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PHOTO-ELECTROCHEMICAL BEHAVIORS OF SEMICONDUCTOR ELECTRODES COATED WITH THIN METAL FILMS

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Contrary to most ordinary semiconductor electrodes, metal-coated semiconductor electrodes have been found to cause photo-currents in aqueous solutions without dissolution into or reaction with the solution, and will be useful as solar-energy convertors.

Recently, the photovoltaic effect at the semiconductor-electrolyte interface has been studied by some authors. Such an effect is of great interest in view of direct conversion of light energy into chemical energy[1,2] and also as a model of photosynthesis in natural plants.[3,4]

There are, however, some serious problems to be solved before realizing the former idea. One is that most of the available semiconductors are photo-electrochemically unstable, either dissolving into electrolyte solutions or forming insulating thin films.[5,6] Another is that the energy levels of the semiconductor electrode are required to be properly located with respect to the equilibrium potentials of redox couples in the electrolyte solutions. For example, a very small quantum yield was reported for the TiO_2/electrolyte/Pt cell and was attributed to the height of the conduction band at the surface of the TiO_2 electrode only barely higher than the reduction potential of hydronium ions.[7]

One possible way to solve these problems is to improve the electrochemical nature of the semiconductors by various surface treatments. In this letter, we are going to report the results of studies on the effect of coating the semiconductor surfaces with thin metal films.

N- and p-type GaP and Si, all single crystals in the form of wafers, were used in the experiments. They were polished successively with polishing cloth and alumina 1.0 - 0.3 μm in size and etched. The ohmic contact was then obtained by evaporating suitable metal or alloy onto one face of the crystal and, if necessary, by heating. After a copper wire was soldered on the evaporated metal, all surfaces, except the face of the crystal which was to be exposed to the electrolyte solution, were covered with epoxy resin.

In the case of GaP, the electrode thus prepared was etched again with warm aqua regia. In the case of Si, etching was done with CPD-2*. Then, they were washed with deionized water, and put in an evaporation chamber as quickly as

* The mixture of HNO_3 (15ml), HF (15ml) and Br_2 (0.02ml)

possible to prevent oxidation of the semiconductor surface. Evaporation of metal was carried out under $(2 - 4)\times10^{-5}$ Torr. The amount of evaporated metal was monitored by measuring the light transmittance of a glass plate held at an equivalent position. In all cases, the transmittance ranged from 5 to 30 %. Polarization curves were measured with a Hokutodenko HA 101 potentiostat. The electrolyte solution was bubbled with highly pure nitrogen gas and stirred with a magnetic stirrer throughout each measurement.

Fig. 1[A] shows the current-voltage curves for an n-type GaP electrode coated with Au (abbreviated hereafter as Au/n-GaP), together with that for an n-GaP electrode as a reference. The dark currents are negligibly small (<0.1 μA) in both cases at potentials more positive than about -1.2 V vs. SCE. Under illumination in the spectral region higher than the band-gap energy of GaP, the current-voltage curves for the Au/n-GaP electrode differ completely from those for the n-GaP electrode, and rather resemble those for an Au electrode, shown in Fig. 1[B], except for the potential shifting toward the negative direction by about 0.6 V. Based on the results of the studies on the electrode reactions on Au,[8] the anodic and cathodic currents for the Au/n-GaP electrode in the region between -0.4 and 0.4 V vs. SCE can be interpreted, respectively, to be the formation and reduction of the oxide film of Au, and the anodic current at potentials more positive than about 0.5 V is attributed to the decomposition of water to O_2. The current saturation observed at potentials above 0.6 V is due to the illumination intensity. A qualitative analysis of the electrolyte gave no indication of dissolution of the electrode materials for the case of Au/n-GaP electrode, contrary to the case of the n-GaP electrode.[9] This supports the above interpretation. It is then concluded that the oxidation of water on the illuminated Au/n-GaP electrode occurs at a potential 0.6 V more negative than that on the Au electrode.

