NOTES

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Flat-band Potential of p-Type GaP in Acetonitrile Solutions

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Synopsis. An interaction of quinone compounds such as tetrachloro-*p*-benzoquinone and *p*-benzoquinone with surface hydroxyl groups of a p-type GaP electrode seems to play an important role in determining the magnitude of photovoltage in acetonitrile solutions. The same holds for p-type InP and Si.

The maximum photovoltage at an illuminated semiconductor electrode in a redox electrolyte is equal to the potential difference between the flat-band potential of the electrode E_{fb} and the redox potential of the electrolyte.[1] In aqueous solutions, E_{fb} is in many cases a function of the solution pH, not being influenced by the redox species. Thus, a theoretical maximum photovoltage can be estimated easily by using E_{fb} measured in a base electrolyte into which a redox species is added. However, this may not be true in nonaqueous electrolytes,[2] although the invariance of E_{fb} has sometimes been assumed.[3-5] This note reports on the finding that the interaction of an organic redox species with hydroxyl groups of the electrode surface changes E_{fb} to a large extent.

Experimental

p-Type GaP, InP, and Si were used. Etching of GaP and InP was carried out with HCl, and that of Si with CP-4A.[6] Immediately after chemical etching, the electrodes were washed with de-ionized water for 15 min, followed by rinsing with acetonitrile (AN), and finally dried under evacuated conditions. An Ag wire immersed in AN containing 0.01 mol dm^{-3} $\mathrm{AgNO_3}$ was used as a reference electrode. The potential given in this paper refers to this electrode.

Acetonitrile was purified according to the procedure reported.[7] Tetraethylammonium perchlorate (TEAP) as a supporting electrolyte was prepared in this laboratory. Its concentration was usually 0.1 mol dm^{-3}. Tetrachloro-*p*-benzoquinone (Chloranil CA) and *p*-benzoquinone (BQ) used as redox species were of reagent grade. The redox electrolytes of $\mathrm{CA/CA^{\cdot-}}$ and $\mathrm{BQ/BQ^{\cdot-}}$ were prepared by electrolyzing CA and BQ in TEAP/AN at -0.45 and -0.95 V, respectively, where $\mathrm{CA^{\cdot-}}$ and $\mathrm{BQ^{\cdot-}}$ denote the anion radicals of CA and BQ. A 500 W xenon lamp was used as a light source.

Results and Discussion

BQ and CA were found to be reduced almost reversibly to give $\mathrm{BQ^{\cdot-}}$ and $\mathrm{CA^{\cdot-}}$, respectively, making it possible to estimate the formal potential E^0 of $\mathrm{BQ/BQ^{\cdot-}}$ and $\mathrm{CA/CA^{\cdot-}}$ from the halfwave potentials of the reduction reaction,[8,9] the estimated E^0 being -0.81 and -0.31 V, respectively. The value of E_{fb} of p-type Si reported[4] is *ca.* -0.4 V; that of p-type GaP would be *ca.* 0.8 V, as judged from the reported value for n-type GaP.[2] The value of E_{fb} of p-type InP determined in TEAP/AN is *ca.* 1.2 V. Although the reproducibility is poor, it is not a serious problem. If the redox species has no significant influence on E_{fb}, the maximum photovoltage values given in Table 1 would be expected. In the case of InP the potential difference between E_{fb} and the redox potential exceeds the bandgap of InP, so that no electrochemical equilibrium can be established.

The open circuit potentials of the semiconductor electrodes in the dark were almost equal to the redox potentials of the electrolytes. When illumination of 1.8 W/cm^2 was made, the electrode potential shifted anodically by the amount of the photovoltage (Table 1). The photovoltage increased by 60—80 mV with increasing illumination intensity from 0.18 to 1.8 W/cm^2, gradually tending to saturation. This suggests that the maximum photovoltage cannot be achieved even under imaginary intense illumination conditions. In addition it should be noted that (1) the photovoltage appeared in the system where it was not expected ($\mathrm{Si{-}CA/CA^{\cdot-}}$), and (2) almost the same photovoltage was obtained at the same electrode independent of the kind of the redox electrolyte. These results suggest that E_{fb} is variable in such a manner that the more negative the redox potential of a chemical species added to TEAP/AN, the larger the negative shift of E_{fb}. This was investigated in detail for p-type GaP.

