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PHOTOELECTROCHEMICAL IMAGING PROCESSES USING SEMICONDUCTOR ELECTRODES

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Photoelectrochemical reactions at semiconductor electrodes in the solution with metallic ions have been applied to the reproducible image formation. Photo-images were the oxide layer in the case of an n-type semiconductor electrode and the metal layer in the case of a p-type semiconductor electrode.

Recently, extensive investigations have been carried out in the field of the photoimage formation employing non-silver halides. The principal interest in this field is focussed on the way of the conversion of light image into visible forms via the photochemical reactions or the photocatalytic reactions.$^{1,2)}$ Electrochromism and photochromism have been also investigated and developed to the imaging devices.$^{3-5)}$

Photoelectrochemical reactions on semiconductor electrodes have been extensively investigated primarily in connection with the solar energy conversion. At a stable photoelectrode such as TiO_2,$^{6)}$ the electrode reaction is the direct oxidation of water resulting in oxygen evolution by the action of holes (p^+) produced in the valence band;

$$2\,H_2O + 4\,p^+ \longrightarrow 4\,H^+ + O_2 \qquad [1]$$

Moreover, the redox reactions of other redox agents dissolved in the electrolyte solution can occur at the illuminated semiconductor electrodes;$^{7)}$

$$\mathrm{Red} + n\,p^+ \longrightarrow \mathrm{Ox} \qquad [2]$$

$$\mathrm{Ox} + m\,e^- \longrightarrow \mathrm{Red} \qquad [3]$$

Therefore, possibility of the photoimage formation has given rise to employing the photoelectrochemical reactions on semiconductor electrodes.

We describe a novel process of an image formation using semiconductor photoelectrodes. The present method of an image formation is different in principle from the former ones.$^{1-5)}$ This imaging system is constructed from a combination of a semiconductor electrode/a solution containing metal ions/a platinum electrode, accompaied with a light source and a voltage supply. Semiconductor materials used in this study were TiO_2 (single crystal, sintered polycrystal, and evaporated thin film), ZnO (single crystal and sintered polycrystal), CdS (single crystal and sintered polycrystal), and GaP (single crystal). For example, as for the ZnO electrode, a ZnO substrate was prepared by pressing a ZnO powder at ca. 1 ton/cm^2 and then sintering at 1300 °C for 2 hrs. Indium was vacuum-evaporated onto one face of the substrate in order to ensure an ohmic contact and a copper lead wire was connected to the indium layer with a silver paste. Then, the ZnO substrate was assembled on a glass plate using a epoxy resin. The surface of the semiconductor electrode was illuminated uniformly by 500 W Xe lamp through the glass cell window .

Photoimages were formed on the n-type or p-type semiconductor electrodes in the solution with metallic redox agents under irradiation with an absorbable light of semiconductors when the n-type semiconductors were polarized anodic or the p-type semiconductors were polarized cathodic. Image vanishing was achieved by the reverse polarization of the semiconductor electrodes. Figure 1 shows a brown image pattern clearly formed on the sintered ZnO photoelectrode in an aqueous solution containing Tl^+ when the electrode was polarized at 3.0 V vs. Pt for 5 seconds under the illumination with a light of ca. 10^{16} photons/sec from 300 to 400 nm.

Current-potential characteristics of this system was investigated by means of a potentiostatic measurement in combination with a platinum electrode as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode (see Figure 2). In darkness, any currents do not appear by the anodic polarization with or without Tl^+ in the solution. In the absence of Tl^+ ions in the electrolyte solution , the photocurrent (curve 1) appears at the potentials more positive than the flatband potential (ca. -0.5 V vs. SCE) of the ZnO photoelectrode due to the photoanodic decomposition reaction;[8)]

$$ZnO + 2\,p^+ \longrightarrow Zn^{2+} + 1/2\,O_2 \qquad [4]$$

In this case a white color of ZnO does not change. In the presence of Tl^+ in the solution, on the other hand, the illuminated part of ZnO electrode was colored brown simultaneously with starting of the photoanodic current (curve 2) by the anodic polarization of the ZnO electrode. The brown image faded away proportionally to the reduction current (curve 3). As for this phenomenon, we assume that the electrode reactions for the image formation and for the image disappearance are the followings, respectively,

$$2\,Tl^+ + 3\,H_2O + 4\,p^+ \longrightarrow Tl_2O_3 + 6\,H^+ \qquad [5]$$

$$Tl_2O_3 + 6\,H^+ + 4\,e^- \longrightarrow 2\,Tl^+ + 3\,H_2O \qquad [6]$$

That is, the imaging step may be the formation of the oxidized layer of Tl^+ on the ZnO surface and the decoloration step may be the reduction of this layer.

This imaging process has a good reversibility during the formation step and the vanishing step (see Figure 3). The positive photocurrent corresponds to the image formation and the negative current to the vanishing of the image. This figure shows that the image formation step needs the illumination and the anodic polarization of the ZnO electrode and that the image fading step needs only the cathodic polarization of the ZnO electrode.

Therefore, this photoelectrochemical imaging process has some unique characteristics: 1) Both the construction of a system and the imaging process are simple. 2) Image formation and fading step can be attained by a low electric power. 3) Rate of image formation depends on the illumination intensity and the concentration of Tl^+. 4) Imaging process has a good reversibility and reproducibility. 5) Image pattern has a high contrast against the ZnO substrate, 6) and is stable more than 8000 hrs in the atmosphere. 7) Acid solution can also vanish the image pattern by the action of chemical dissolution.

