (α), of a crystalline material depends on the photon energy according to following equation:

$$\alpha = A(h\nu - E_g)^n / h\nu \quad (1)$$

where A is a constant, h is the Plank constant, and ν is the frequency of the phonon (thus $h\nu$ is the photon energy). For crystalline semiconductors, n depends on the electron transition type; $n = 1/2$ for direct transition, and $n = 2$ for indirect transition. However $n = 2$ has been frequently used for an amorphous semiconductor such as

passive film, but the electronic transition occurring in passive film is called nondirect to distinguish it from the indirect one in crystalline semiconductor.¹⁵⁾ The E_g is determined by extrapolating the $(i_{ph} \cdot h\nu)^{1/n}$ vs. $h\nu$ plot to the photon energy axis, provided that the photocurrent (i_{ph}) for the film is proportional to the absorption coefficient; $i_{ph} = A'(h\nu - E_g)^n / h\nu$.

Based on the data in Fig. 2, both $(i_{ph}h\nu)^2$ vs $h\nu$ and $(i_{ph}h\nu)^{0.5}$ vs $h\nu$ plots were drawn to determine the nondirect and direct band gap energies, and presented in Figs. 4(a) and 4(b), respectively. In the same methods, the direct and nondirect band gap energies for the passive film formed in an artificial seawater were determined from both $(i_{ph}h\nu)^2$ vs $h\nu$ and $(i_{ph}h\nu)^{0.5}$ vs $h\nu$ plots presented in Figs. 5(a) and 5(b), respectively. The photocurrent spectra for the passive films on Ti showed straight lines in $(i_{ph}h\nu)^2$ vs $h\nu$ plot and $(i_{ph}h\nu)^{0.5}$ vs $h\nu$ plot, suggesting that the passive films have the direct and nondirect electron transition sources.

The E_g for the passive films formed on Ti in pH 8.5 buffer solution was measured to be $E_g^{n=2} = 3.7$ eV for nondirect electron transition, and $E_g^{n=0.5} = 3.4$ eV for direct electron transition. These values are found to be almost same as those for the passive films formed on Ti in the artificial seawater, indicating that Cl^- didn't affect E_g for the passive films on Ti. The anodic current in the photocurrent spectra in Figs. 2 and 3 confirms that the passive films on Ti are n type semiconductors.

3.4 Structure of the passive film

The structure of passive film on Ti can be characterized by comparing the photocurrent spectrum and band gap

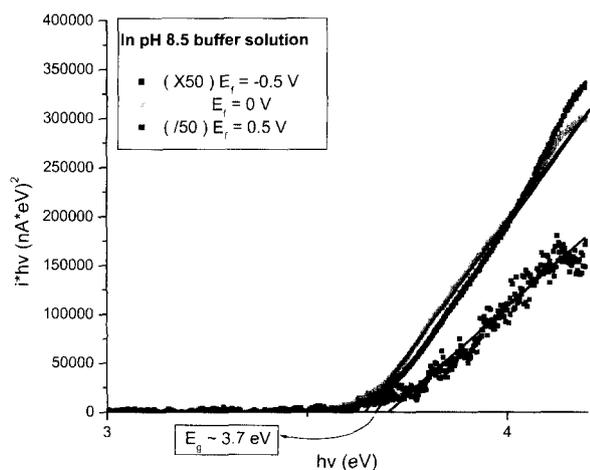


Fig. 4(a). $(i_{ph}h\nu)^2$ vs $h\nu$ plots for the passive film formed on Ti at various potentials (-0.5V~0.5V) in deaerated pH 8.5 buffer solution.

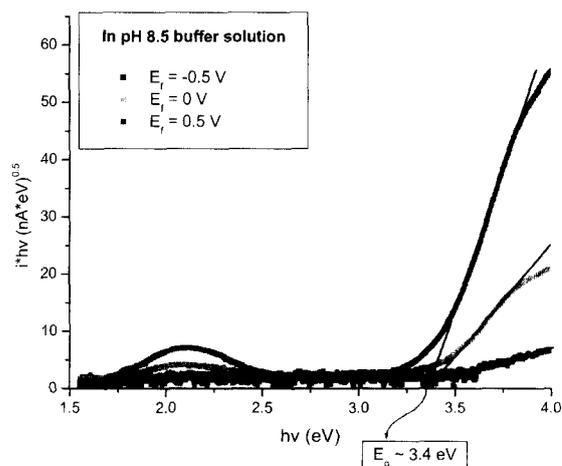


Fig. 4(b). $(i_{ph}h\nu)^{0.5}$ vs $h\nu$ plots for the passive film formed on Ti grade 2 at various potentials (-0.5V~0.5V) in deaerated pH 8.5 buffer sol.

