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Analysis of photocurrent responses of oxide films formed on stainless steel

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ABSTRACT

The photocurrent responses of the oxide films formed on 304L stainless steel in high temperature and high pressure water was investigated in borate buffer solutions. The photocurrent responses showed transient characteristics. The oxide films exhibited a p-type semiconductor but presented negative steady photocurrents and positive photocurrent spikes under certain applied bias and incident light. A theoretical model was developed to analyze the transient photocurrent behaviors. This model was derived on the basis of continuity equation for carriers and can give a reasonable explanation for the transient photocurrent waveform patterns. The transient photocurrent waveform pattern is mainly dependent on the electric field inside the space charge region of the outer layer at oxide film/electrolyte interface. The effects of applied bias and incident light on photocurrent waveform patterns result from their impacts on the electric field. The values of calculated electric field by fitting the measured photocurrent data show a good agreement with the prediction of the model.

1. Introduction

The corrosion resistance of stainless steel (SS) depends on the corrosion resistances of their surface (passive/oxide) film which exhibit semiconductor properties [1]. Besides the composition, structure, thickness and other physical or chemical properties of the films, their semiconductor properties are also very important to understand the corrosion mechanism of SS. Photocurrent spectroscopy (PCS) of surface films contains composition, electronic structure [2,3] and other information of the films, and is often employed to investigate the semiconductor properties of surface films on metals.

The passive/oxide films formed on SS in various kinds of solutions consist of duplex layers, both of which behave as a semiconductor. And the electronic band structure model of oxide film on SS is often described as that shown in Fig. 1 [2,4]. In many cases, the inner layer of p-type semiconductor is a rich-chromium layer and the outer layer of n-type is a rich-iron oxide or nickel oxide/hydroxide.

The photocurrent responses of the passive/oxide films on SS often show transient characteristics [5] as shown in Fig. 2(a)–(d). In Fig. 2(a) and (b), the photocurrent showed the simple exponential rising and falling transient, and in Fig. 2(c) and (d), a spike of photocurrent was observed when the specimen was illuminated and then decayed immediately and exponentially. The opposite spike of photocurrent was observed also when illumination was interrupted. The waveforms (transient patterns) and value of photocurrent spike or steady photocurrent were affected by applied bias and incident light [3–15].

The photocurrent waveforms of Fig. 2(a)–(g) will be referred to as “pattern A” to “pattern G”, respectively.

There were two kinds of existing theory to analyze the transient photocurrent response.

Some papers considered that the spike of photocurrent is caused by the chemical reactions in solutions. The photocurrent is considered to be closely related to the reaction velocity. When the incident light is turned on, the positive reaction velocity is relatively big at the beginning. That is the reason for the presence of the spike of photocurrent. And then as the reaction products in the solution are accumulated gradually, the reverse reaction occurs, and the reverse reaction velocity increased from zero to its maximum value. At this moment, the photocurrent decays to the steady state. And when the light is turned off, similar photocurrent responses are gotten. This theory could analyze the waveforms like pattern C and pattern D. Abrantes [6] considered that the transient features of photocurrents observed on a passivated iron electrode can be attributed to the build-up and decay of surface intermediates (hydroxyl radicals stabilized at iron sites).

Others indicated that the transient phenomenon was caused by the accumulation of photo-induced carriers at the film/electrolyte interface. As the light was on, the photo-induced carriers were accumulated at the surface and they could not to diffuse into the bulk or solution in a short period. Therefore, the photocurrent spikes were happened, and when carriers diffused by concentration gradient, the photocurrent decayed to a steady value gradually. Hara and

