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Capacitance Relaxation Method for Detecting Surface States and Bulk Traps at Semiconductor-liquid Junctions

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To detect surface (or bulk trapping) states with small state density at a semiconductor-liquid junction, we have developed a capacitance relaxation method. This method is applied to studies of the electronic structure at the TiO_2/H_2O interface.

In recent years, the electronic structure of the semiconductor electrode surface in contact with electrolyte solutions has been studied by using some techniques developed for detecting interface states at MIS devices.[1-3] For instance, we have determined properties of surface states at the TiO_2/H_2O interface by employing the low frequency capacitance method.[1] This method is simple but its usage is restricted to surface states with large state density. On the other hand, the conductance method has higher sensitivity if no leakage current flows at a semiconductor and liquid (S-L) junction.[3,4] However, electrochemical reactions occur at an interface of a semiconductor and an electrolyte solution containing redox species. Such electrochemical reactions raise the background of a. c. conductance at the S-L junction and result in a lowering of the sensitivity.

In the present work, we develop a capacitance relaxation method in which the frequency dependence of $-\omega dC/d\omega$ is measured (ω : angular frequency), and we apply this method to the investigation of the electronic structure of the TiO_2/H_2O interface.

A single rutile crystal (1 mm thick) was heated to 900 °C at 2×10^{-6} Torr for 5 h. An ohmic contact was made to one side of the crystal by depositing In metal. The electrolytic solution contained 0.25 M HNO_3 and 0.5 M KNO_3. The capacitance and resistance were measured by using an impedance analyser(4192A YHP). Impedance measurements were performed at frequencies ranging from 5 Hz to 13 MHz. Values of the capacitance and resistance measured by the impedance analyser were transmitted to a computer(9801F NEC). Impedance measurements were repeated 50 times, and subsequently data stored in the computer was averaged.

Application of an a. c. impedance analyser with four probe terminals to an electrolytic cell enables us to obtain separately the impedance of a S-L junction alone. When the internal impedance of a reference electrode is large, a value of the impedance measured at a higher frequency is remarkably affected by the presence of stray capacitance of sample holders and electrical lead wires. Thus, in an a. c. impedance measurement, an electrode with the small internal impedance should be

employed as a reference electrode, instead of a saturated calomel electrode(SCE). In the present work, a platinum electrode with the surface area of 50 cm^2 was used as a reference electrode. The d. c. electrode potential was measured with respect to SCE by using an electrometer with the high internal impedance(TR8651 TAKEDA).

An electric equivalent circuit of a S-L junction is illustrated in Fig. 1.[5] R_o and C_o denote the resistance and capacitance of an ohmic contact. R_b and R_{so} are the resistance of the semiconductor bulk and of the electrolytic solution, respectively. C_{ss} and R_{ss} are the capacitance and resistance of surface states, respectively. The resistance R_t and capacitance C_t originate from bulk trapping states in the space charge layer. We assume that there is no redox species in an electrolyte solution which interacts with surface states. Under this assumption, one can eliminate the resistance R_{sr} which represents the reciprocal of the electron transfer rate between surface states and redox species in solution. The Faradaic resistance R_i is associated with the leakage current arising from electrochemical reactions which occur via the conduction(valence) band at the semiconductor surface. There is possibility that surface states are newly formed by species which are produced in the process of electrochemical reactions.[5] For simplicity, however, the density of surface states is assumed to be not varied by the electrochemical reactions. The Helmholtz layer capacitance C_H is larger than the depletion layer capacitance C_{sc}, so that the parallel equivalent capacitance C_p and conductance G_p of the space charge layer are respectively given by[5,6]

$$C_p = C_{sc} + C_{ss}/(1+\omega^2\tau_s^2) + C_t/(1+\omega^2\tau_t^2) \quad (1)$$

and

$$G_p = 1/R_i + \omega^2\tau_s C_{ss}/(1+\omega^2\tau_s^2) + \omega^2\tau_t C_t/(1+\omega^2\tau_t^2) \quad (2)$$

where τ_s and τ_t denote the relaxation time of the surface states and that of the bulk trapping states in the space charge layer, respectively. In the depletion region, the relaxation times τ_s and τ_t for a n-type semiconductor are written as[6]

$$\tau_s^{-1} = C_{ns} N_c [\exp(E_f - E_c - eV_s)/kT + \exp(-E_s/kT)] \quad (3)$$

$$\tau_t^{-1} = 2 C_{nt} N_c \exp(-E_t/kT) \quad (4)$$

where C_{ns}(or C_{nt}) is the probability per unit time for an electron to be captured by an empty surface (or bulk trapping) state, N_c is the effective density of the conduction band, eV_s represents the band bending, $E_s(E_t)$ is the depth energy of surface(bulk trapping) states with respect to the bottom of the conduction band, E_f is the energy of the Fermi level, and E_c is the energy of the bottom of the conduction band in the semiconductor bulk. In the conductance method, the relaxation time and state density of surface (bulk trapping) states are determined from a peak frequency and a peak value in a plot of G_p/ω vs. $\omega/2\pi$. The decrease of R_i raises the background of G_p/ω in the low frequency range and shifts the peak frequency toward lower values. Thus, the presence of the leakage current is especially severe for detecting surface(bulk trapping) states with a long relaxation time. As is evident from Eqs. 1 and 3, the parallel equivalent capacitance C_p is not affected by the leakage

