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THE CONCEPT OF "SURFACE-TRAPPED HOLE" IN n-TYPE SEMICONDUCTORS AND THE CONDITIONS FOR EFFICIENT AND STABLE PHOTOELECTROCHEMICAL CELLS[1)]

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The competition between decomposition and electron transfer reactions at an n-GaP electrode under illumination was explained on the basis of the concept of the "surface-trapped hole". It is concluded that an efficient and stable photoelectrochemical cell can be constructed by use of a redox couple having the standard redox potential slightly more negative than the redox potential of the surface-trapped hole.

The employment of the photoelectrochemical systems with semiconductor electrodes is one of the most promising methods for solar energy conversion. The difficulty in this method lies in that most of the small bandgap semiconductors corrode in electrolyte solutions. To secure a stable photocell without lowering the energy conversion efficiency is the crucial point in this technique.

It was pointed out by some workers[2-6)] that an n-type semiconductor having a thermodynamic decomposition potential, ε_d, can be stabilized only by a redox couple with the standard redox potential more negative than ε_d. According to this theory, the maximum photovoltage attainable for a semiconductor with the conduction band edge at the surface E_c^s is given approximately by the difference between ε_d and $-(E_c^s/e)$, which is often much smaller than the bandgap (E_g). For example, it is only 0.7 V for n-GaP[5)] (E_g = 2.26 eV).

We proposed a concept of "surface-trapped hole" as a precursor of various anodic reactions of semiconductor electrodes,[7)] and showed that the shift of the surface band energies, the photocurrent-potential behavior and the electroluminescence could be well explained by this concept.[7,8)] In the present work we studied the competition between electrode dissolution and redox reaction at an n-GaP electrode, and found that stable photocells generating photovoltages much larger than expected from the ε_d can be constructed.

We investigated the effects of various redox couples at various pH on the surface band energies and photocurrent-potential curves. Fig. 1 shows the results for solutions containing 0.05 M $Fe(CN)_6^{3-}$ and 0.05 M $Fe(CN)_6^{4-}$ (b), and 0.05 M $Fe(C_2O_4)_3^{3-}$ and 0.05 M $Fe(C_2O_4)_3^{4-}$ (c) (M = mol/dm^3), as compared to those for a solution containing 0.05 M Na_2SO_4 as the supporting electrolyte (a). As reported previously,[7)] the surface-trapped hole is energetically characterized by a redox potential, ε_h. For the case of n-GaP, the ε_h was estimated experimentally to be

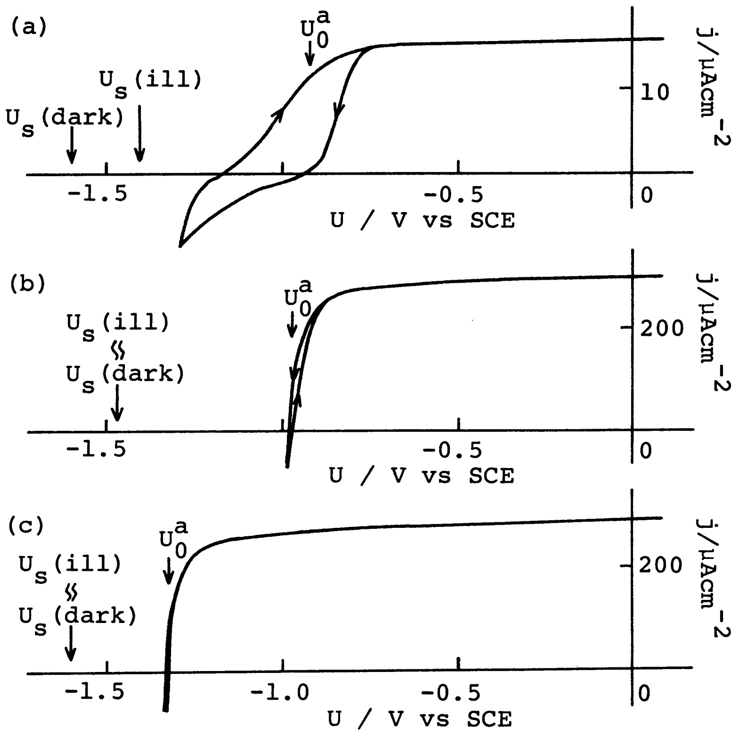

Fig. 1 U_s values and photocurrent-potential curves for the Ga-face of an n-GaP electrode at pH 6.0, (a) in the absence of a redox couple, (b) in the presence of a $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ couple, and (c) in the presence of a $Fe(C_2O_4)_3^{3-}$/$Fe(C_2O_4)_3^{4-}$ couple.

