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Photoelectrochemical study of hydrogen in zirconium oxide

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Abstract

The chemical states of hydrogen in a zirconium oxide film were studied by photoelectrochemical (PEC) measurements and electrochemical impedance spectroscopy (EIS) measurements. The oxide films were prepared by the oxidation of a zirconium sheet (purity 99.7%) in air at 673 K for 18 h. In order to obtain a hydrogen-implanted oxide film, the oxide film was implanted with 100 keV H^+ ions to a dose of 10^{17} cm^{-2} at room temperature. From the PEC measurements, the band gap energy for the hydrogen-free oxide film was determined to be about 4.8 eV and it was reduced to 3.5 eV by hydrogen implantation. The distribution of the carrier density in the band gap was obtained by EIS measurements using Mott–Schottky analysis. Hydrogen implanted into the oxide film caused the impurity level in the original band gap. This result was consistent with that of PEC measurements. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photocurrent; Photoelectrochemistry; Zirconium oxide film; Hydrogen; Impurity level

1. Introduction

Zirconium alloys have been widely used as cladding materials for light water reactors (LWRs). In recent years, the behavior of hydrogen in the cladding has been studied because of the high burn up of nuclear fuel required for economic reasons. Oxidation of the alloy involving hydrogen absorption through the oxide film determines the lifetime of the fuel cladding. However, the chemical states of hydrogen in zirconium oxide films are not known.

Photoelectrochemical (PEC) measurement is now recognized as being a useful tool for investigating the electronic structure of metal oxides. Photoelectrochemistry has been developed for studying oxide electrodes, especially TiO_2 [1,2]. The effect of hydrogen charging on the PEC properties of TiO_2 has also been investigated [3–5]. Oxide electrodes can readily be modified by hydrogen charging during electrochemical measurements. Photoelectrochemistry, therefore, is a useful method for studying the properties of hydrogen in oxides. In the present study, the PEC properties of a zirconium oxide film with or without hydrogen were studied, and the distribution of the impurity level induced by hydrogen charging discussed.

2. Experimental

Zirconium electrodes were cut in the form of a disk (about 23 mm×15 mm) from a commercial zirconium sheet (Nilaco) of 99.7% purity and 1.0 mm thickness. Before oxidation, all the specimens was placed in a vacuum (~10^{-6} Torr) at 523 K for 3 h in order to remove adsorbed gases on the surface; zirconium specimens were oxidized in air at 673 K for 18 h to form thin oxide films on the surface. In order to produce a hydrogen-implanted oxide film, the oxide film was implanted with 100 keV H^+ ions to a dose of 10^{17} cm^{-2} at room temperature. The electrodes used for electrochemical measurements were made by spot-welding a zirconium wire onto a section of the backside of the specimen to eliminate the oxide film and to ensure an ohmic contact throughout the experiment. The wire and the specimen were covered with insulating silicon sealant (GE Toshiba Silicone, TSE392-C) except for an area of 0.56 cm^2 (0.8 cm×0.7 cm) exposed to the aqueous solution and light illumination.

A schematic diagram of the experimental apparatus for the PEC measurements is shown in Fig. 1. The experiments were conducted at room temperature in a three-electrode PTFE (polytetrafluoroethylene) electrochemical cell with quartz optical window through which light could illuminate the surface of the specimens. A saturated Ag/AgCl (in sat. KCl) electrode as the reference electrode and a square platinum foil (Nilaco) as the counter electrode

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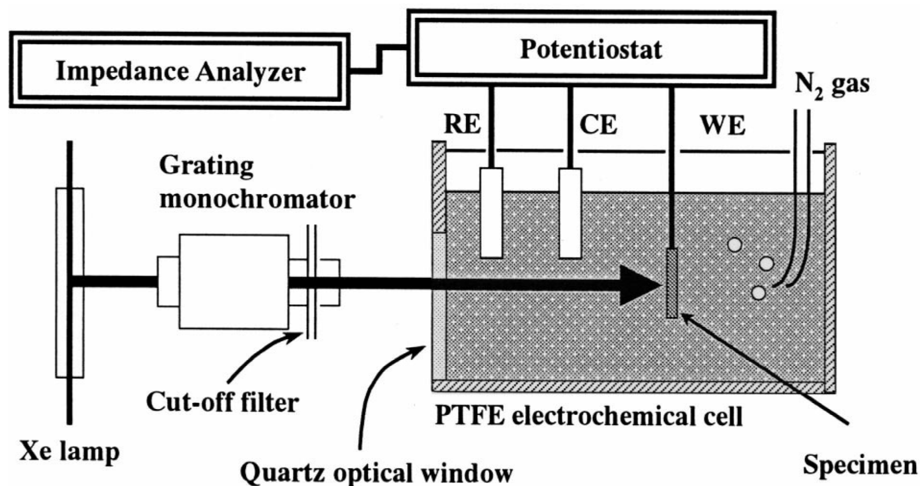

