Mechanism of Stabilization of ZnO Photoanodes in High pH Solutions

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(Received February 16, 1989)

Stabilization of ZnO photoanodes was investigated using ZnO thin film electrodes under controlled potential in various pH solutions; the effects of light intensity and agitation were also studied. The photocorrosion of ZnO photoanodes was suppressed at sufficiently cathodic potentials and/or at low light intensity. Agitation of solution also suppressed photocorrosion. On the basis of the experimental results, the mechanism of the stabilization in high pH solutions is discussed and a model is proposed.

Zinc oxide (ZnO) is one of the most popular semiconductor photoelectrodes. Although it shows a large anodic photocurrent, it has been difficult to use ZnO for solar energy conversion[1] or photoelectrochemical synthesis[2-4] because of its photocorrosion.[5-10] We recently showed that ZnO photoanodes could be stabilized in high pH solutions,[11,12] but the mechanism of the stabilization still remains unknown. On the other hand, the photocorrosion of ZnO can be used for other applications such as imaging systems,[13] and micro-processing of ZnO for optoelectric devices.[14,15] In these systems, it is necessary to control film thickness, and therefore speed of the photocorrosion, during the photoetching process. Thus it is still important to understand the details of the mechanism of the photocorrosion of ZnO photoelectrodes. In the present work we studied the effects of pH of the solution, electrode potential, light intensity, and agitation of the solution on the photocorrosion of ZnO photoelectrode. We have developed a new simple technique for monitoring the dissolution of ZnO electrode. ZnO thin films on transparent SnO_2-coated glass were used as photoelectrodes. A change in thickness of the ZnO film was detected by observing a change in interference colors. In addition, the surface morphology could be monitored with a scanning electron microscope. The experimental results are explained in terms of competition between the photocorrosion of ZnO and the oxidation of hydroxide ion in the electrolyte solution.

Experimental

A ZnO thin film was deposited onto a SnO_2-coated glass (Asahi Glass Co., Ltd.) by a spray-pyrolysis technique.[16] Figure 1 shows the structure of the ZnO film electrode. The thickness of the film was estimated to be 200±20 nm. X-Ray diffraction analyses showed that the c-axis was oriented vertically to the surface. The photocorrosion of ZnO was investigated under a controlled bias in a solution of $NaClO_4$ (0.2 mol dm^{-3}) containing an adequate amount of NaOH for pH control. A He-Cd laser (Kinmon Denki Co., Ltd. wavelength 325 nm, output 8 mW) was used as a light source; the diameter of the light beam was controlled with a quartz lens so that the incident photon flux was maintained constant.

The amount of charge passed, C, which resulted in the dissolution of the irradiated spot of the ZnO films, can be calculated as follows:

$$C = \frac{\pi \cdot r^2 \cdot d \cdot D \cdot n \cdot F}{4 \cdot M} \quad (1)$$

Here r is beam diameter, d thickness of the films, D the specific gravity of ZnO, n number of electrons transferred, F the Faraday constant, and M formular weight of ZnO. For n=2, r=1.2±0.1 mm, and d=200±20 nm, C is 2—4 mC. However, the photocurrent from SnO_2 must be taken into account as a background. Thus, characterization of the electrode surface was carried out after a charge of 5 mC was passed, which took several minutes under the present conditions.

The relation between the interference color and the thickness of the film can be written as follows

$$4 \cdot n \cdot d = (2 \cdot M + 1) \cdot \lambda \quad (2)$$

Here, d is the thickness of the film, n the refractive index of

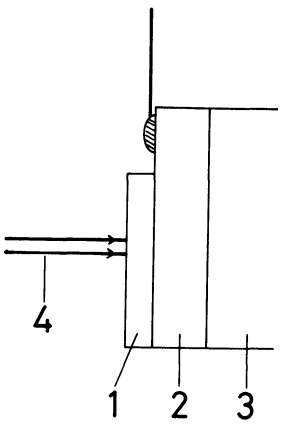

Fig. 1. The structure of the ZnO film electrode. 1: ZnO film, 2: SnO_2 layer, 3: glass substrate, 4: laser beam.

ZnO, λ the wave length of the interference light, and M an integral constant. Since the refractive index of ZnO is about 2.0, $\lambda=8\cdot d$ when $M=0$, and a change in λ of ca. 40—50 nm can be detected by the observation with naked eyes. Thus a thickness change of 5 nm could be easily detected. When the interference color of the irradiated spot was the same as that of the substrate SnO_2 film, it was judged that the ZnO film had completely been removed. When there was no change in the interference color after the irradiation, it was regarded that photocorrosion did not occur. Between these two cases, it was concluded that incomplete photocorrosion had occurred.

