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# POTENTIAL VARIATION AT THE SEMICONDUCTOR-ELECTROLYTE INTERFACE THROUGH A CHANGE IN pH OF THE SOLUTION

Tadashi WATANABE, Akira FUJISHIMA*, and Ken-ichi HONDA
Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo 106
*Faculty of Technology, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama-shi, Kanagawa 221

Flatband potentials of n-type $TiO_2$ and CdS single crystal electrodes have been measured as a function of the pH of the electrolyte solution. The potential drop across the electrical double layer at the $TiO_2$ electrode surface was found to depend regularly on the solution pH, while that of CdS remained constant in the pH range from 2 to 13.

In a semiconductor electrode, a major part of the externally applied potential difference falls within the space charge layer inside the semiconductor, owing to the much lower carrier concentration in the electrode (normally $10^{14}$ - $10^{18}$ $cm^{-3}$) than in the solution (ca. $10^{20}$ $cm^{-3}$ for an ordinary 0.1 M electrolyte). The electrode potential at which the potential drop within the space charge region is zero is called the flatband potential, a quantity analogous to the p.z.c. of metal electrodes.

The flatband potential naturally controls the band bending in the space charge region under a given electrode potential, and is of vital importance in the study of semiconductor electrode processes, such as the photosensitized electrolytic oxidation$^{1)}$, where the energy band structure in the space charge region can be a decisive factor. The position of the flatband potential can sometimes be shifted by the pretreatment of the electrode surface or by a change in the solution composition. Such a shift is often caused by the change in the potential drop in the electrical double layer at the interface, and therefore can affect the rate of electron transfer reaction, e.g., the spectrally sensitized photocurrent by organic dyes$^{2)}$.

Measurements of flatband potentials have so far been reported on Ge$^{3),4)}$, ZnO$^{3),4)}$, GaAs$^{3),4)}$, CdS$^{3),4)}$ and GaP$^{5)}$ electrodes, but few investigations have been carried out relating the flatband potential with the rate of electron transfer across the electrical double layer.

In the present study we measured the flatband potentials of n-type $TiO_2$ and CdS single crystal electrodes as a function of the solution pH. An outstanding difference in the pH-dependence between these two electrodes was found, which would prove to be a clue for further investigations of semiconductor electrode reactions.

## EXPERIMENTAL

$TiO_2$ single crystal electrode employed was an n-type semiconductor, with (001) face exposed. The form of the electrode was a wafer of 1.5 mm thick, with the surface area of 0.7 $cm^2$. For an ohmic contact with the conducting wire, indium was evaporated on to the surface. Before measurements the electrode was polished with alumina powder, immersed in nitric acid for a constant period of time, and then washed with water. The electrolyte was a 0.5 M KCl aqueous solution, and the pH of the solution was controlled by means of Clark-Lubs or Michaelis buffer solutions.

CdS single crystal was also of n-type, with (001) face exposed. The electrode was 2 mm thick, with the surface area of 1.0 $cm^2$. Pretreatments of the electrode were mechanical polishing, etching in hydrochloric acid, and subsequent water washing. The electrolyte was a 0.2 M $Na_2SO_4$ aqueous solution, and the pH of the solution was varied with a small amount of $H_2SO_4$ or NaOH.

Of the two methods for the determination of flatband potentials, i.e., the capacitance measurement[6)] and the instantaneous photopotential measurement[7)], the former method was employed here with the use of an a.c. bridge illustrated in Fig. 1. For the calculation, the measured system was conveniently assumed to have only one capacitance in the semiconductor space charge region, because other capacitance components (those of the Helmholtz layers at semiconductor-electrolyte and counter electrode-electrolyte interfaces) have normally too large values to affect the overall capacitance.

## RESULTS AND DISCUSSION

The determination of the flatband potential of a highly doped semiconductor electrode is based upon the application of the Mott-Schottky relationship[3),4)] which is expressed as

$$\frac{1}{C_s^2} = \frac{2}{q\varepsilon\varepsilon_o N}\left( V - V_{fb} - \frac{kT}{q} \right) \qquad (1)$$

where $C_s$ represents the space charge capacitance per unit area, q the electronic charge, $\varepsilon$ the dielectric constant of the semiconductor, $\varepsilon_o$ the permittivity of vacuum, N the carrier concentration (practically equals the donor concentration in the present case), V the electrode potential, and $V_{fb}$ the flatband potential. This relationship is applicable when the capacitance of the space charge layer is much smaller than those of any other regions. Such a situation can be attained at the anodic polarization for n-type semiconductors where a depletion layer is formed for the majority carriers (electrons). Thus the intercept of the V axis of the $1/C^2$ (approximately equals $1/C_s^2$) vs V curve gives a potential differing from the flatband potential by kT/q.

Fig. 2 shows a typical $1/C^2$ - V plot for CdS electrode. The slope in the potential range from -0.85 to -0.25 V agrees fairly well with the theoretical one (broken line) predicted by Eq. (1) using the values $\varepsilon = 8.64$ and $N = 7.38 \times 10^{16}$ $cm^{-3}$ (determined by measurement of the Hall effect). A break appears at -0.25 V, presumably caused by ionization under further anodic polarization of deep donors which are not ionized in the bulk of the semiconductor. A similar phenomenon has once

