Photoelectrochemical Properties of Anodic Oxide Film on Niobium

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Photoelectrochemical properties of niobium oxide film formed by anodic oxidation in a saturated boric acid solution have been studied. The oxide film is considered as an n-type semiconductor from the polarization curves measured in 0.5N sulfuric acid solution. Anodic photocurrent is observed when the oxide film is illuminated by an ultraviolet light while it is anodically polarized. From the spectrum of the photocurrent of the film, the band gap energy of the oxide is determined to be about 3.3 eV.

When the specimen is polarized at a cathodic potential before the photocurrent measurements, the film shows an additional photoresponse for the light with longer wavelength than that corresponds to the band gap energy. This can be explained by the formation of new electron levels in the band gap by cathodic hydrogen charging.

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I. Introduction

Photoelectrochemical reactions of semiconductor electrodes have been studied extensively in recent years for the application to solar energy conversion. Especially, TiO_2 has been the material examined for the photoanode in photoelectrochemical cells⁽¹⁾. On the other hand, since the photoelectrochemical behavior of semiconductive oxides gives much information about electrical and optical properties of the oxide, photoelectrochemical measurements have also been used for studying passivation of metals and alloys, e.g. iron, stainless steels, and some valve metals⁽²⁾⁽³⁾. The photoelectrochemistry would have a great deal of possibilities and importance in studying the electrical and optical properties of oxides formed on metals and alloys.

Among the oxides of valve metals, the niobium oxide has been known to be stable and insoluble in various solutions⁽⁴⁾, and it has been studied in terms of the properties of electrochromism⁽⁴⁾⁽⁵⁾ and metal/oxide diode⁽⁶⁾. Reichman *et al.* reported that niobium oxide showed coloration by cathodic hydrogen charging in sulfuric acid. Hayashi *et al.*⁽⁵⁾ studied its spectroscopic and optical properties. Sciri *et al.*⁽⁶⁾ studied niobium oxide/metal diode, and discussed the mechanism of electron conduction at the contact of metal/oxide. But there are few reports on photoelectrochemical studies of niobium oxide⁽⁷⁾. In this work, the photoelectrochemical properties of the niobium anodic oxide film have been studied, and the effects of cathodic hydrogen charging on these properties are discussed.

II. Experimental Procedure

The oxide film was formed by anodic oxidation on a

niobium sheet. Before the oxidation the niobium sheet was mechanically polished and etched in a solution of 15HF, 85HNO₃ (parts by volume). For the oxidization, a saturated boric acid solution was used at 293 K. The sheet was oxidized at a constant current of 10 A/m² until the cell voltage reached 210 V, and then held at this voltage for 10 min. A platinum sheet was used for a counter electrode. This specimen was sealed by silicone sealant except for the area of 1.2 cm² on one surface, and was used for electrochemical experiments.

The equipment of the photoelectrochemical measurements is shown in Fig. 1. A three electrode cell having a quartz window was used. The specimen or working electrode was kept at various steady potentials by a potentiostat (Hokuto Denko HA-301) and the controlling currents were measured. The counter electrode was a plati-

Fig. 1 Equipment for photoelectrochemical measurements.

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num sheet, and the reference electrode was a saturated Ag/AgCl electrode (0.1999 V vs NHE at 298 K, all the electrode potential in this paper is referred to this electrode). The electrolyte used in the photoelectrochemical measurements was mainly 0.25 kmol/m³ H₂SO₄. Solutions having pH values ranging from 2 to 13, prepared from 0.25 kmol/m³ H₂SO₄, 0.5 kmol/m³ Na₂SO₄ and 0.5 kmol/m³ NaOH, were also used for the measurement of pH dependence. All the experiments were done at a constant temperature, 298 K. The light source of a 150 W Xe lamp (Hamamatsu L2273) and a grating monochromator with cutoff filters (Nihon Bunko CT-10) were used to obtain a monochromatic light beam whose wavelength was chosen between 200 and 1000 nm. The light beam from the Xe lamp was intercepted by a shutter to a rectangular wave (0.1 to 0.25 Hz) and illuminated vertically to the specimen. The photocurrent was measured as a difference between the current under illumination and in dark. The absolute power of the illuminating light was measured by a silicon probe powermeter (Advantest Corporation TQ8210, TQ82017) and a photomultiplier (Hamamatsu R-375). The quantum efficiencies were calculated from the measured photocurrent as the flow rate of electrons induced per one incident photon.