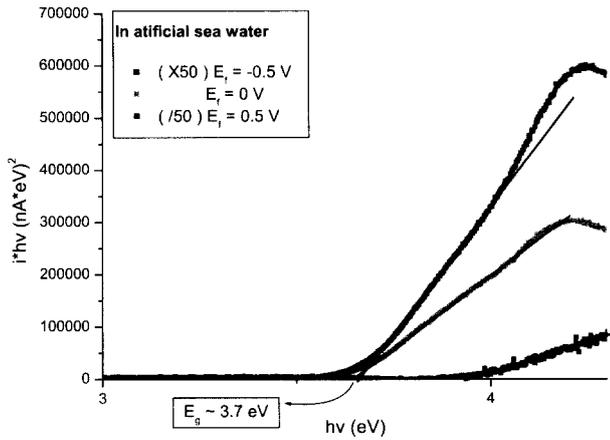


Fig. 5(a). $(i_{ph}h\nu)^2$ vs $h\nu$ plots for the passive film formed on Ti at various potentials (-0.5V~0.5V) in deaerated artificial seawater.

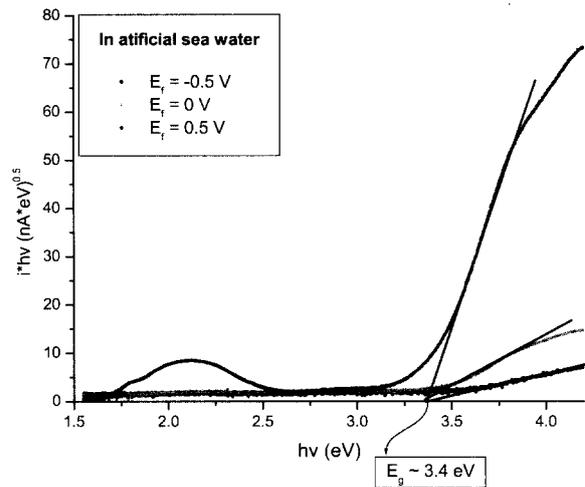


Fig. 5(b). $(i_{ph}h\nu)^{0.5}$ vs $h\nu$ plots for the passive film formed on Ti grade 2 at various potentials (-0.5V~0.5V) in deaerated artificial seawater

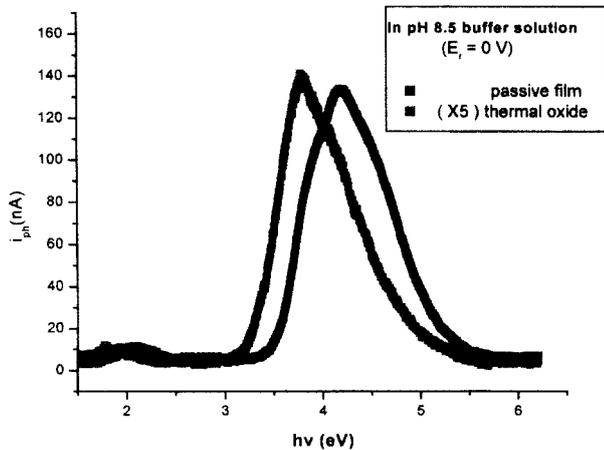


Fig. 6. Photocurrent spectra for the passive film and thermal oxide film formed on Ti at applied potential of 0V in deaerated pH 8.5 buffer solution