Results

Figure 2 shows the typical current-time curves for the following three cases; no ptotocorrosion, incomplete photocorrosion and complete photocorrosion. Since the power of the light beam was 8 mW and the irradiated area was 1.3 ± 10^{-2} cm^2, the light intensity was calculated to be 0.6 W cm^{-2}. The quantum efficiency of the ZnO photoelectrodes used here is 40—70% in ordinary circumstances. However, the total quantum efficiency was decreased to 10—20% under these experimental conditions, because the light intensity was so high that the recombination of the carrier occurred. In addition, I_{ph} was not saturated at the potential regions employed here. Thus, it is reasonable that the I_{ph} values observed here were smaller than that expected from the amount of incident photons. When the photocorrosion did not occur (Fig. 2(a)), I_{ph} was almost constant. Figure 2(b) corresponds to the cases with incomplete photocorrosion. I_{ph} initially showed a large decrease and then became almost constant. These two results imply that reaction other than photocorrosion takes place at the electrode surface. This reaction is the oxidation of OH^- ions to gaseous oxygen. However, we could not visually detect gas evolution because of the small photocurrent. Figure 2(c) shows the case of complete photocorrosion; I_{ph} exhibited a large decrease after an initial small increase. The photocorrosion roughens the electrode surface, and thus increases the surface area. This is the reason why I_{ph} increases at first. The thickness of the ZnO film decreases with the occurrence of photocorrosion, and consequently I_{ph} decreases. A small constant I_{ph} is probably due to I_{ph} from the SnO_2 substrate.

It was found that pH of the solution, electrode

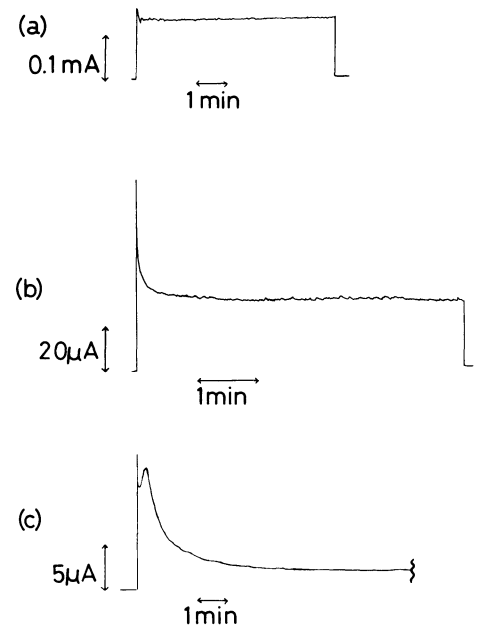

Fig. 2. Typical current-time curves: light intensity 0.6 W cm^{-2}. (a) pH 13, −0.3 V vs. SCE: no photocorrosion. (b) pH 12, −0.1 V vs. SCE: incomplete photocorrosion. (c) pH 11, 0.0 V vs. SCE: complete photocorrosion.

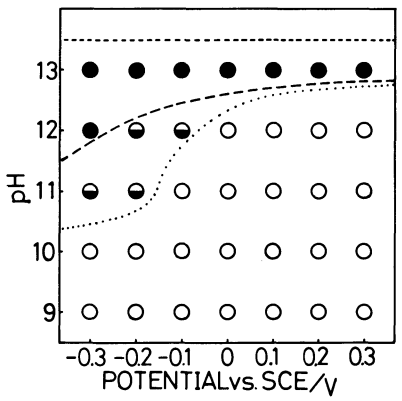

Fig. 3. Summary of the effects of pH and potential. ○: complete photocorrosion. ◒: incomplete photocorrosion. ●: no photocorrosion.

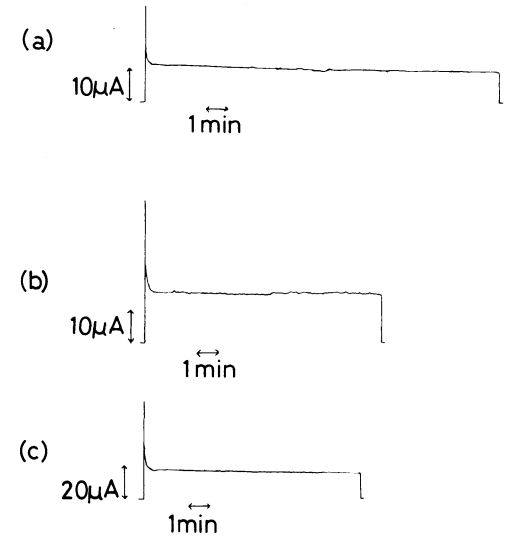

Fig. 4. Photocurrent-time curve in a pH 12 solution, light intensity 0.6 W cm^{-2}. (a) potential −0.3 V vs. SCE. (b) potential −0.2 V vs. SCE. (c) potential −0.1 V vs. SCE.