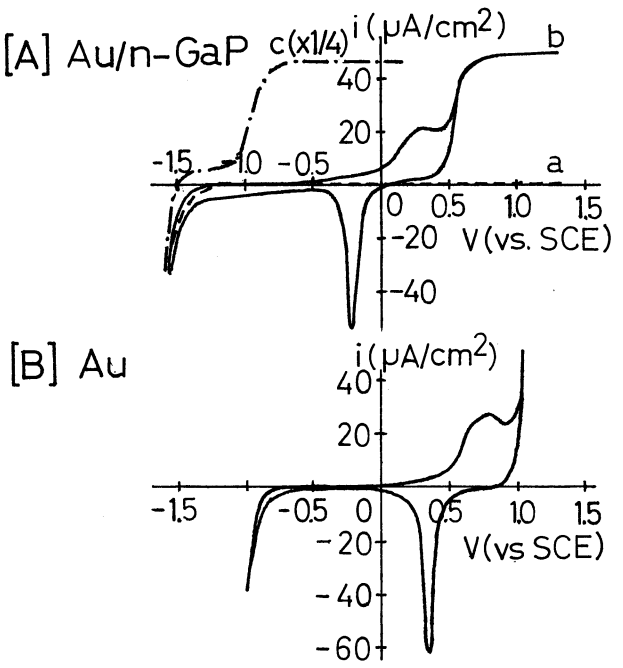

Fig. 1
Current-voltage curves for the Au/n-GaP electrode [A] and the Au electrode [B], in the borate buffered 0.5 M K_2SO_4 aqueous solution (pH = 9.2). (a) For the Au/n-GaP electrode in the dark. (b) For the Au/n-GaP electrode under illumination. (c) For the n-GaP electrode under illumination.

Fig. 2 shows the current-voltage curves for the Au/n-GaP and Au electrodes when a redox system, $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$, is added in the electrolyte. Similar to the former result, the anodic reaction for the Au/n-GaP electrode occurs at a

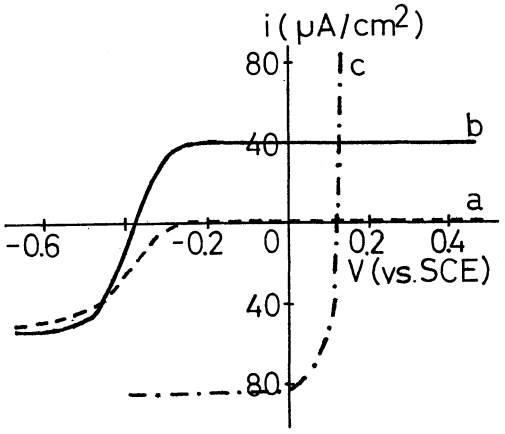

Fig. 2
Current-voltage curves in the presence of a redox system. Acetate buffered 0.5 M K_2SO_4 aqueous solution(pH = 4.7), containing 5.4×10^{-3} M $K_4[Fe(CN)_6]$ + 1.8×10^{-4} M $K_3[Fe(CN)_6]$. (a) For the Au/n-GaP electrode in the dark. (b) For the Au/n-GaP electrode under illumination. (c) For the Au electrode.

Table 1
The shift of current-voltage curve between metal and metal coated semiconductor electrode (ΔU)

Electrode	ΔU volt	Electrode Reaction
Au/n-GaP	-0.56	A
	-0.48	B
	-0.55	C
Pd/n-GaP	-0.60	A
Au/n-Si	-0.17	A
	-0.07	B
	-0.13	C
Pd/n-Si	-0.15	A
Ag/p-GaP	+0.20	D
Ag/p-Si	+0.35	D

A: $H_2O \longrightarrow 1/2O_2 + 2H^+ + e$
B: $[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + e$
C: $Fe^{2+} \longrightarrow Fe^{3+} + e$
D: $H^+ + e \longrightarrow 1/2H_2$

potential 0.5 V more negative than that for the Au electrode.

Experiments were made for other semiconductor electrodes coated with various kinds of metal. Similar behaviors and shifts of the current-voltage curves were observed in all cases. The results are summarized in Table 1. It is seen that the amount of the shift, ΔU, is nearly constant for each semiconductor, independent of the kind of the metal and the electrode reaction.

