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THE CONCEPT OF "SURFACE-TRAPPED HOLE" AS AN INTERMEDIATE OF ANODIC REACTION OF A GALLIUM PHOSPHIDE SEMICONDUCTOR ELECTRODE[1)]

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The concept of "surface-trapped hole", acting as a precursor in various photoanodic processes, is proposed on the experimental basis of the surface band energy and electroluminescence of GaP in contact with redox solutions.

The study of the photoelectrochemical systems has been quite active recently, in relation with solar energy conversion. It is growingly recognized that the details of the photoelectrochemical behavior of semiconductor electrodes are understood in view of the presence of surface states. We reported previously that the surface band energy of an n-GaP electrode is shifted by illumination under anodic polarization.[2)] The shift was explained by accumulated surface intermediates formed from photo-produced holes. We have further studied the properties of such intermediates, and found that a surface state, which may be called the "surface-trapped hole", plays important roles in various photoelectrochemical processes of semiconductor electrodes.

Mott-Schottky plots were made to determine the surface band energies of n-type GaP single crystals. As described previously,[2)] the potential at the intercept of a Mott-Schottky plot with the abscissa is taken to be (U_s + kT/e). The U_s value thus determined is related to the lower energy limit of the conduction band at the surface, E_C^S, as shown below:

$$E_C^S = -eU_S + \Delta$$

where Δ is a small energy difference (See Fig. 1).

Figure 2 shows the U_s values observed for the (111)-face (Ga-face) of n-GaP. U_s(d) designates the values observed at dark in aqueous solutions containing only 0.05 mol/dm^3 Na_2SO_4 and pH buffer, and U_s(ill,R) designates those observed under illumination in the presence of 0.05 mol/dm^3 $Fe(CN)_6^{4-}$ ions. U_s(d,Ox/R) designates the U_s values observed at dark in solutions containing 0.05 mol/dm^3 $Fe(CN)_6^{3-}$ and 0.05 mol/dm^3 $Fe(CN)_6^{4-}$ ions. It was confirmed that the U_s(d) values are unchanged by adding the $Fe(CN)_6^{4-}$ ions at various pH. Therefore, the change for U_s(ill,R) from U_s(d) must be caused by illumination i.e., by photo-injected holes. Holes are also injected into the valence band of GaP by the $Fe(CN)_6^{3-}$ ions, because hole injection current flows at a p-GaP electrode in $Fe(CN)_6^{3-}$ solutions, as reported.[3)] Therefore, the change for U_s(d,Ox/R) from U_s(d) is explained by the holes injected by the oxidant in solution. Thus, both curves for U_s(ill,R)

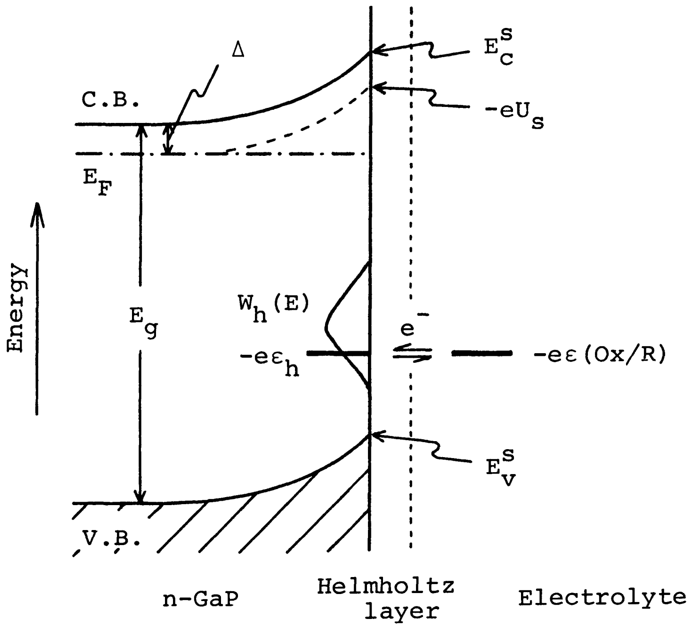

Fig. 1 An energy level diagram showing an electron transfer equilibrium between the surface-trapped hole and a redox couple in solution.