potential, light intensity and agitation of the solution affected the photocorrosion of ZnO. The effects of the electrode potential and pH of the solution are summarized in Fig. 3 (light intensity 0.6 W cm^{-2}, in stationary solution). The effect of electrode potential was apparent in the region near 0 V vs. SCE. The I_{ph} increases with the electrode potential in this potential region. From pH 7 to 10, the photocorrosion was observed for all the applied potentials. The photocorrosion was incomplete at −0.3 V vs. SCE for pH 11 and at −0.2 to −0.1 V vs. SCE for pH 12. The photocorrosion was not observed at −0.3 V vs. SCE for pH 12 and in the potential region from −0.3 to −0.8 V vs. SCE for pH 13.

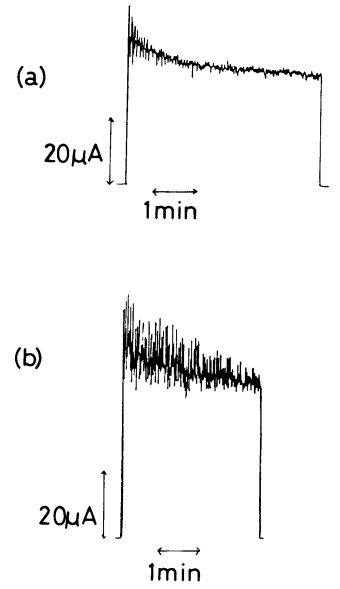

Fig. 5. Photocurrent-time curve in an agitated solution, pH 12, light intensity 0.6 W cm^{-2}. (a) potential −0.1 V vs. SCE. (b) potential 0.0 V vs. SCE.

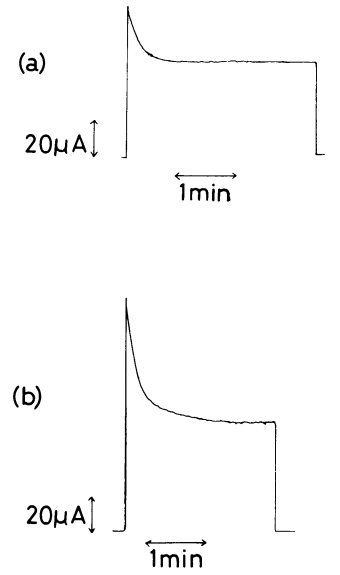

Fig. 6. Photocurrent-time curve in pH 12 solution, light intensity 0.1 W cm^{-2}. (a) Potential −0.1 V vs. SCE. (b) Potential 0.0 V vs. SCE.

The effects of agitation and light intensity are shown in Figs. 4—6. Photocorrosion was observed in a stationary solution of pH 12 when the light intensity was 0.6 W cm^{-2} and the electrode potential was −0.1 V vs. SCE (Fig. 4(c)), but it was not observed when the solution was agitated (Fig. 5(a)) or when the light intensity was 0.1 W cm^{-2} (Fig. 6(a)).

Discussion

Here we consider the competition reaction between the photocorrosion and the oxidation of OH^- ions in order to explain the experimental results observed. The photocorrosion of ZnO and the oxidation of OH^- can be summarized by Eqs. 3—8.

$$ZnO + h\nu \longrightarrow ZnO + p^+ + e^- \quad (3)$$

$$ZnO + 2p^+ \longrightarrow Zn^{2+} + \cdot O \quad \text{(slow)} \quad (4)$$

$$OH^- + p^+ \longrightarrow \cdot OH \quad \text{(slow)} \quad (5)$$

$$Zn^{2+} + nH_2O \longrightarrow Zn^{2+}(H_2O)_n \quad \text{(fast)} \quad (6)$$

$$2\cdot O \longrightarrow O_2 \quad \text{(fast)} \quad (7)$$

$$2\cdot OH \longrightarrow H_2O + 1/2O_2 \quad \text{(fast)} \quad (8)$$

We did not consider the chemical dissolution of ZnO which takes place at extremely high pH and low pH. The rate-determining step of the photocorrosion is given by Eq. 4 and that of the oxidation of OH^- by Eq. 5. Now, we write the rate of the reaction (4) as V_1 and that of the reaction (5) as V_2. According to this model, the current efficiency of the ZnO decomposition, C_d becomes as follows,