Fig. 1. Schematic diagram of the experimental apparatus for PEC measurements.

were purchased from commercial sources and used without any further purification. All electrochemical measurements were carried out in aqueous solutions containing 0.25 M H_2SO_4. The PEC measurements were performed in an optical setup consisting of a 150 W Xe lamp (Hamamatsu, L2273) used as the light source and a grating monochromator with cut-off filters (Bunkou Keiki, M10-T), which allows monochromatic illumination. The samples were vertically illuminated. The system was interfaced to a computer with a data acquisition system (Scribner Associates, CorrWare ver. 2.1). The photocurrent was evaluated as the change in the current due to exposure to the light. The absolute power of the light beam was measured by a silicon probe powermeter (Ophir Optronics, Nova PD300-UV).

Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 10^5 to 5×10^{-4} Hz under alternating current conditions with an a.c. voltage amplitude of 100 mV utilizing an Impedance/Gain-Phase Analyzer system (Solartron, SI 1260) coupled to the potentiostat used in the PEC measurements.

3. Results and discussion

3.1. Photoelectrochemical properties of the zirconium oxide film

The polarization curves show that the hydrogen-free and hydrogen-implanted zirconium oxide films behave as n-type semiconductors. The flat-band potential (U_{fb}), which is defined as the potential at which there is no band bending in the semiconductor and the anodic photocurrent vanishes, is shown in Fig. 2, a plot of the photocurrent vs. applied potential, producing a straight line with intercept U_{fb} on the abscissa. The U_{fb} measured in 0.25 M H_2SO_4 with respect to a Ag/AgCl (in sat. KCl) electrode was −1.29 V for the hydrogen-free oxide film, and −0.27 V for the hydrogen-implanted oxide film. According to the literature [1,6], U_{fb} for a semiconductor electrode in aqueous solution exhibits a pH dependence, 59 mV/pH. The U_{fb} shifts to a more negative potential when the pH of the electrolyte increases. Clechet et al. observed the U_{fb} of hydrogen-free ZrO_2 at pH 7 and reported a value of −1.5 V vs. SCE [7]. Since the electrode potential measured with respect to SCE differs from that measured with respect to a Ag/AgCl (in sat. KCl) electrode by 0.04 V at 25°C, we corrected the value (U_{fb} vs. SCE=−1.5 V at pH 7) to that with respect to Ag/AgCl (in sat. KCl) at pH 1.1 assuming a shift of 59 mV per pH unit. The corrected U_{fb}, now with a Ag/AgCl (in sat. KCl) electrode as reference, was −1.19 V, which is slightly more positive than our values for the hydrogen-free oxide film. However, U_{fb} for the hydrogen-implanted oxide film was quite different from that for the hydrogen-free oxide film. This result shows that the energy

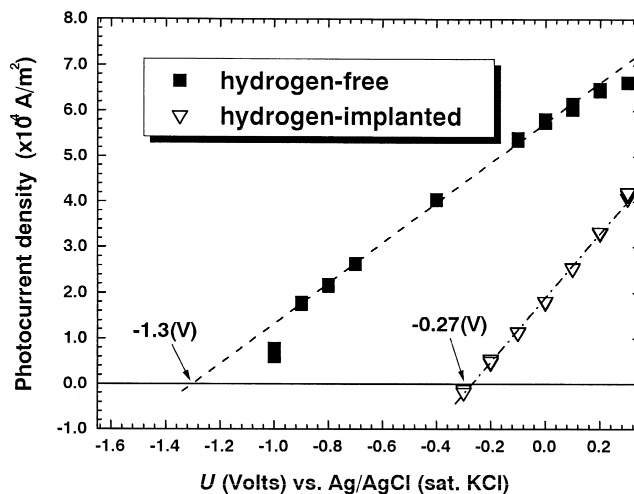

Fig. 2. Plot of photocurrent density versus applied potential U vs. Ag/AgCl (in sat. KCl) with Xe light illumination at 230 nm producing a straight line with intercept U_{fb} on the abscissa.