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e	electronic charge (C)
p	hole concentration (cm^{-3})
n	electron concentration (cm^{-3})
Δp	concentration difference of holes inside the space charge region (cm^{-3})
Δn	concentration difference of electrons inside the space charge region (cm^{-3})
x	distance (cm)
t	time variable (s)
E_f	Fermi level (eV)
V_D	the inherent potential difference on the semiconductor/electrolyte interface (V)
V_{bias}	the applied potential difference (V)
V_L	the photo-induced potential difference (V)
ξ	the electric field ($V\,cm^{-1}$)
$(\Delta J_n)d$	the electron diffusion current density per unit surface (nA/cm^2)
$(\Delta J_p)d$	the hole diffusion current density per unit surface (nA/cm^2)
$(\Delta J_n)e$	the electron drift current density per unit surface (nA/cm^2)
$(\Delta J_p)e$	the hole drift current density per unit surface (nA/cm^2)
ΔJ_n	the electron current density per unit surface (nA/cm^2)
ΔJ_p	the hole current density per unit surface (nA/cm^2)
ΔJ	the total current density per unit surface (nA/cm^2)
J_{sp}	the photocurrent spike per unit surface (nA/cm^2)
J_{st}	the steady photocurrent per unit surface (nA/cm^2)
μ_p	mobility of holes ($cm^2\,V^{-1}\,s^{-1}$)
μ_n	mobility of electrons ($cm^2\,V^{-1}\,s^{-1}$)
D_p	diffusion constant of holes ($cm^2\,s^{-1}$)
D_n	diffusion constant of electrons ($cm^2\,s^{-1}$)
U_n	the net recombination rate of electrons ($cm^{-3}\,s^{-1}$)
U_p	the net recombination rate of holes ($cm^{-3}\,s^{-1}$)
G	the optical generation rate of photo-induced carriers ($cm^{-3}\,s^{-1}$)
G_p	the optical generation rate of photo-induced holes ($cm^{-3}\,s^{-1}$)
G_n	the optical generation rate of photo-induced electrons ($cm^{-3}\,s^{-1}$)
α_p	the optical absorption coefficient of holes (cm^{-1})
α_n	the optical absorption coefficient of electrons (cm^{-1})
β	the quantum efficiency
I	the light intensity (a.u)
I_0	the light intensity on surface of oxide film (a.u)
$h\omega$	photon energy of incident light (eV)
τ_p	the time constant of holes including traps in surface states, reaction in the film/electrolyte interface and combination/recombination in space region (s)
τ_n	the time constant of electrons including traps in surface states, reaction in the film/electrolyte interface and combination/recombination in space region (s)
N_p	the concentration of holes per area at the moment with light on (cm^{-2})
N_n	the concentration of electrons per area at the moment with light on (cm^{-2})
k_0	Boltzmann constant ($J\,K^{-1}$)
T	thermodynamic temperature (K)
$1/\alpha$	the depth penetration of the incident light (cm)
L	the thickness of the external part of the film (cm)

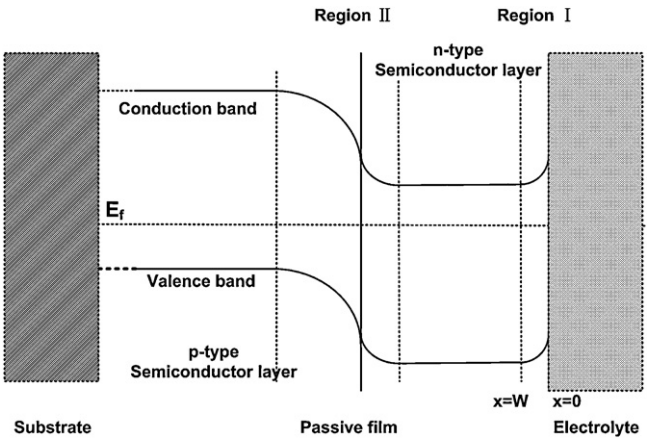

Fig. 1. Schematic illustration showing electronic structure of duplex oxide films formed on 304L SS in high temperature water.

Sugimoto [7] pointed out from an analysis of transient photocurrent and photo-induced potential difference measured for CVD·α·Fe_2O_3 that the transient photocurrent behavior can be explained by the accumulation of photo-induced carriers in the surface states on the film.

The theories mentioned above could only analyze the waveforms like pattern A to pattern D. More recently, relevant experimental and theoretical studies have been carried out. Some investigators made the simple quantitative interpretation for pattern A and pattern B by equivalent circuit [2,9]. Azumi et al. [8] analyzed a simulation to explain the transient behavior of the photocurrent by assuming an equivalent circuit with generation of a photo-induced free carrier pair in the n-type passive film on iron in pH 6.5 borate solution, and explained the dependence of photocurrent responses on the thickness of the passive film, the recombination rate of photo-induced carriers in the film, the density of surface states, and the charge transfer from or to the redox system in the solution. Others analyzed qualitatively the photocurrent waveforms for pattern A to pattern D by using band model [2] and other methods [8–10]. Silver et al. [9] had shown an elementary Monte Carlo approach which can calculate the main features of the experimentally observed transient photocurrent in low mobility material. Azumi et al. [10] attributed the photocurrent transient curves measured on oxide layer in TiN to the charge or discharge of free carriers. They proposed that the values of photocurrent spike reflected the charging/discharging process of the photo-induced free carriers, and the polarity of steady photocurrent depended on the potential. Hoffman et al. [11] proposed that the photocurrent

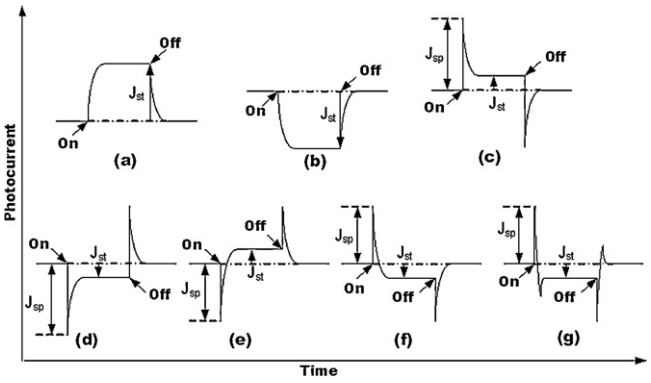

Fig. 2. Various patterns of transient photocurrent response for oxidation films formed on metal surface.