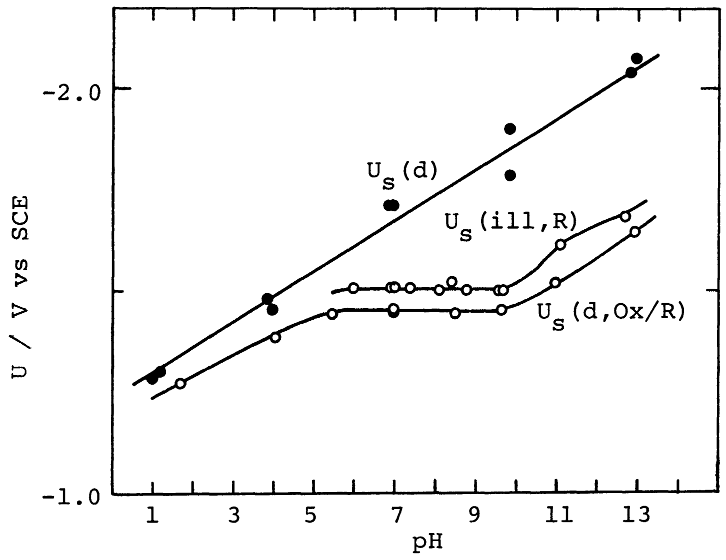

Fig. 2 U_s values for the Ga-face of an n-GaP electrode under various conditions. $U_s(ill,R)$ was observed under a constant illumination intensity, with the photoanodic saturation current kept at 200 μA/cm^2.

and $U_s(d,Ox/R)$ are resulting from hole injection.

It is to be noted that quite similar curves for $U_s(ill,R)$ and $U_s(d,Ox/R)$ are obtained (Fig. 2). They are both kept nearly constant in the range of pH 6 to 10, in contrast to $U_s(d)$. Since the redox potential of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple, $\varepsilon(Ox/R)$, observed is also constant in pH $\geq$ 4, one can explain the above result of the U_s values fixed from pH 6 to 10 by taking account of an establishment of an electron transfer equilibrium between the redox couple in solution and a surface state on the electrode, by analogy to the Bardeen barrier in metal-semiconductor contacts.[4)]

The relevant surface state above proposed can best be visualized by the concept of "surface-trapped hole". This implies that the energy of a hole relaxing at the surface is not at the upper energy limit of the valence band at the surface, E_v^s, as is often assumed, but lies slightly above E_v^s, owing to the stabilization due to the distortion of the GaP framework at the surface and the solvation.

The surface trapped hole is regarded to be an electron deficient Ga-P bond in the surface framework. Then, this and the original surface Ga-P bonds form a surface redox system, characterized by a redox potential, ε_h. The energy intervals between E_c^s, E_v^s and

$-e\varepsilon_h$ can be shown to be nearly constant unless the density of the surface-trapped hole is too low, as will be discussed in detail elsewhere. Injection of holes by illumination or by an oxidant in solution will accumulate the surface-trapped hole, in case where it is chemically stable to some extent, shifting the potential at the Helmholtz layer, and therefore U_s and ε_h, to the positive, because of the positive charge of the surface trapped hole. An electron transfer equilibrium is attained in case where the n-GaP electrode is in contact with the redox solution at dark when ε_h becomes equal to $\varepsilon(Ox/R)$ in the solution, as is shown in Fig. 1, from which the U_s value can be determined. The $-e\varepsilon_h$ value for the n-GaP electrode is estimated to be ca. 0.5 eV above E_V^S, by using observed values for U_s and $\varepsilon(Ox/R)$, E_g of 2.26 eV, and Δ of 0.1 eV (See Fig. 1). Similarly, in case where the n-GaP is illuminated at a constant intensity in the presence of the reductant, a stationary state is attained at the point where the rate of photo-formation of the surface-trapped hole becomes equal to the rate of electron transfer from the reductant to it, that is to say, at the point where ε_h is shifted to a potential near $\varepsilon(Ox/R)$.