Moreover, when various reducing agens (such as Pb^{2+}, Co^{2+}, Mn^{2+}, and Cr^{3+}) besides Tl^+ were used for the n-type semiconductor TiO_2 or ZnO, the image pattern from yellow to dark brown were formed on the electrode surfaces by the same procedures as described above and also have similar characteristics to the n-type ZnO electrode with Tl^+. In these cases, the image formation reactions may be also oxidation reactions of metallic ions (M^{n+}) by the action of photogenerated holes;

$$M^{n+} + a\,H_2O + b\,p^+ \longrightarrow M_xO_y + 2a\,H^+ \qquad [7]$$

In the case of soluble semiconductor photoanode such as ZnO, the image formation reaction competes with the oxidative decomposition of the photoelectrode per se. In the case of a stable semiconductor photoanode such as TiO_2, the image formation reaction competes with the photoelectrochemical oxidation of water.$^{7,8)}$ As for an n-type CdS semiconductor, the image formation process was an oxidation process of the photoelectrode per se;

$$CdS + 2\,p^+ \longrightarrow Cd^{2+} + S \qquad [8]$$

In the case employing a p-type GaP semiconductor as a photoelectrode and Ag^+ as an oxidizing agent, an image pattern of metallic silver was formed on the reddish brown GaP substrate as a result of the photocathodic reaction;

$$Ag^+ + e^- \longrightarrow Ag \qquad [9]$$

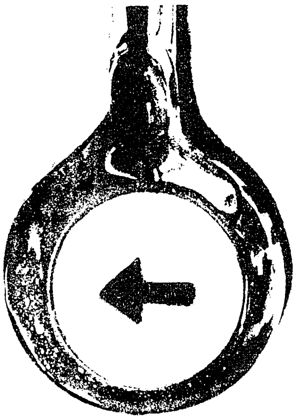

Fig. 1. Photograph of an image pattern made of the thallium oxide on the ZnO semiconductor electrode. Electrolyte solution was 0.2 M Na_2SO_4 and 0.02 M Tl_2SO_4 aqueous solution.

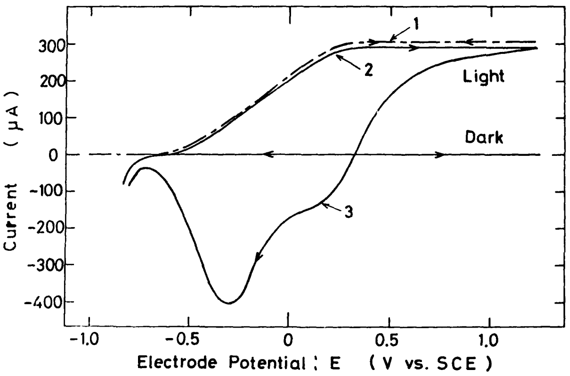

Fig. 2. Current-potential curves for the n-type ZnO electrode.
— — — in 0.2 M Na_2SO_4 solution
———— in 0.2 M Na_2SO_4 + 0.02 M Tl_2SO_4 solution.

and other image patterns of several metals (such as In, Cu, Fe, and Ni) were also formed on the p-type semiconductor substrates.

The kinetic scheme of this photoelectrochemical imaging process can be elucidated based on the electrode reaction of the illuminated semiconductors. When a semiconductor electrode absorbs photons, electrons and holes are produced in a conduction band and a valence band, respectively. Then, the reducing agent (metal ions) in the solution captures the photogenerated holes (minority carriers) in the depletion layer of an n-type semiconductor electrode in the condition of anodic polarization and makes an image pattern of an oxide layer. Furthermore, the oxidizing agent (also metal ions) captures the photogenerated electrons (also minority carriers) in the depletion layer of a p-type semiconductor electrode in the condition of cathodic polarization and makes a metallic image pattern. Fading processes of the photoelectrochemically-formed images come from the reduction of the image layer on n-type semiconductor electrodes and from the oxidation on p-type semiconductor electrodes by actions of majority carriers obtained in the condition of the polarization in reverse to the image formation.

However, the concrete optical characteristics of the image and the detailed kinetics of the electrode reactions have not been well confirmed and are currently under investigation in this laboratory.

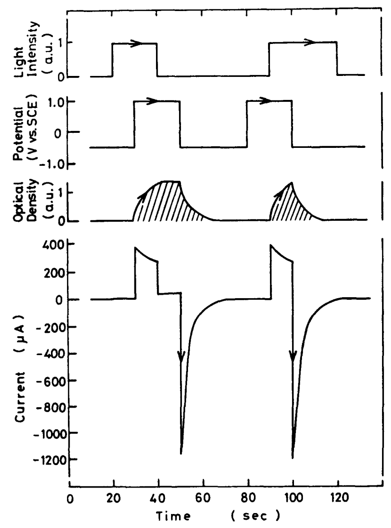

Fig. 3

Time-dependences of current and optical density of an image on light intensity and ZnO electrode potential. The hatched parts in the optical density-time curve indicate the appearance of the image. As for the current-time curve, the positive currents refer to the image formation and negative currents to the image disappearnce

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