III. Results and Discussion

The oxide film showed a brilliant interference color. The thickness of the oxide film was determined by the TEM observation of the cross section of the specimen; for example, the thickness of the film formed at the oxidation voltage of 210 V was about 0.5 μm. Since the thickness of the films were proportional to the oxidation voltage, the film formed by anodic oxidation is composed of a barrier layer.

1. Photoelectrochemical properties of the niobium oxide film

Figure 2 shows the polarization curves of the niobium oxide film under illumination and in dark. The potential was scanned from +4.0 V to less noble potentials, and the wavelength of the light was 310 nm. In the dark condition the film showed a good rectifying property, that is cathodic current flows under cathodic polarization but very low anodic current under anodic polarization. By the illumination of light, anodic photocurrent was observed at noble potentials. This shows that the oxide film has a characteristics of an n-type semiconductor.

Now, we define the flat band potential U_{fb} as the potential where the anodic photocurrent vanishes in scanning the electrode potential. This is an electrode potential at which the potential slope in the oxide becomes flat. The U_{fb} in 0.25 kmol/m³ H₂SO₄ was 0.2 V, and the U_{fb} shifted to less noble potential when the pH of electrolyte became higher. In the region of pH < 4 a linear relationship was obtained between U_{fb} and pH, and the slope was about 60 mV/pH. Therefore, the electrochemical reaction would involve one electron transfer. The value of U_{fb} determined by scanning the electrode potential from

Fig. 2 Current-Potential characteristics of a niobium oxide electrode in 0.25 kmol/m³ H₂SO₄. The potential was swept from anodic to cathodic direction. The sweep rate was 10 mV/s.

cathodic to anodic was lower than that determined by the reverse scan of the potential. The quantum efficiency is expressed by eq. (1) and means the flow rate of electrons induced per one incident photon:

$$\Phi = \frac{I_p h\nu}{Pe} \quad (1)$$

where I_p is the photocurrent (A), $h\nu$ the photon energy (eV[†]), P the illuminating light power (W) and e the charge of an electron 1.6×10^{-19} (C).

The quantum efficiency was calculated from the photocurrent measurements. The spectrum of the quantum efficiency, Φ , at the electrode potential of 1.0 V is shown in Fig. 3. In Fig. 3, the quantum efficiency increases in the region of the wavelength shorter than about 400 nm. In the region where photon energy is near the band gap energy, E_g , the light absorption coefficient, α , depends on the photon energy and expressed by the following equation⁽²⁾:

Fig. 3 Spectrum of quantum efficiency, Φ at the potential of +1.0 V.

[†] 1 eV = 0.160218 aJ

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (2)$$

where A is a constant. In eq. (2), $n=1/2$ describes the process of the photon absorption by direct transition, and $n=2$ corresponds to the indirect transition. On the assumption that Φ is proportional to α , the type of transition and a band gap energy can be determined from the plot of the following equation:

$$(\Phi h\nu)^{1/n} = A'(h\nu - E_g) \quad (3)$$

where A' is a constant. The plot $\Phi h\nu^{1/2}$ v.s. $h\nu$ with $n=2$ is shown in Fig. 4. A linear relationship obtained shows the excitation process of this film is an indirect transition. From the extrapolation of the plot the band gap energy of the oxide is determined to be about 3.3 eV. This value agrees well with the E_g value, 3.4 eV, of the niobium oxide obtained in sulfuric acid⁽¹⁾⁽⁷⁾.

