

# A STUDY ON THE SEMICONDUCTING PROPERTIES OF PASSIVE FILMS ON STAINLESS STEELS BY PHOTO-ELECTROCHEMICAL TECHNIQUES

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**Abstract.** Semiconducting properties of the passive films on ferrite stainless steels were examined in a pH 7.8 buffer solution by photo-electrochemical techniques (Photocurrent measurements and Mott-Schottky analyses). By passivation of stainless steel in an aqueous mixture of nitric acid and hydrofluoric acid, surface morphology and composition were dramatically changed. Under unbiased UV-illumination, all passive films tested showed p-type photocurrent, while air formed oxide film showed n-type photocurrent in buffer solution. It was found that p-type photocurrent and stability of stainless steel was strongly dependent on Cr content.

## 1. INTRODUCTION

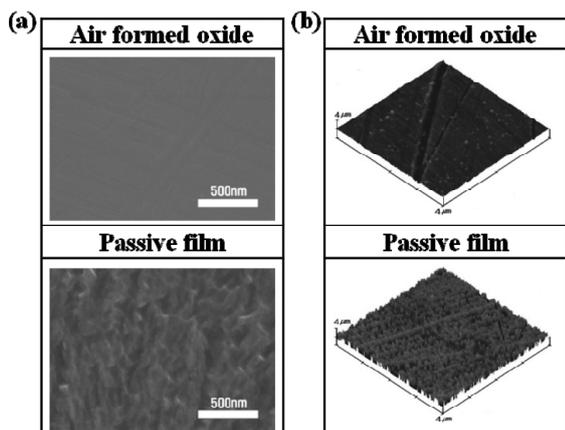
Because corrosion phenomena of stainless steel are closely related to the passive film on the surface [1-3], both electronic properties and semiconducting properties of passive films have been of great interest for understanding of the corrosion behaviors of metals and alloys [4-10]. Although the analyses of the passive films by ex-situ methods such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and X-ray diffraction (XRD) have been extensively studied [11], the properties of passive films still remain controversial. For the investigation of semiconducting properties of passive films, many researchers have reported the bandgap energy ( $E_g$ ) of passive films formed on Fe, Cr, and Fe-Cr alloys [12-15]. However, different band gap energies of the passive films have been reported. This is mainly due to experimental difficulties in probing the passive film whose thickness may not ex-

ceed a few nanometers, and also due to its structure and composition liable to be changed with environmental [16].

Recently, photo-electrochemical technique and Mott-Schottky analysis by capacitance measurement have proved to be powerful techniques for in situ analysis of passive films on metal and alloy. These techniques make it possible to determine the in situ semiconducting properties of the passive film such as bandgap energy ( $E_g$ ), flat band potential ( $E_{fb}$ ), type of semiconductor, and density of defects that are very sensitive to structure and composition [17].

In this study, the physical and chemical properties of the passive films on ferrite stainless steels were studied using three kinds of stainless steels with different Cr content. Photocurrent measurements and Mott-Schottky analyses in a pH 7.8 buffer solution were employed to examine the semiconducting properties of the passive films.

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**Fig. 1.** (a) SEM images of Sample #1 before and after passivation and (b) AFM images of Sample #1 before and after passivation.

## 2. EXPERIMENTAL DETAILS

Three kinds of stainless steels with different Cr contents (Sample 1 (Fe-19%Cr), Sample 2 (Fe-26%Cr), Sample 3 (Fe-30%Cr)) were used, and before test all samples were rinsed and polished with SiC papers and diamond suspensions. Air formed films were removed in a sulfuric acid solution, and all samples were re-passivated in an aqueous mixture of nitric acid and hydrofluoric acid.