The breakdown of the constancy of U_s at high pH ($\gtrsim$ 10) shown in Fig. 2 is explained by assuming that the surface-trapped hole is too reactive to accumulate enough in this pH range. At high pH, the nucleophillic attack of hydroxide anion, OH^-, on the surface-trapped hole will lead to too short a life time for it to accumulate, causing rapid dissolution of GaP.

We have observed electroluminescence spectra when the n-GaP electrode was under slightly cathodic potentials in a $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ solution as shown in Fig. 3. Similar but somewhat different spectra were reported previously in the literature.[3,5] These spectra are best assigned to a recombination luminescence between the surface-trapped hole formed by hole injection by the $Fe(CN)_6^{3-}$ ions and the electron in the conduction band at the surface. According to this interpretation, the luminescence spectrum gives the energy difference between the surface-trapped hole and conduction band edge, the spectral shape mainly reflecting the energy level distribution of the surface-trapped hole, denoted as $W_h(E)$. The $W_h(E)$ thus estimated from the spectra is drawn in Fig. 1. It is to be noted that the redox

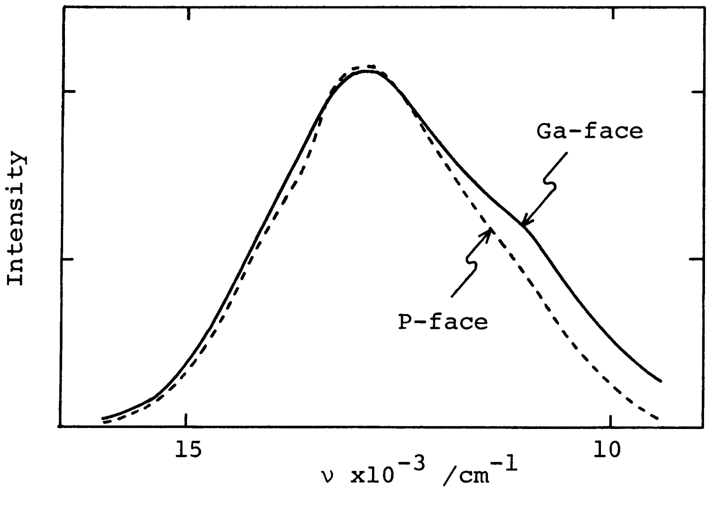

Fig. 3 Electroluminescence spectra from the Ga- and P-face of an n-GaP electrode observed under ca. -1.9 V vs SCE in a solution containing 0.3 mol/dm^3 $Fe(CN)_6^{3-}$ and 0.3 mol/dm^3 $Fe(CN)_6^{4-}$ at pH 8.0.

potential, ε_h, is located between the $W_h(E)$ and the valence band, the latter of which approximately represents the energy distribution of the electron in the surface Ga-P bonds. Thus, the correlation between ε_h and $W_h(E)$ is very good, strongly supporting our present conclusion.

It is to be noted that the luminescence spectra for the Ga- and the P-face are similar to each other (Fig. 3), though the electrochemical properties of these faces are considerably different. This might suggest that the positive charge in the surface-trapped hole is still delocalized over a certain range of surface Ga-P bonds, because in such a case the energy of the surface-trapped hole is not affected much by the surface chemical structure.

The surface-trapped hole acting as a precursor of photoanodic reactions gives a theoretical basis for considering the kinetic stability of semiconductors, and the similar surface-trapped holes are expected to exist in various n-type semiconductors from its theoretical model mentioned above. Very recently, Bard et al.$^{6)}$ proposed the presence of surface states on n-GaAs, p-GaAs, or p-Si, based on constant open-circuit photovoltages observed for photoelectrochemical cells using non-aqueous solvents. In their discussion, the surface state is assumed to be of the pre-existing nature, originating from surface defects or adsorbed species. Therefore, their surface state is quite different in the origin, generality, and in the relation to the electrode decomposition from the surface-trapped hole proposed in the present letter.

References

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