From the results the energy diagram for the system, sulfuric acid/niobium oxide/niobium, at +1.0 V polarization is drawn as Fig. 5. Drawing the diagram we assumed that the oxide was an uniform n-type semiconductor and

Fig. 4 Plot of $(\Phi h\nu)^{1/2}$ against $h\nu$.

Fig. 5 Energy level diagram for the niobium/niobium oxide/0.25 kmol/m³ H₂SO₄ system.

the Fermi level of the oxide lay close to the bottom of the conduction band. We also assumed that the anodic electrochemical reaction in the electrolyte was an oxygen evolution. The photoelectrochemical behavior in this system is described as follows: At the interface of metal/oxide, since the work function of metal, ϕ_M , is smaller than that of oxide or semiconductor, $\phi_{sc}^{(6)}$, there will be no energy barrier formed. While at the oxide/electrolyte interface, the Schottky barrier and a space charge layer appear when the electrode potential is higher than the flat band potential, $U > U_{fb}$. And the photon energy of the illuminating light is higher than 3.3 eV of the band gap energy of the oxide; therefore electron and hole pairs are formed in the conduction and valence band respectively. By the potential slope in the space charge layer of the oxide, electrons are driven to the inside of the oxide and through the niobium metal to the external circuit. While holes are driven to the oxide/electrolyte interface and oxidize a reductant in the redox couple of the electrolyte; oxygen evolves.

2. The effect of hydrogen charging by cathodic polarization

In Fig. 6 the spectra of quantum efficiency of photocurrent after cathodic polarization are shown. The specimen was cathodically polarized at various potentials for 5 min and then polarized at +1.0 V. After 15 min holding at +1.0 V spectra of photocurrent were measured at this potential. An additional photo-response was observed in the longer wavelength region than that corresponds to E_g . When the cathodic polarization becomes less noble, the additional photo-response becomes more remarkable. The spectra in Fig. 6 have some peaks and valleys. These peaks and valleys agree with the interference oscillation of the reflectivity spectrum of the oxide, so that this is also due to the interference of light in the oxide film.

The recovery of the additional photo-response during the anodic potential hold is shown in Fig. 7. The specimen was cathodically polarized at -1.0 V for 1 min and polarized at +1.0 V, and the photocurrent spectra were measured after 15, 45, 750 min holding and also after

Fig. 6 Spectra of quantum efficiency after cathodic polarization at various potentials.

Fig. 7 Transient property of the spectrum of quantum efficiency after cathodic polarization.

illumination with lights of 520 nm for 60 min additionally. During anodic polarization at +1.0 V, the additional photo-response in the longer wavelength region decreases with the holding time. The rate of decrease of this photo-response is accelerated by the illumination with lights. By the illumination with lights and a prolonged anodic polarization, the quantum efficiency additionally observed in the long wavelength region vanishes and the property before the cathodic polarization is recovered.

The change of quantum efficiencies at various wavelengths, which are longer than that of the band edge, is shown in Fig. 8 with the amount of electric charge in galvanostatic cathodic polarization. The electrode was polarized with the current density of $-40 \mu\text{A}/\text{cm}^2$ for various periods of time, then anodically polarized at +1.0 V for 15 min, and the quantum efficiencies were measured at this potential subsequently. The quantum efficiencies become larger with the increase in electric charge in cathodic polarization. The change in the quantum efficiencies at long wavelengths considered to be related to the amount of hydrogen introduced by electrochemical charging.