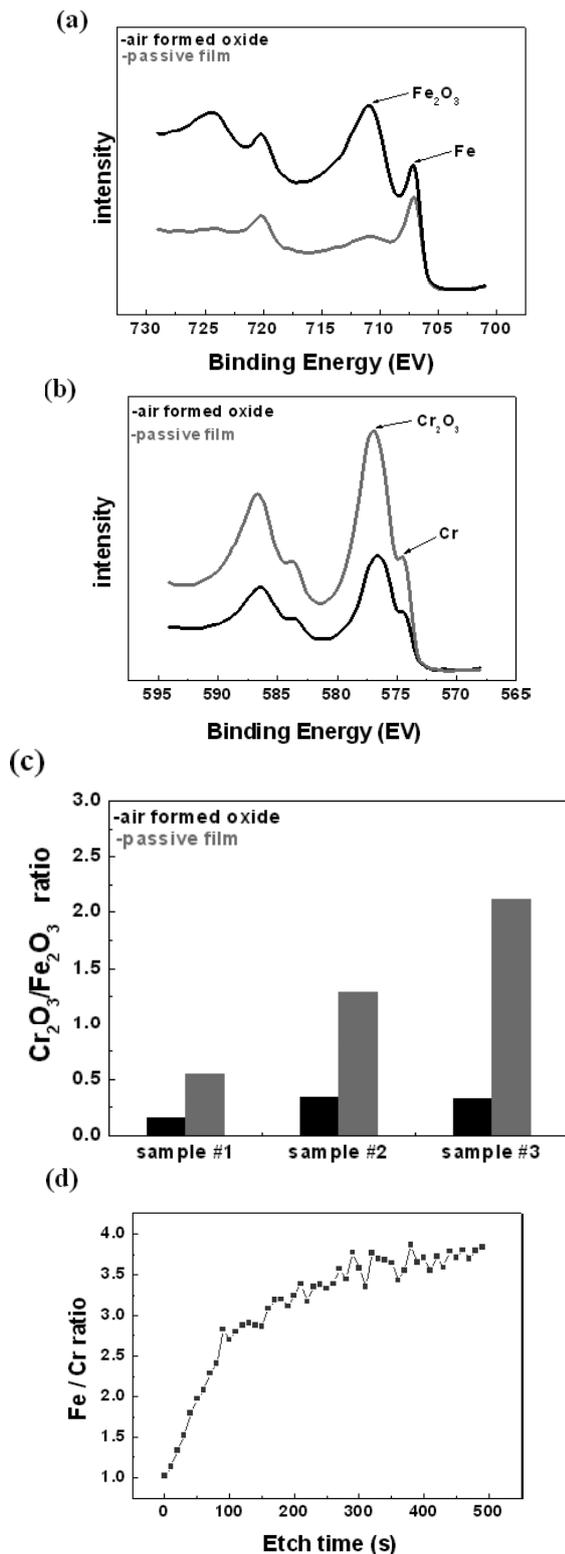
Surface composition and oxidation states of components were determined by X-ray photoelectron spectroscopy, and surface morphology was investigated by scanning electron microscopy (SEM) and scanning probe microscopy (SPM).

All the measurements of semiconducting properties were carried out in a pH 7.8 buffer solution at room temperature. Photocurrent measurement was conducted in a conventional three-electrode cell using a Pt wire and Ag/AgCl as a counter and reference electrode, respectively. Both unbiased photocurrent and IV behavior were measured under an 1 kW Xenon arc lamp illumination using an automatic shutter.

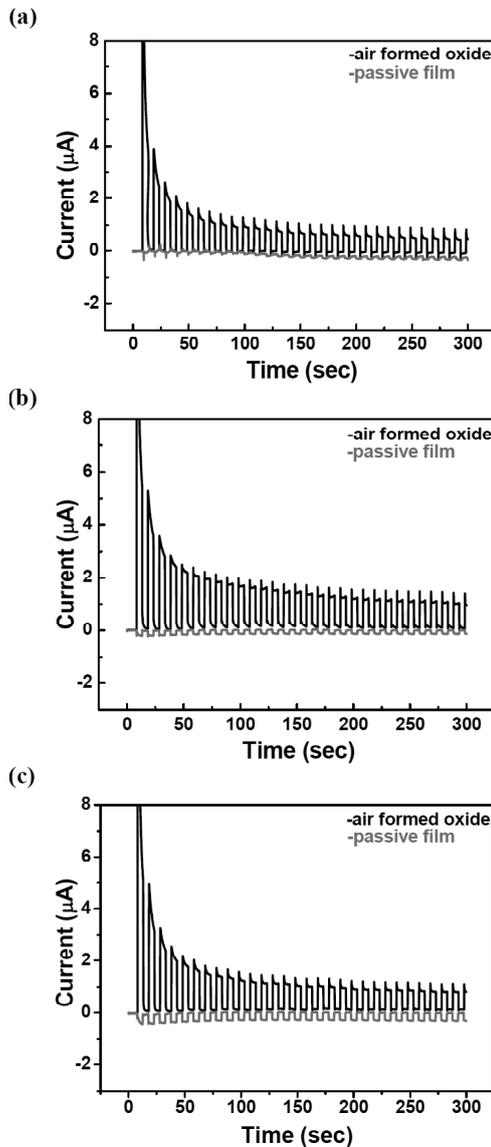
In order to investigate the density of donor/acceptor and flat band potential ( $E_{fb}$ ), Mott-Schottky analysis was carried out in the voltage range between -1.5 and 0.5 V vs Ag/AgCl.