These experimental results can be understood from the energy level scheme for the metal-coated semiconductor electrode in contact with the electrolyte solution, as schematically shown in Fig. 3. In the dark thermal equilibrium state, the Fermi level of the semiconductor, E_F, agrees with that of the metal film and also with the equilibrium potential of the redox system, U_{redox} (Fig. 3). When an external voltage is applied to this electrode, the potential drop occurs mostly within the space charge layer formed near the surface of the semiconductor. Let us designate an electrode potential at which the band of the semiconductor near the surface is flat as a flat-band potential, U_{fb}, as usually done for the bare semiconductor electrodes. On illumination of the surface of the semiconductor under the electrode potential more positive than U_{fb}, hole-electron pairs are formed. They are separated into holes near the surface and electrons in the interior of the semiconductor owing to the electric field existing within the space charge layer. The holes at the surface pass the metal film and oxidize the redox system. Since

these processes occur at any potentials more positive than U_{fb}, it follows that the onset potential of the anodic photocurrent agrees with U_{fb}. It can also be seen that the shift of the current-voltage curve, ΔU, observed (Table 1), corresponds to the difference between U_{fb} and U_{redox}, or the contact potential difference between the semiconductor and the metal. Bardeen showed that the contact potential difference between a semiconductor and a metal is controlled by the surface states on the semiconductor, if the density of the surface states is fairly high, being independent of the kind of metal.[10] The present results of the observed values of ΔU, nearly constant for each semiconductor, can thus be understood by assuming the presence of the surface states.

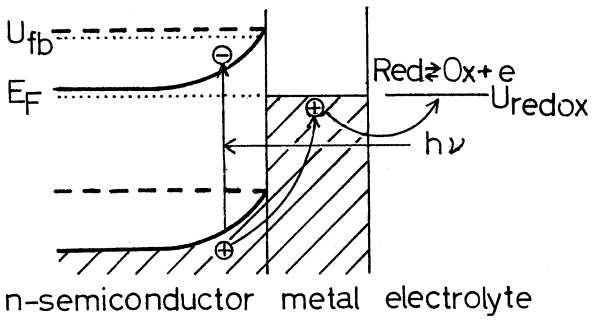

Fig. 3
The energy level scheme for metal-coated semiconductor electrode in contact with the electrolyte, for a dark, equilibrium state (——) and for the case at a electrode potential of U_{fb} (----).

It has been found in the present work that the semiconductor electrode coated with thin metal film is electrochemically stable, and the electrode reactions on this electrode under illumination are of the same type as those on the metal electrode, but the current-voltage curve for this electrode shifts in potential from that of the metal electrode. This type of electrodes can thus be useful for an electrochemical photo-cell which transforms light energy into electric energy and works stably for a long period of time in the presence of a suitable redox system.

Reference

1) A. Fujishima and K. Honda, Nature, 238, 37 (1972), A. Fujishima, K. Kohayagawa, and K. Honda, Bull. Chem. Soc. Japan, 48, 1041 (1975).
2) H. Gerischer, Electroanal. Chem. Interfacial Electrochem., 58, 263 (1975).
3) H. Tributsch, Photochem. Photobiol., 16, 261 (1972).
4) M. Calvin, Science, 184, 375 (1974).
5) H. Gerischer, Advances in Electrochem. and Electrochem. Engineering, 1, 139 (1961).
6) A. K. Vijh, "Electrochemistry of Metals and Semiconductors", Marcel Dekker, Inc., New York (1973).
7) T. Ohnishi, Y. Nakato, and H. Tsubomura, Ber. Bunsenges. Phys. Chem., 79, No. 6 (1975), to be published.
8) T. Takamura, K. Takamura, W. Nippe, and E. Yeager, J. Electrochem. Soc., 117, 626 (1970).
9) R. Memming and G. Schwandt, Electrochim. Acta, 13, 1299 (1968).
10) J. Bardeen, Phys. Rev., 71, 717 (1947).

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