The same effect has been reported on Ta_2O_5 in a review article by Stimming⁽²⁾, but none on niobium oxide. Ac-

Fig. 8 Quantum efficiencies at 407 and 560 nm as a function of electrolytic charge in the galvanostatic cathodic polarization.

cording to Stimming defects created in Ta_2O_5 by hydrogen penetration or a partial reduction of the film during the cathodic pretreatment gives rise to the sub-bandgap response. The effect of cathodic polarization on photoelectrochemical properties in TiO_2 was reported by Clechet *et al.*⁽⁸⁾. Using a nuclear analysis they confirmed that hydrogen was introduced into TiO_2 after the cathodic polarization. They also showed that photocurrent increased by the cathodic polarization, though they showed no spectroscopic data of photoresponse. The occurrence of photoresponse or light absorption band at a longer wavelength than that of the fundamental band edge induced by ion implantation has also been reported by other authors⁽²⁾⁽⁹⁾.

Some transition metals show the electrochromic coloration by cathodic hydrogen charging in aqueous solutions. In Fig. 9 the reflectivity spectra at various electrode potentials in $0.25 \text{ kmol}/\text{m}^3 \text{ H}_2\text{SO}_4$ for niobium oxide formed by thermal oxidation in air are shown. At +1.0 V, the absorption edge exists around 350–400 nm. This wavelength corresponds to the E_g value of 3.3 eV obtained by the photoelectrochemical experiments. At this potential the oxide film is free from hydrogen. As the electrode potential becomes less noble the reflectivity reduces in the region of the longer wavelengths than the absorption edge. The decrease in reflectivity becomes more pronounced as the electrode potential becomes less noble. The mechanism of this coloration would be described by the following equation⁽⁴⁾:

By the cathodic polarization, protons are introduced from the electrolyte interface and electrons from backward contact, then oxide becomes colored $\text{H}_x\text{Nb}_2\text{O}_5$. This proton injection is considered to be the origin of the additional photo-response observed in the longer wavelength region.

We propose following explanation for the additional photo-response: Hydrogen introduced in the oxide by the cathodic polarization forms new electron levels as donor or acceptor in the band gap of the oxide. The photo-excitations by the lights with a lower energy than

Fig. 9 Spectra of reflectivity of a niobium oxide prepared by thermal oxidation.

the band gap energy become possible. Then the photo-response to lower energy photons comes up. Hydrogen charged by the cathodic polarization is extracted by the anodic polarization. A complete extraction of hydrogen needs a great deal of time without illumination, so this photoresponse can be observed when the electrode is polarized anodically.

In Figs. 6 and 9, the photo-response band and the absorption band, induced by hydrogen charging, lie in the wavelength region from the intrinsic band edge to longer wavelengths, and no clear cut-off energy is observed. Therefore, the newly formed electron levels exist in a wide energy levels between valence band and conduction band of the oxide and no definite impurity level is formed.

In the measurements of polarization curve the onset potential of the anodic photocurrent during the potential scanning from cathodic potential to anodic was less noble than the potential of zero photocurrent in the inverse potential sweep. In other words, the value of U_{fb} changed after the cathodic polarization. This result suggests that the electron states in the oxide changes by hydrogen charging.

The recovery rate of hydrogen induced additional photocurrent was accelerated by the illumination with lights. That is, the release of hydrogen from the oxide is accelerated by the illumination. Lower energy of the illuminating light than the intrinsic band gap energy was also effective for the acceleration of the hydrogen extraction. It seems that hydrogen ion conduction in the space charge region of the oxide film would participate in this recovery process. A further investigation on the behavior of ions

in the oxide is still required in order to make clear this effect.

IV. Conclusions

Photoelectrochemical properties of a niobium oxide formed by anodic oxidation in a boric acid solution have been studied. The main conclusions are as follows:

(1) Anodic photocurrent is observed when the oxide is illuminated by an ultraviolet light. The niobium anodic oxide film is an n-type semiconductor with a band gap energy of about 3.3 eV.

(2) After the cathodic polarization an additional photoresponse, which is excited by the illumination with lights with a wavelength longer than the intrinsic band edge wavelength, is observed. This is attributed to the formation of new electron levels by cathodic hydrogen charging.

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