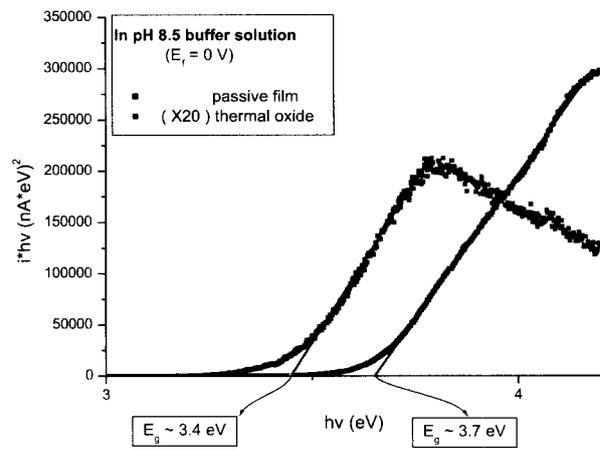


Fig. 7. $(i_{ph}h\nu)^2$ vs $h\nu$ plots for the passive film and thermal oxide(400°C, 1 hour) formed on Ti in deaerated pH 8.5 buffer solution

energy of the film with those of well defined material. The photocurrent spectrum for the passive film is compared with that for the thermal oxide film formed in air at 400 C in Fig. 6. The photocurrent spectrum for the thermal oxide film was measured at 0 V in pH 8.5 buffer solution after immersed for 1 h in the solution. Further the band gap energies for both the passive film and the thermal oxide film are compared in the $(i_{ph}h\nu)^2$ vs $h\nu$ and $(i_{ph}h\nu)^{0.5}$ vs $h\nu$ plots in Figs. 7 and 8. The values of $E_g^{n=2}$ (3.7 eV) and $E_g^{n=0.5}$ (3.4 eV) for the passive film were greater than the values of $E_g^{n=2}$ (3.4 eV) and $E_g^{n=0.5}$ (3.1 eV) for thermal oxide film formed on Ti in air at 400 °C. It is significant that whereas the photocurrent for the thermal oxide film begin to increase sharply, that for the

passive film exhibited an Urbach tail,¹⁵⁾ a characteristic of amorphous or highly disordered semiconductor.

The Urbach tail was presented by the equation (2);

$$\alpha = \alpha_0 \exp[\gamma(h\nu - E_g) / kT] \quad (2)$$

where α is the absorption coefficient, h is the Plank constant, $h\nu$ is the frequency of the phonon (thus $h\nu$ is the photon energy), γ is a constant. The slop (β) of a linear part in the $(\log i_{ph})$ vs $h\nu$ plot, shown in Fig. 9, was associated with the disorder energy($1/\beta$) of the film.¹⁷⁾

The disorder energy for the passive film was measured to be 176 meV that was much greater than that(60 meV)

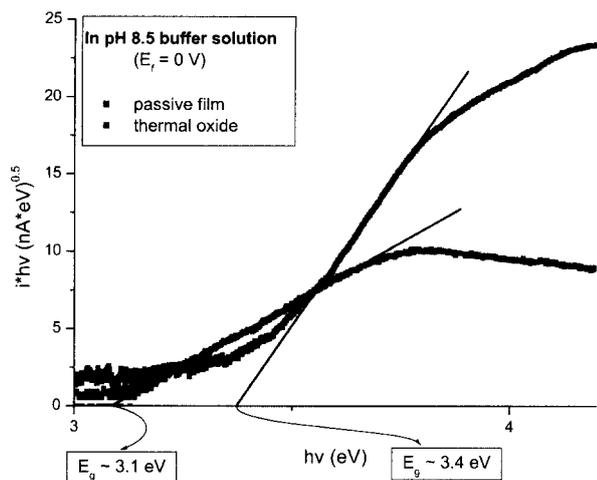


Fig. 8. $(i_{ph}h\nu)^{0.5}$ vs $h\nu$ plots for the passive film and thermal oxide(400°C, 1 hour) formed on Ti in deaerated pH 8.5 buffer solution