## 3. RESULTS AND DISCUSSION

Fig. 1 compares the morphologies between air-formed film and passivated film of Sample 1 (19% Cr), examined by SEM (a) and AFM (b). All passive films tested showed rough surface, while air formed oxide film showed smooth surface.

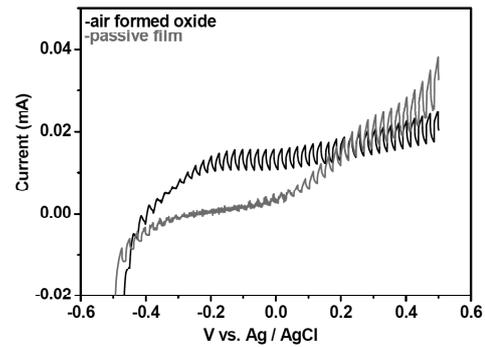


**Fig. 2.** (a) Fe2P XPS spectra of Sample #2 before and after passivation, (b) Cr2P XPS spectra of Sample #2 before and after passivation, (c) Change of  $\text{Cr}_2\text{O}_3/\text{Fe}_2\text{O}_3$  ratio before and after passivation, measured by XPS, and (d) Depth profile of Fe/Cr ratio of sample #2 after passivation.



**Fig. 3.** Unbiased photocurrents before and after passivation; (a) Sample #1, (b) Sample #2, and (c) Sample #3.

XPS analysis was carried out to examine the change in surface composition by passivation, and the Cr2p and Fe2p spectra of Sample 2 (26%Cr) are shown in Figs. 2a and 2b, respectively. Although metal and metal oxide peaks for both Cr and Fe were clearly observed for all air-formed and passivated films, remarkable change was found after passivation. The peaks of  $\text{Fe}_2\text{O}_3$  were remarkably decreased by passivation, while more  $\text{Cr}_2\text{O}_3$  was observed to be formed by passivation. This phenomenon was clearly observed for all samples, implying surface composition change by passivation. The changes in  $\text{Cr}_2\text{O}_3/\text{Fe}_2\text{O}_3$  ratio before and after passivation are shown in Fig. 2c, and for all samples  $\text{Cr}_2\text{O}_3/$

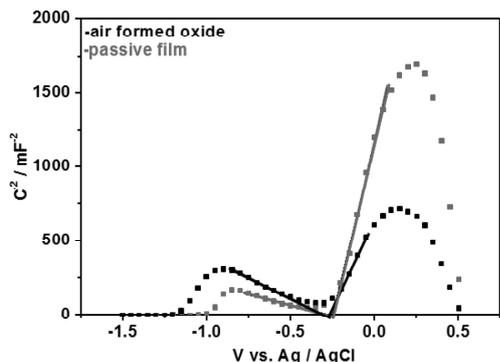


**Fig. 4.** Potentiodynamic scans under chopped illumination for Sample #3 before and after passivation.

$\text{Fe}_2\text{O}_3$  ratio was remarkably increased by passivation. In addition, with increase of Cr content from 19% to 30%, the  $\text{Cr}_2\text{O}_3/\text{Fe}_2\text{O}_3$  ratio was also increased. These results imply that surface is reconstructed by passivation from  $\text{Fe}_2\text{O}_3$ -rich toward  $\text{Cr}_2\text{O}_3$ -rich surface, which is a p-type semiconductor. Depth profile of Fe/Cr ratio was also determined by XPS with argon etching at an etching rate of 0.03 nm/s, and Fig. 2d shows the Fe/Cr ratio of Sample 2 after passivation with respect to depth. At the near surface Fe/Cr was very low, indicating Cr-rich surface. The ratio increased with depth, and reached a constant value. From the results of SEM, AFM, and XPS analyses, it could be concluded that both surface morphology and composition are significantly changed by passivation.