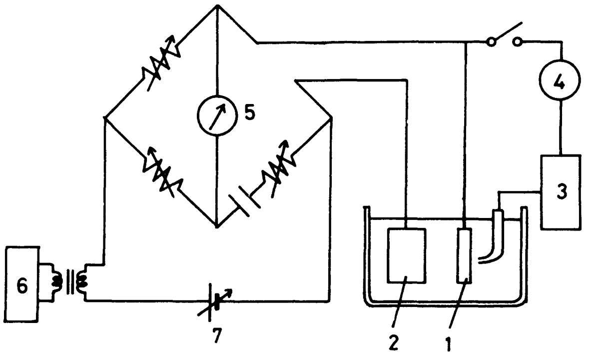

Fig.1 CAPACITANCE BRIDGE

1 SEMICONDUCTOR ELECTRODE
2 Pt COUNTER ELECTRODE
3 S.C.E.
4 VOLTMETER
5 NULL DETECTOR
6 OSCILLATOR
7 DRY CELL

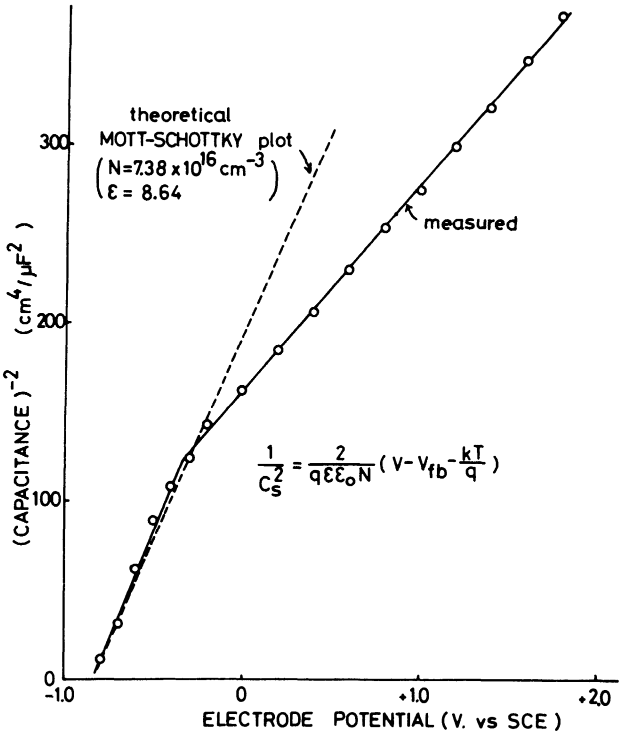

Fig. 2 TYPICAL $C^{-2}\sim V$ PLOT FOR CdS (pH 8.9)

been reported on GaAs[8].

The flatband potentials of $TiO_2$ and CdS single crystal electrodes thus determined are shown in Fig. 3 as a function of the solution pH. The flatband potential of $TiO_2$ electrode depends almost linearly on pH with the slope of -59 mV/pH, while that of CdS holds a constant value of -0.88 V vs SCE. This fact could be elucidated by the following consideration.

Suppose the following dissolution equilibrium be established at the $TiO_2$ electrode surface,

$$\mathrm{Ti{-}O^{2-}} + \mathrm{H^+} \rightleftharpoons \mathrm{Ti{-}OH^-} \qquad (2)$$

where $\mathrm{Ti{-}O^{2-}}$ represents an element of the $TiO_2$ lattice at the surface, $H^+$ a proton in the bulk (beyond the electrical double layer) of the electrolyte solution, and $\mathrm{Ti{-}OH^-}$ the lattice element protonized. A thermodynamic reasoning leads to the following formula for the shift in the equilibrium potential $\Delta\Phi$ of the $TiO_2$ electrode.

$$\Delta\Phi = \mathrm{const.} + \frac{RT}{F} \ln \frac{a_{\mathrm{Ti-O^{2-}}}}{a_{\mathrm{Ti-OH^-}}} - \frac{2.3RT}{F}\,\mathrm{pH} \qquad (3)$$

Provided that the pH-dependence of the second term is negligible, a change in pH by unity produces a change in the potential difference within the Helmholtz layer of 2.3RT/F (ca. 59 mV at room temperature). This is what can be seen in Fig. 3 for the $TiO_2$ electrode. Analogous explanations have been proposed for the pH-dependence of Ge and GaAs electrodes assuming the oxide formation at the surface[3),4)].

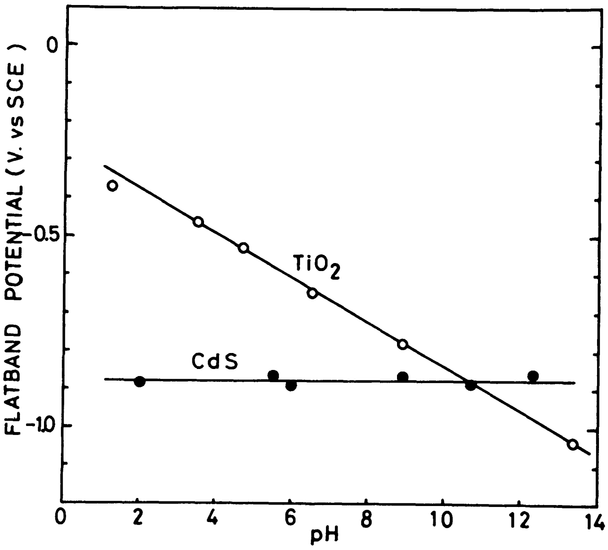

Fig. 3 pH-DEPENDENCE OF FLATBAND POTENTIAL OF $TiO_2$ AND CdS ELECTRODES

In the case of CdS electrode, a dissolution equilibrium similar to Eq. (2) seems to be unlikely by the fact that no variation of the flatband potential with respect to the solution pH was observed.

Such a conspicuous difference described above is suggestive of a further difference in the pH-dependence of the electrode reactions occurring on these two semiconductor electrodes, which we have found in the investigation of the spectrally sensitized photocurrents of $TiO_2$ and CdS electrodes[9].

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