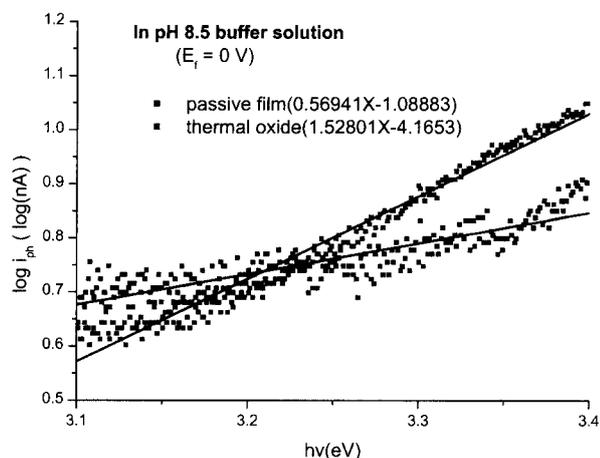


Fig. 9. $\log(i_{ph})$ vs $h\nu$ plots for the passive film and thermal oxide film (400°C, 1 hour) formed on Ti in deaerated pH 8.5 buffer solution solution

for the thermal oxide film. It was reported previously that the disorder energy of about 200 meV was corresponded to the value for a high amorphous state.¹⁷⁾ The higher the disorder energy and the greater the E_g , the more disordered or the more amorphous is the structure of the film. The straight lines in the $(i_{ph}h\nu)^2$ vs $h\nu$ plots shown in Fig. 7, however, suggests that both the passive film and the thermal oxide film exhibits a characteristics appeared only for crystalline semiconductors.¹⁶⁾ It was reported that the characteristic peaks of anatase and rutile were observed on Ramam spectra for passive films formed on Ti at low potentials (0-5V).¹³⁾ So we conclude that the passive film on Ti is composed of a disordered structure, and has some amount of crystalline Ti oxide in a mixture of amorphous

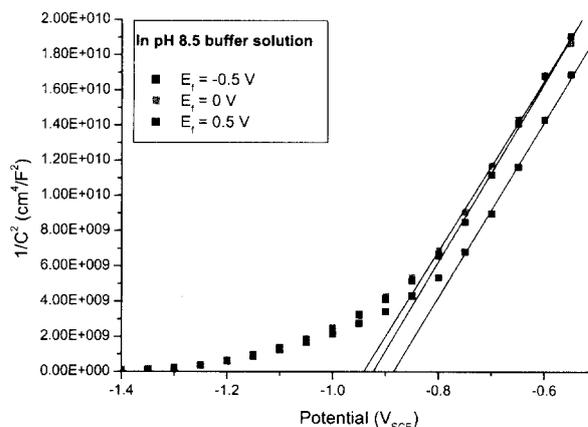


Fig. 10. Mott-Schottky plots at various potential for the passive film formed on Ti in deaerated pH 8.5 buffer solution.solution solution.

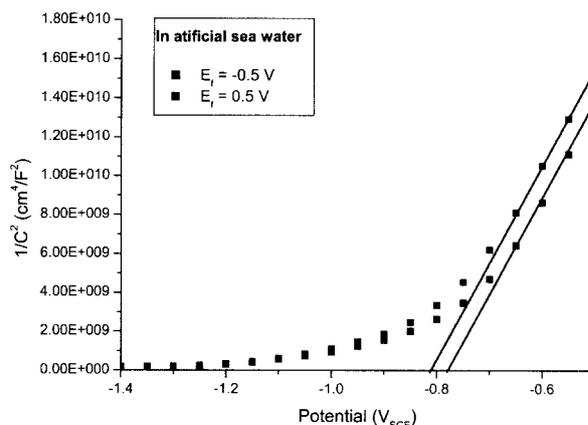


Fig. 11. Mott-Schottky plots at various potential for the passive film formed on Ti in deaerated artificial seawater.solution.

and crystalline structure or duplex layer structure.

To investigate effects of Cl^- on electronic properties of passive film on Ti, the electronic properties of passive film on Ti in pH 8.5 buffer solution is compared with those in artificial seawater. The photocurrent spectra and band gap energy of the passive film were not influenced by Cl^- in the solution.