0.5 V above $-(E_v^s/e)$, where E_v^s refers to the energy of the valence band edge at the surface. If the ε_h value at dark in a solution containing no redox couple is defined as ε_h°, the redox potential, ε(Ox/R), of the $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ couple is only ca. 0.15 V below ε_h°, while that of the $Fe(C_2O_4)_3^{3-}$/$Fe(C_2O_4)_3^{4-}$ is ca. 0.3 V above ε_h°, as shown in Fig. 2(b) and (c) respectively. These potential relations are very important, causing large difference in the electrochemical behavior of the electrode (Fig. 1(b) and (c)). It is also to be noted that ε(Ox/R) of these redox couples are both far below $\varepsilon_d$$^{5)}$ (Fig. 2).

The surface band energy E_c^s is nearly the same as $-eU_s$, where U_s is a potential determined from the intercept of a Mott-Schottky plot with the abscissa.$^{8)}$ The U_s values observed are also included in Fig. 1. For the solution where no redox couple is present, the U_s value is shifted by illumination from U_s(dark) to U_s(ill) (case (a) in Fig. 1). This is mainly attributable to the accumulated surface-trapped hole, as explained in a previous paper.$^{8)}$ The U_s(dark) in a $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ solution, case (b) in Fig. 1, is more positive than that in case (a), owing to the surface-trapped hole produced by the $Fe(CN)_6^{3-}$ ions.$^{7)}$ In this case, however, the U_s value is not changed by illumination, even with an illumination intensity 20 times higher than in case (a). This means that the density of the surface-trapped hole is not increased by illumination, determined by an electron transfer equilibrium, $\varepsilon_h = \varepsilon$(Ox/R) (Fig. 2(b)). Since U_s(ill) in this case is more negative than U_s(ill) in case (a), we can conclude that the density of the surface-trapped hole under illumination is less than that in case (a). As the electrode dissolution is thought to become fast with the accumulated surface-trapped hole,$^{8)}$ this suggests that the electrode dissolves in case (b) more slowly than in case (a). In agreement with this conclusion, it was reported$^{5)}$ that the photoanodic dissolution of n-GaP was prevented by the $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ couple.

The U_s(dark) in a $Fe(C_2O_4)_3^{3-}$/$Fe(C_2O_4)_3^{4-}$ solution, case (c) in Fig. 1, is nearly the same as U_s(dark) in case (a) and is not shifted by illumination. It is

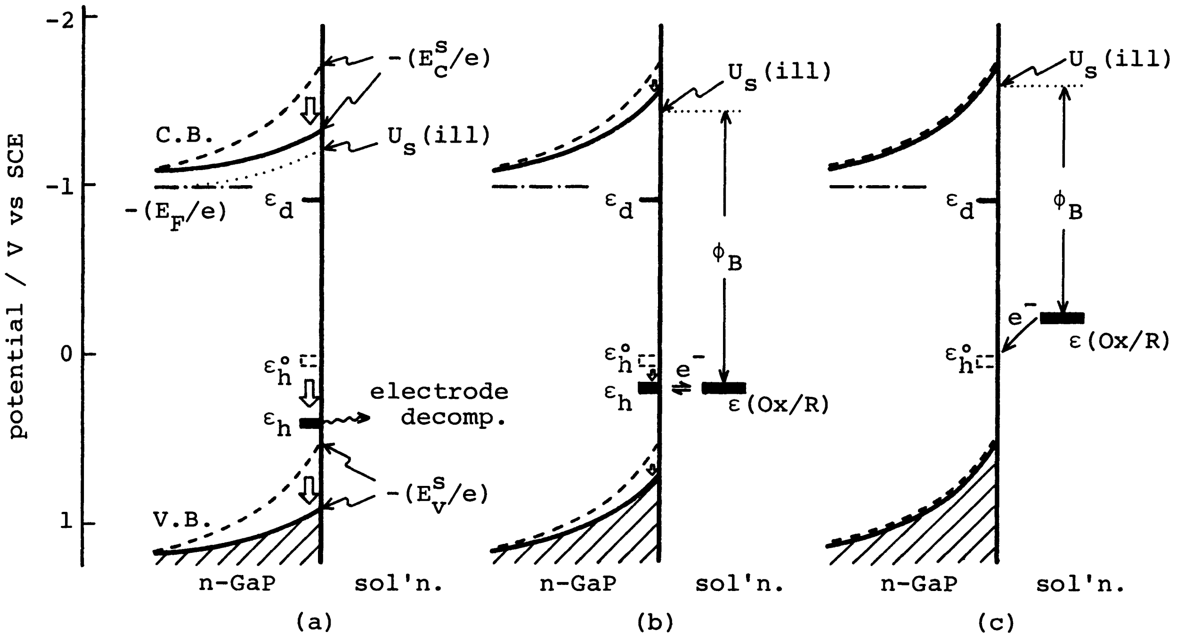

Fig. 2 Energy level diagrams of n-GaP/solution interfaces (————) under illumination, (a) in the absence of a redox couple, (b) in the presence of a $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ couple, and (c) in the presence of a $Fe(C_2O_4)_3^{3-}$/$Fe(C_2O_4)_3^{4-}$ couple, as compared to those (-------) at dark in the absence of a redox couple.

therefore concluded that the surface-trapped hole is effectively reduced by the reductant in solution and not accumulated in this case even under illumination (Fig. 2(c)). This means that the electrode dissolution is prevented almost completely by this redox couple.