$$C_d = \frac{V_1}{V_1 + V_2} \quad (9)$$

The steady state is attained with respect to the surface concentrations of OH^- ion and p^+ when the photocurrent is constant with time. These conditions are satisfied when the thickness of the ZnO films is sufficiently larger than that of the space charge layer, or when the photocorrosion does not occur. The following relations hold under the steady state;

$$I_p = V_1 + V_2 \quad (10)$$

$$f = V_2 \quad (11)$$

Here I_p and f denote the photocurrent density and the current density induced by the flux of OH^- ion, respectively. We obtain the following equation by using Eqs. 9—11.

$$C_d = \frac{I_p - f}{I_p}$$

$$= 1 - \frac{f}{I_p} \quad (12)$$

This analysis shows that C_d is determined by I_p and f. I_p is a function of the electrode potential and the light intensity. The flux f is a function of the thickness of the diffusion layer (d), concentration of OH^- ion in bulk ($[OH^-]_b$) and at surface ($[OH^-]_s$). The conditions where the photocorrosion does not occur, that is, $C_d=0$ can be realized when $I_p=f$. When diffusion along the surface is neglected, f can be approximately expressed as

$$f = \frac{D}{d} \cdot F \cdot ([OH^-]_b - [OH^-]_s) \quad (13)$$

Here D is the diffusion coefficient of OH^- ions, F the Faraday constant. We write the f as f_{max} when $[OH^-]_s$ is zero. Under the conditions where d and $[OH^-]_s$ are constant, f_{max} is constant. When I_p is equal or smaller than f_{max}, $I_p=f$ is approximately realized, and consequently C_d becomes zero. When I_p is larger than f_{max}, $I_p=f$ cannot be realized then $C_d=1-f_{max}/I_p>0$, and photocorrosion occurs.

From the experimental results, we can make a quantitative analysis. The diffusion coefficient of OH^- ion, D, was estimated from the molar conductivity, to be ca. 3×10^{-5} cm^2 s^{-2}. The thickness of diffusion layer, d, can be estimated from the time needed for the photocurrent to become constant. It was ca. 3×10^{-3} cm when the light intensity was 0.6 W cm^{-2} for pH 12 ($[OH^-]_b=1\times10^{-2}$ mol l^{-1}), and photocorrosion was not observed. Under this condition, f_{max} becomes ca. 1×10^{-3} A cm^{-2}. We can compare this estimation with the results of Figs. 4(a) and 4(b). Photocorrosion was not observed for Fig. 4(a) where $I_p=8.8\times10^{-4}$ A cm^{-2}, and photocorrosion was observed for Fig. 4(b) where $I_p=1.2\times10^{-3}$ A cm^{-2}. These results support our competition model.

In an agitated solution of pH 12 (Fig. 5), photocorrosion was not observed even when I_p was 3.0×10^{-3} A cm^{-2} (Fig. 5(a)), but was observed when I_p was 4.2×10^{-3} A cm^{-2} (Fig. 5(b)). This result shows that the f_{max} value was 3—4 times larger than that in a stationary solution. This is because d was decreased by the agitation.

In the case where the light intensity was 0.1 W cm^{-2}, photocorrosion did not occur when I_p was 6.6×10^{-4} A cm^{-2} (Fig. 6(a)), but was observed when I_p was 8.8×10^{-4} A cm^{-2} (Fig. 6(b)). From the time needed for the photocurrent to become constant, d was estimated to be 4×10^{-2} cm, and f_{max} was calculated to be 7×10^{-4} A cm^{-2}. This f_{max} value is smaller than that estimated from Figs. 4(a) and 4(b). In the potential region employed in these experiments, the photocurrent was not saturated, so a large part of the energy of the incident photons was converted into heat. Thus, there was heat convection around the irradiated spot. In a stationary solution, this heat convection reduces the thickness of the diffusion layer. Thus when the light intensity is large, heat convection will be intense and the thickness of the diffusion layer will be small. Hence f_{max} for the light intensity of 0.1 W cm^{-2} became smaller than that for the light intensity of 0.6 W cm^{-2}.

Conclusion

Photocorrosion of ZnO is suppressed when the concentration of OH^- ion at the surface is large or when the concentration of p^+ at the surface is small. These results can be explained in terms of competition reaction between the oxidation of OH^- ion and the photocorrosion of ZnO.

We would like to thank Professor B. H. Loo for his kind advice and appreciate financial support from the Ministry of Education, Science and Culture, Grant-in-Aid.

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