3.5 Mott-shottky relation

Influence of film formation potential on the Mott-Shottky plots for the passive film formed on Ti in pH 8.5 buffer solution, and also in an artificial seawater (pH 7.5) were drawn in Figs. 10 and 11. Donor densities (N_d) of the passive films were determined from the slope of the Mott-Schottky plots in Figs. 10 and 11. Evidently, the donor density of the film or the slope in the Mott-Schottky relation appears to be almost insensitive to the film

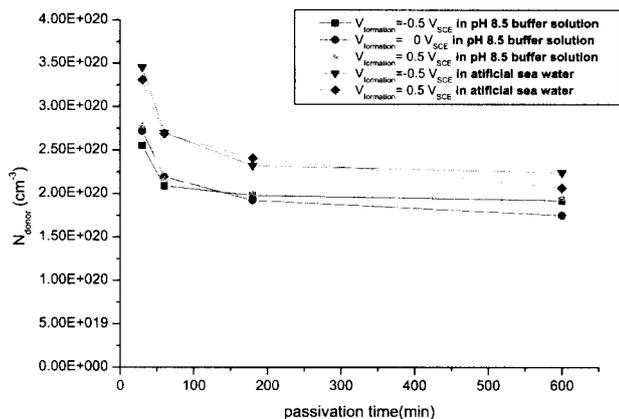


Fig. 12. Donor density vs passivation time plot for the passive film formed on Ti. Permittivity number of 40 for passive film on Ti was used.

formation potential in both solutions. Electronic properties of passive film may be influenced by the passivation time under a potentiostatic condition, due to stabilization of the film. Fig. 12 demonstrates the effects of passivation time on the donor density of the films formed in either pH 8.5 solution or an artificial sea water. Clearly, the donor density of the films decreased with passivation time up to 200 min., and then attained a limiting value for further passivation, a result of stabilization of the film.

The E_{fb} and N_d for passive film formed in the same solution were not affected by E_f as shown in Figs. 10 and 11. However, the donor density (about $2.4 \times 10^{20} \text{ cm}^{-3}$) for the passive film formed in artificial seawater was greater than that (about $2.0 \times 10^{20} \text{ cm}^{-3}$) for the film formed in pH 8.5 buffer solution, indicating that Cl⁻ increased the donor density for the passive film on Ti. The high defect density of the passive films confirms again that the passive films on Ti is composed of a highly disordered structure. It is noted that the flat band potentials (E_{fb}) for the passive film in pH 8.5 solution is determined to be -0.91 V that is lower than that (-0.80 V) in artificial seawater (pH 7.5), as shown in Figs. 10 and 11. This small difference in the E_{fb} may arise from the difference of pH between two solutions. It was examined and confirmed that the E_{fb} for the passive films was almost same when measured in 8.5 pH buffer solutions with or without 3.5 % NaCl.

4. Conclusions

1. The passive film on Ti exhibited a n-type semiconductor in both pH 8.5 buffer solution and an artificial sea water. The overall features of photocurrent spectrum for the passive film formed in both solutions were almost same, irrespective of the film formation potential. How

ever, the peak photocurrent for the films increased with an increase in the film formation potential.

2. The photocurrent spectrum for the passive film on Ti resulted from both direct and nondirect electronic transitions. The E_g for the film was measured to be $E_g^{n=2} = 3.7 \text{ eV}$ for nondirect transition, and $E_g^{n=0.5} =$ for direct transition. These values of band gap energy were almost insensitive to the film formation potential and the addition of Cl⁻ in solution.

3. There were some differences in the photocurrent behaviors between the passive film and the thermal oxide film; the sharp increase in photocurrent and the smaller E_g for the thermal oxide film compared with that for the passive film. The disorder energy (176 meV) for the passive film much greater than that (60 meV) for the thermal oxide film. The Urbach tail, the occurrence of direct electronic transition, the larger E_g , and the greater disorder energy for the passive film compared with those for the thermal oxide film demonstrates that the passive film on Ti is composed of a highly disordered structure or a duplex layers of amorphous and crystalline structures.

4. The E_{fb} and N_d for passive film formed in the same solution were not affected by E_f . However, the donor density (about $2.4 \times 10^{20} \text{ cm}^{-3}$) for the passive film formed in artificial seawater was greater than that (about $2.0 \times 10^{20} \text{ cm}^{-3}$) for the film formed in pH 8.5 buffer solution, indicating that Cl⁻ increased the donor density for the passive film on Ti. The high defect density of the passive films confirms again that the passive films on Ti is composed of a highly disordered structure.

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