It was pointed out[8)] that the potential at which the photocurrent becomes zero, U_0^a, is considerably more positive than U_s(ill) in case where the surface-trapped hole is accumulated, because it captures electrons in the conduction band under decreased band bending and therefore acts as an electron-hole recombination center. The deviation of U_0^a from U_s(ill) in case (c) of Fig. 1 is much smaller than in case (a) or (b), suggesting also that the surface-trapped hole is scarcely accumulated in this case.

Based on the discussions made so far, we now consider which redox couple is better for a photoelectrochemical cell, (n-GaP | redox sol'n. | Pt). Table 1 shows the characteristic values of the two cells using (1) the $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ couple and (2) the $Fe(C_2O_4)_3^{3-}$/$Fe(C_2O_4)_3^{4-}$ couple. As is seen from Fig. 2, the height of Schottky-type potential barrier, ϕ_B, for cell (1) is given by $\phi_B = \varepsilon_h - U_s$(ill), while that of cell (2) is given by $\phi_B = \varepsilon$(Ox/R) $- U_s$(ill). Though the former is ca. 0.3 V larger than the latter, the open-circuit photovoltages, V_{oc}, observed are nearly the same (Table 1). This result shows that a redox couple having ε(Ox/R) more positive than ε_h° has no merit, partly because the barrier height ϕ_B gets small by the surface-trapped hole and partly because the surface-trapped holes act as recombination centers or electron transfer mediators, as mentioned before, leading to a large positive shift of U_0^a from U_s(ill) (Fig. 1), or a

Table 1 Characteristic values of photoelectrochemical cells, (n-GaP (Ga-face) | redox electrolyte, pH 6.0 | Pt).

Redox	ϕ_B/V	V_{oc}/V	j/mAcm^{-2}
(1) $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	1.76	1.15	0.30
(2) $Fe(C_2O_4)_3^{3-}/Fe(C_2O_4)_3^{4-}$	1.48	1.10	0.36

large decrease of V_{oc} relative to ϕ_B. The surface-trapped holes produced by such a redox couple also induce the long-range instability of the electrode. Consequently, we can conclude that a redox couple having $\varepsilon(Ox/R)$ slightly more negative than ε_h°, as seen in such cases as $Fe(C_2O_4)_3^{3-}/Fe(C_2O_4)_3^{4-}$, is the most appropriate, keeping the electrode stability without a significant loss in V_{oc}. It is also noted that the surface-trapped hole gives a better theoretical basis for considering the electrode stability and the cell efficiency than the previously proposed thermodynamic decomposition potential (ε_d).2,3)

It is pointed out that the above argument can be extended generally to the criterion of photoelectrochemical cells using other n-type semiconductors, including photoelectrolysis cells, because the surface-trapped hole more or less exists in any semiconductors, as seen from its theoretical model.7,9) We conclude that the best photocell can be constructed by using a semiconductor having stable surface-trapped holes with their ε_h very close to $-(E_v^s/e)$ and a suitable redox couple.

References

1) Part of the results was presented by Y. Nakato, A. Tsumura, and H. Tsubomura at the Symposium on "Photochemical and Electrochemical Surface Science: Photoeffects at Semiconductor-Electrolyte Interfaces" in the 179th American Chemical Society National Meeting, Houston, Texas, March 1980.
2) H. Gerischer, J. Electroanal. Chem., 82, 133 (1977).
3) A. J. Bard and M. S. Wrighton, J. Electrochem. Soc., 124, 1706 (1977).
4) A. Fujishima, T. Inoue, T. Watanabe, and K. Honda, Chem. Lett., 1978, 357.
5) R. Memming, J. Electrochem. Soc., 125, 117 (1978).
6) T. Kobayashi, H. Yoneyama, and H. Tamura, Chem. Lett., 1979, 457.
7) Y. Nakato, A. Tsumura, and H. Tsubomura, ibid., 1981, 127.
8) Y. Nakato, A. Tsumura, and H. Tsubomura, J. Electrochem. Soc., 127, 1502 (1980).
9) This is also supported by our preliminary experimental results.

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