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SURFACE STATES OF n-TYPE TiO_2 ELECTRODE IN AQUEOUS SOLUTION

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The basic properties of surface states were studied by the capacitance measurements for TiO_2 electrode to elucidate the role of the surface states on the charge transfer at electrode-electrolyte interface. The surface state density and its energy were obtained respectively to be $N_t=1.5\times10^{12}$ cm^{-2} and $E_t=0.4$ eV below the bottom of the conduction band.

For recent years, it has been recognized that the surface states play an important role on the charge transfer at the semiconductor/liquid interface. For example, some workers$^{1)}$ reported that the cathodic dark current was observed at the potential more positive than the flat band potential at an n-type TiO_2 electrode. Although the above observation was interpreted in terms of the charge transfer via surface states, the experimental results were not quantitatively discussed because they could not determine the energy level and the state density of the surface states. The curve of the surface state capacitance vs. the electrode potential directly gives the energy level and state density of the surface state. The surface state capacitance was not detected at high frequency because of the relaxation time of the surface states. In the present paper, the surface state energy and the state density of TiO_2 single crystal were determined from the low frequency capacitance measurements in order to clarify the charge transfer processes via surface state.

A TiO_2 crystal(Nakazumi Crystal Co.) was reduced in vacuum (2×10^{-6} Torr = 2.7×10^{-4} Pa) at 1100 °C for 4 h. The aqueous solution of 0.25 M HNO_3 and 1 M KNO_3 was used as the electrolyte solution. The capacitance of this system was measured by using a 2 mV sine wave of 0.6 - 2000 Hz superimposed onto the dc bias. The 90° component of the resultant current was determined by a lock-in amplifier. The system was calibrated by replacing the electrochemical cell by a standardized capacitor.

The capacitance was measured mainly at 0.6 Hz in order to enhance the contribution of the slow relaxation component at the surface. The hump of the capacitance was observed in the potential region -0.2 to 0.2 V vs. SCE. The capacitance which was obtained by subtracting the depletion layer capacitance from the total capacitance is plotted against the electrode potential in Fig.1. The shape of the plot is a typical one for the surface state capacitance$^{2)}$ whose electrode potential dependence is given by

$$C_{ss}(E) = \frac{N_t e^2}{kT} \frac{\exp((E_t - E)/kT)}{(1+\exp((E_t - E)/kT))^2} \qquad (1)$$

where e is the elementary charge, C_{ss} is the capacitance divided by surface area, and E_t and N_t are the energy and surface density of the surface states, respectively, and E represents the Fermi level of the semiconductor. The Theoretical curve of C_{ss} vs. E is a symmetrical one with the peak value, $C_{ss} = 0.25e^2N_t/kT$ at $E = E_t$. The experimental curve of the surface state capacitance vs. electrode potential in Fig.1 has a peak at 0.0 V vs. SCE and a peak value of 2.2 $\mu F/cm^2$, so we can estimate that the surface state is located at 0.0 V vs. SCE and the surface state density, N_t, is 1.5×10^{12} cm^{-2}. From the slope of the Mott-Schottky plot(Fig.2) in the potential region where no surface state was observed, the carrier density of 8×10^{19} cm^{-3} was estimated by assuming that the surface factor was two. The flat band potantial of -0.4 V vs. SCE was obtained from the potential axis intercept of the Mott-Schottky plot. In the TiO_2 crystal with such a large carrier density as 8×10^{19} cm^{-3}, the Fermi level is adjacent to the bottom of the conduction band. This explains the fact that the surface state is located at 0.4 eV below the bottom of the conduction band. The surface state capacitance was independent of the kind of the supporting electrolyte (H_2SO_4-Na_2SO_4, HNO_3-KNO_3, $HClO_4$, HCl). Therefore, the surface states are not those caused by the specific adsorption on the electrode surface but the states caused by the impurity or defect in the bulk of TiO_2. It is known from the temperature dependence of the electrical conductivity that the reducing treatment of titanium dioxide will introduce a level due to the oxygen vacancy or Ti^{3+} ion at 0.3 eV below the bottom of the conduction band.3) The surface state level observed in the present experiment lied close to this level; but the assignment is not definitive at the present.

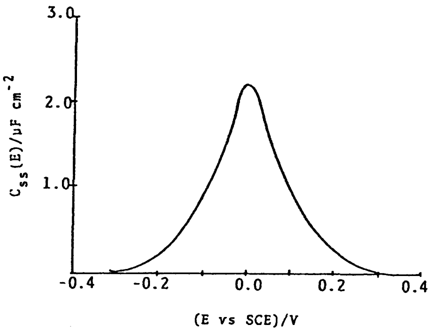

Figure 1. Surface states capacitance vs. electrode potential for TiO_2 electrode in 0.25 M HNO_3 and 1 M KNO_3.

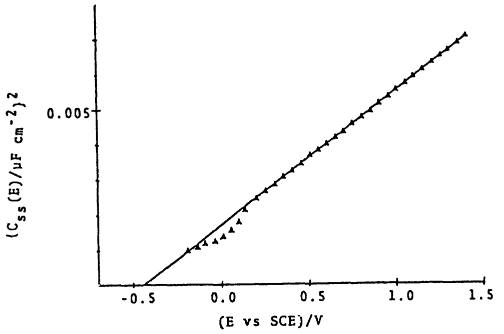

Figure 2. Mott-Schöttky plot for TiO_2 electrode in 0.25 M HNO_3 and 1 M KNO_3(frequency:0.6 Hz).

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