The unbiased photocurrent was measured for all samples before (air-formed film) and after passivation as shown in Fig. 3. For all samples, air formed films (before passivation) showed anodic photocurrent (n-type photocurrent) and the unbiased photocurrent decreased with time on stream. In cases of passive films, however, p-type photocurrent was clearly observed and was stable with time. Both air formed and passivated films are composed of  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ , as confirmed by XPS analysis. Surface concentration of  $\text{Cr}_2\text{O}_3$  was remarkably increased by passivation, resulting in the increase of p-type semiconducting properties. Moreover, p-type photocurrent (cathodic photocurrent) of passivated film increased with the increase of Cr content from 19% to 30%. Judging from photocurrent change with time, the air-formed films are not stable under UV illumination, while passivated films are stable.

Fig. 4 shows current-voltage behaviors of Sample 3 (30% Cr) for both air formed and passivated films under chopped illumination. Two distinct regions were observed for all air-formed and passivated films. As



**Fig. 5.** Mott-Schottky plot of Sample #3 before and after passivation.

voltage increased toward cathodic direction, p-type photocurrent increased, and n-type photocurrent increased with anodic direction.  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  must be responsible for p-type photocurrent generation and n-type photocurrent generation, respectively. Generally, p-type photocurrent increased and n-type photocurrent decreased after passivation, which was evidenced by XPS results. By passivation,  $\text{Cr}_2\text{O}_3$  concentration on the surface increased, resulting in the increase of p-type photocurrent.

The electrochemical capacitance was measured in order to characterize the semiconducting properties of the passive film [18]. The linear relation between  $1/C^2$  and potential is expressed as the following Mott-Schottky equation;

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 qN} \left( E - E_{fb} - \frac{kT}{q} \right),$$

where  $N$  is the carrier density,  $\epsilon$  the dielectric constant,  $\epsilon_0$  the vacuum permittivity,  $q$  the elementary charge,  $k$  the Boltzman constant,  $T$  the absolute temperature, and  $E_{fb}$  the flat band potential. The density of donor/acceptor and flat band potential ( $E_{fb}$ ) can be determined by the equation above, and they are summarized in Table 1. Mott-Schottky plot of

Sample 3 (Cr 30%) is shown in Fig. 5. For all samples, general trends were clearly observed; 1. Two distinct regions (positive slope and negative slope) were clearly observed, which means the existence of both p-type and n-type semiconductors. 2. Donor density decreased after passivation, while acceptor density increased. This behavior corresponds well to the photocurrent measurements. 3. Flat-band potentials calculated from Mott-Schottky equation is a little bit different from those observed from potentiodynamic scans. Morphology, composition and structure of surface, and ion conductivity of electrolyte must be considered because flat band potential depends on the space charge layer of surface/electrolyte interface.

## 4. CONCLUSIONS

Photo-electrochemical technique and Mott-Schottky analysis were used to investigate semiconducting properties of passive films.

By passivation of stainless steel in an aqueous mixture of nitric acid and hydrofluoric acid, surface morphology and composition were dramatically changed. Surface roughness increased, and the surface was reconstructed from  $\text{Fe}_2\text{O}_3$ -rich to  $\text{Cr}_2\text{O}_3$ -rich surface by passivation. Air-formed films showed n-type behavior, while passivated films exhibited p-type behavior, which was confirmed by the measurement of unbiased photocurrent and Mott-Schottky plots. P-type character of the passivated film increased with Cr content of stainless steel.

## ACKNOWLEDGEMENTS

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**Table 1.** Donor density, acceptor density, and flat band potential ( $E_{fb}$ ) calculated from Mott-Schottky equation.

	Donor density	Acceptordensity	Flat band potential ( $E_{fb}$ )
Sample #1_air formed film	$2.5 \times 10^{19}$	$3.9 \times 10^{19}$	-0.43 ~ -0.26
Sample #1_passive film	$1.9 \times 10^{19}$	$5.2 \times 10^{20}$	-0.25 ~ -0.16
Sample #2_air formed film	$3.7 \times 10^{19}$	$2.7 \times 10^{20}$	-0.27 ~ -0.17
Sample #2_passive film	$1.6 \times 10^{19}$	$2.9 \times 10^{20}$	-0.28 ~ -0.25
Sample #3_air formed film	$5.1 \times 10^{19}$	$2.2 \times 10^{20}$	-0.28 ~ -0.27
Sample #3_passive film	$2.4 \times 10^{19}$	$4.0 \times 10^{20}$	-0.27 ~ -0.25

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