Values of E_{fb} of a p-type GaP electrode in a variety of electrolytes, obtained by Schottky-Mott plots of the electrode capacitance, are given in Table 2. The capacitance was measured at 0.5, 1.0, and 5 kHz, the same E_{fb} being obtained. However, E_{fb} was scattered to about ±0.2 V when pretreatment of the electrode was repeated in each run. The scatter was large enough to shadow a small change in E_{fb} which

TABLE 1. THE MAXIMUM PHOTOVOLTAGE PREDICTED AND VALUES EXPERIMENTALLY OBTAINED WITH ILLUMINATION OF 1.8 W/cm^2

Electrode	Redox species[a)]	ΔE_{max}/V	ΔE_{expt}/V
p-Si	$\mathrm{BQ/BQ^{\cdot-}}$	0.4	0.23
p-Si	$\mathrm{CA/CA^{\cdot-}}$	0	0.21
p-GaP	$\mathrm{BQ/BQ^{\cdot-}}$	1.6	0.40
p-GaP	$\mathrm{CA/CA^{\cdot-}}$	1.1	0.42
p-InP	$\mathrm{BQ/BQ^{\cdot-}}$	—	0.41
p-InP	$\mathrm{CA/CA^{\cdot-}}$	—	0.42

a) The concentration was 9.1×10^{-3} mol dm^{-3} CA/ 7.1×10^{-4} mol dm^{-3} $\mathrm{CA^{\cdot-}}$, and 8.5×10^{-3} mol dm^{-3} BQ/6.6×10^{-4} mol dm^{-3} $\mathrm{BQ^{\cdot-}}$.

TABLE 2. FLAT-BAND POTENTIAL OF A p-TYPE GaP IN A VARIETY OF ACETONITRILE SOLUTIONS

	Solution[a)]	E_{fb}/V
1	0.1 M TEAP/AN	0.75
2	0.01 M CA	0.3
3	0.01 M BQ	−0.3
4	1.0×10^{-4} M CA	0.6
	1.0×10^{-3} M CA	0.5
	1.0×10^{-2} M CA	0.4
5	4.6×10^{-3} M HCl	0.72
	4.6×10^{-2} M HCl	0.78
	4.1×10^{-1} M HCl	0.84
6	5.6×10^{-2} M HCl$+1.0\times10^{-4}$ M CA	0.80
	5.6×10^{-2} M HCl$+1.0\times10^{-3}$ M CA	0.80
	5.6×10^{-2} M HCl$+1.0\times10^{-2}$ M CA	0.80

a) M = mol dm^{-3}.

should have been brought about by changing the electrolyte from one kind to another. Thus, the pretreatment of the electrode was made only at the beginning of a series of runs. In this way, a small change was noticeable.

The following results were obtained. (1) Addition of CA and BQ to the base electrolyte of TEAP/AN greatly shifts E_{fb} towards negative potentials. The shifts is higher for BQ than for CA. (2) E_{fb} shifts cathodically with an increase in the concentration of CA, but a reverse tendency was obtained in the case of HCl. (3) When HCl and CA coexist, E_{fb} is primarily determined by HCl. The results were obtained in the electrolytes containing 150—500 ppm water. The water content increased steadily during the course of measurements, and it was not possible to clarify the effect of water on E_{fb}. A trial was made to decrease the water content to 34 ppm in the initial stage of the measurments, but no appreciable difference was observed.

The results (1)—(3) show that a dissociative equilibrium of surface hydroxyl groups of the electrode with the electrolyte should be a principal factor in determining E_{fb}. The positive shift of E_{fb} by addition of HCl should be related to

$$-\mathrm{GaOH} + \mathrm{H}^+ \rightleftharpoons \mathrm{Ga}^+ + \mathrm{H_2O} \qquad (1)$$

as in the cases of aqueous solutions.[10)] On the other hand, the negative shift by addition of the quinone compounds indicates that negatively charged sites become abundant at the electrode surface by the addition. A tentative model for explanation is

$$-\mathrm{GaOH} + \mathrm{Q} \rightleftharpoons \mathrm{GaO}^- + \mathrm{QH}^+ \qquad (2)$$

where Q denotes the quinone molecule. The magnitude of the change in E_{fb} caused by the addition of a quinone compound to the base solution of TEAP/AN would be high for a molecule having a large effective electron density of the quinone ring, which is in agreement with the results. $\mathrm{BQ/BQ^{\cdot-}}$ has a more negative E^0 value than $\mathrm{CA/CA^{\cdot-}}$. A large photovoltage is expected for the former redox electrolyte than the latter if E_{fb} does not differ a great deal. However, the larger negative shift of E_{fb} in the former cancels the advantage of E^0, so that almost the same photovoltage is obtained.

Equation 2 gives a tentative explanation of the observed phenomena. Any model is applicable if the formation of negative sites by addition of quinone compounds is reasonably explained. The interaction of organic species with the electrode surface was postulated in the case of GaAs in AN solutions,[11)] but its mechanism has not been clarified.

According to the present results, the invariance of E_{fb} may be expected when complete elimination of hydroxyl groups on the electrode surface is achieved. In order to prepare such an electrode, anodic polarization of the electrode in an electrolyte free of water may be useful. However, the preparation of such an electrolyte is practically difficult at least for AN,[12)] so that E_{fb} will be varied more or less by adding an organic redox species to AN solutions.

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