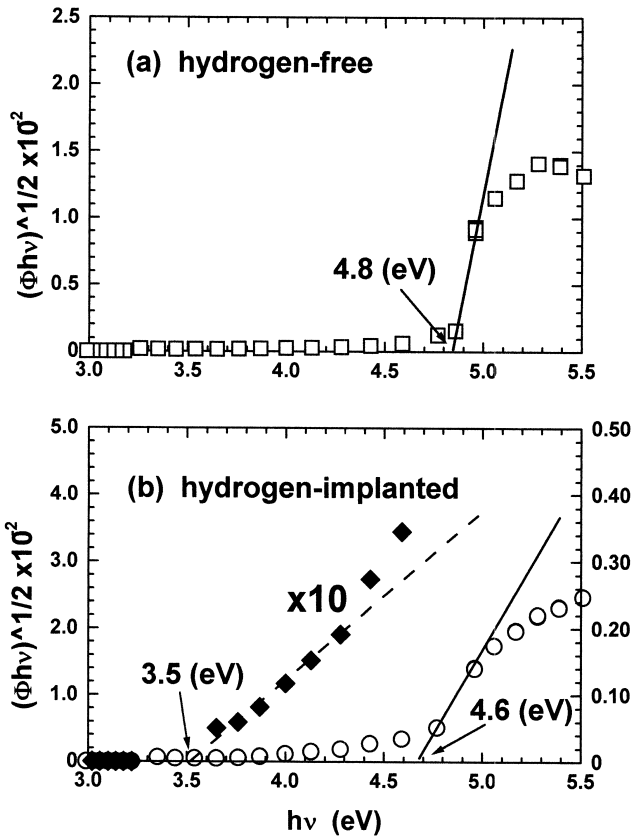

Fig. 3. Quantum efficiency spectrum for (a) the hydrogen-free and (b) the hydrogen-implanted oxide film at a potential of U_{fb} +1.0 V with Xe light illumination of 200–350 nm in 0.25 M H_2SO_4 solution.

level structure is somewhat changed and the original band gap energy is reduced by hydrogen implantation.

The slopes of the lines in Fig. 2 correspond to the electrical conductivity of the oxide [8]. The slope for the hydrogen-free oxide film was relatively smaller than that for the hydrogen-implanted oxide film. The difference between the slopes of the hydrogen-free and hydrogen-implanted oxide films, the film thicknesses being almost the same, suggests that the electrical conductivity of the hydrogen-implanted oxide film was higher than that of the hydrogen-free oxide film.

The photocurrent action spectrum of each specimen as a function of the photon energy, $h\nu$, is plotted in Fig. 3. The value of the quantum efficiency, Φ, in Fig. 3 was calculated using

$$\Phi = \frac{I_p h\nu}{Pe} \tag{1}$$

where P is the illuminating light power (W) and e is the charge of the electron, 1.6×10^{-19} C. In the photocurrent action spectrum measurement, the applied potential of each specimen was held at the value U_{fb} +1 V vs. Ag/AgCl (in sat. KCl). In Fig. 3, the hydrogen-implanted oxide film shows an increase in quantum efficiency for 270–350 nm compared with the hydrogen-free oxide film. This is further evidence that the band gap energy is reduced by hydrogen implantation.

The absorption coefficient, α, of a crystalline material depends on the photon energy, $h\nu$, according to the equation

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

where E_g is the semiconductor band gap energy, A is a constant and n is an integer which depends on whether the electron excitation is direct ($n = 1$) or indirect ($n = 4$). On the assumption that Φ is proportional to α, the type of transition and the band gap energy can be determined from a plot of the equation

$$(\Phi h\nu)^{2/n} = A'(h\nu - E_g) \tag{3}$$

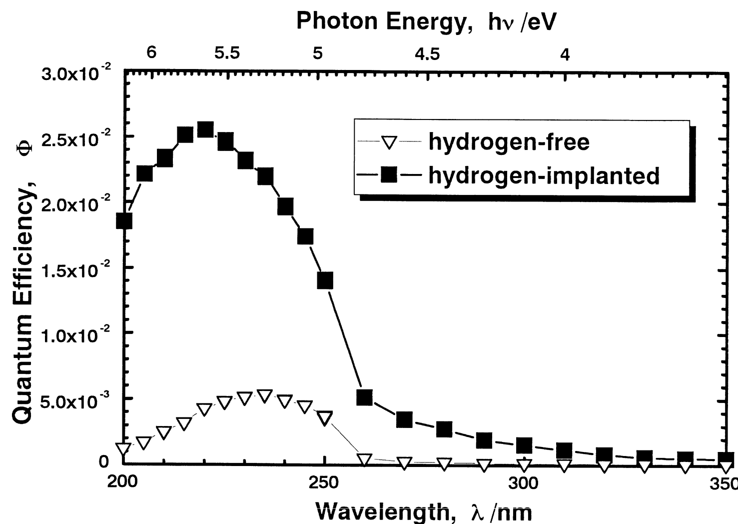

Fig. 4. Plots of $(\Phi h\nu)^{1/2}$ versus photon energy for (a) the hydrogen-free and (b) the hydrogen-implanted oxide film. The additional photoresponse of the hydrogen-implanted oxide film is magnified 10-fold.

where A' is a constant [9–12]. Fig. 4 shows plots of $(\Phi h\nu)^{1/2}$ vs. $h\nu$. A good linear relationship was obtained near the band gap energy for each specimen for the hypothesis of indirect (non-direct for amorphous materials) optical transitions. Plots with $n = 1$ did not yield straight lines for all oxide films. This indicates that the excitation process of all oxide films is an indirect transition. From extrapolation of the plots near the band gap, the band gap energy for the hydrogen-free oxide film was estimated to be 4.8 eV. This value agrees well with the previously reported band gap energy for anodic ZrO_2 films of 4.8 eV [13,14]. The plots for the hydrogen-implanted oxide film show that the band gap energy was reduced to 3.5 eV. This may be attributed to the formation of a new impurity level in the band gap by hydrogen implantation.

3.2. Distribution of electron states induced by hydrogen charging

In order to verify the results obtained by our PEC measurements, the distribution of the carrier density in the band gap was estimated from the EIS using the Mott–Schottky relationship. This relationship is represented by the equation

$$\frac{1}{C^2} = \frac{2}{e\varepsilon\varepsilon_0 N_d}(U - U_{fb}) \tag{4}$$

where ε is the dielectric constant, ε_0 is the permittivity in vacuum and N_d (impurity density) is the carrier density. A detailed description of the Mott–Schottky analysis has been reported previously [5,15]. As seen in Fig. 5, a new peak appears at about 1.5 V for the hydrogen-implanted oxide film. The remarkable change in the distribution with hydrogen implantation is possibly due to the formation of an impurity level in the original band gap. The value of the band gap energy conflicts with that of the PEC measurements for the hydrogen-implanted oxide film, 3.5 V. The photocurrent detection limit for light illumination above 350 nm in our experimental system was mostly responsible for the discrepancy. However, it should be noted that the EIS result is qualitatively consistent with the PEC results in that the decrease of the band gap energy can be explained as the production of an impurity level in the band gap.

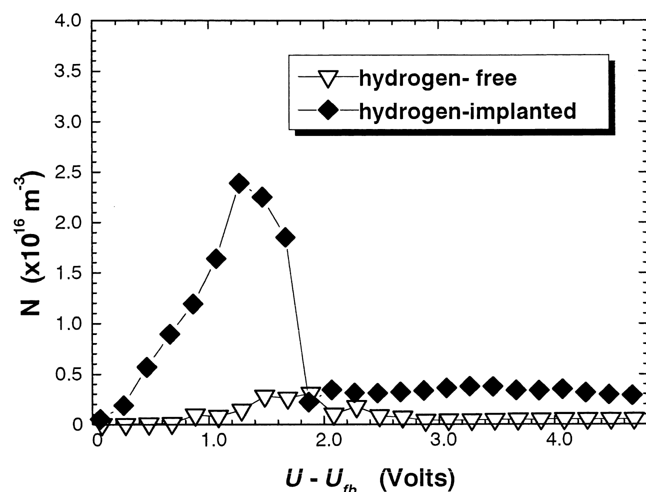

Fig. 5. Mott–Schottky plots measured in 0.25 M H_2SO_4 solution. The carrier density, N, is shown as a function potential, $U - U_{fb}$.

4. Conclusion

The effect of hydrogen implantation into a zirconium oxide film was studied by PEC measurements and Mott–Schottky analysis. Hydrogen implantation into the oxide film produced an additional PEC response for light with a wavelength longer than that corresponding to the band gap energy of the hydrogen-free oxide film. This additional response was explained by the formation of an impurity level in the original band gap. The distribution of the carrier density obtained by Mott–Schottky analysis showed that only the specimen containing hydrogen formed the new impurity level in the band gap. The hydrogen implanted into the zirconium oxide film caused the impurity level in the band gap and reduced the band gap energy.

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