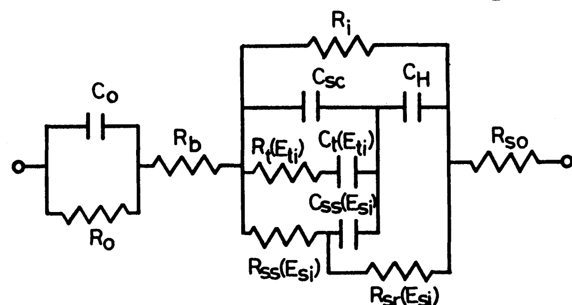

Fig. 1. Electric equivalent circuit of S-L junction.

current. However, since values of C_{ss} and C_t are generally small in comparison with a value of C_{sc}, it is difficult to distinguish C_{ss} or C_t from C_{sc}. Tomkiewicz[2] assumed that a capacitance value approaches to a value of the depletion layer capacitance with increasing the measurement frequency, and he took a value of capacitance at about 50 kHz as a value of C_{sc}. As will be discussed later, however, values of C_p decreased gradually with frequency in the range of 10 kHz to 10 MHz. Consequently, it is not easy to evaluate experimentally an accurate value of the depletion layer capacitance.

We define the capacitance relaxation signal S as follows

$$S = -\omega dC_p/d\omega = 2\omega^2\tau_s^2 C_{ss}(1+\omega^2\tau_s^2)^{-2} + 2\omega^2\tau_t^2 C_t(1+\omega^2\tau_t^2)^{-2} \quad (5)$$

The function $2(\omega\tau)^2/(1+(\omega\tau)^2)^2$ is plotted against angular frequency in Fig. 2 (solid line). For comparison, the function $\omega\tau/(1+(\omega\tau)^2)$ included in G_p/ω is also shown in Fig. 2 (dotted line). In the plot of $2(\omega\tau)^2/(1+(\omega\tau)^2)^2$ vs ω, a peak emerges at an angular frequency equal to $1/\tau$. It should be noted that the plot of $2(\omega\tau)^2/(1+(\omega\tau)^2)^2$ vs. ω is sharp compared with the plot of $\omega\tau/(1+(\omega\tau)^2)$ vs. ω. This implies that the capacitance relaxation method has higher resolution than the conductance method.

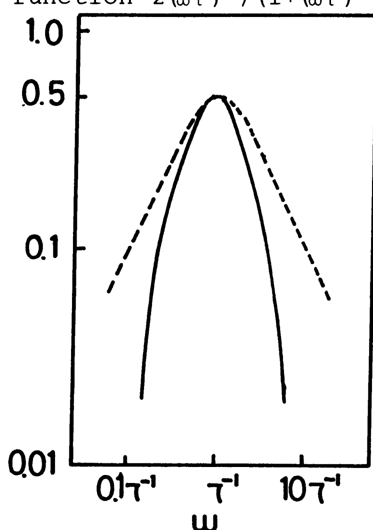

Fig. 2. $2\omega^2\tau^2/(1+\omega^2\tau^2)^2$ vs ω (solid line), and $\omega\tau/(1+\omega^2\tau^2)$ vs. ω (dotted line).

Complex impedance plots for the TiO_2/H_2O interface are shown in Fig. 3. The intercept of loci on the resistance axis yields $R = R_b + R_o + R_{so} = 50\ \Omega$. The values of C_p and G_p are calculated by the following equations:

$$G_p = (R_{ob} - R)/((R_{ob} - R)^2 + X_{ob}^2) \quad (6)$$

and

$$C_p = \omega^{-1}X_{ob}/((R_{ob} - R)^2 + X_{ob}^2) \quad (7)$$

where R_{ob} and X_{ob} are the measured resistance and reactance. Inductive reactance appears at frequencies higher than 2 MHz. This is due to the inductance of electrical lead wires connecting a sample to terminals of an impedance analyser. The inductance of the electrical lead wires is estimated to be 10^{-6} H. At frequencies lower than 300 kHz, the inductive reactance ωL of the electrical lead wires is less than 0.5% of the capacitive reactance, so that in this frequency range the contribution of the inductance of the electrical lead wires is negligible. In Fig. 4, values of C_p are plotted as a function of the frequency. The value of C_p is gradually decreased with frequency. No plateau is observed in the plots of C_p vs. $\omega/2\pi$ in the range of 10 kHz to 1 MHz. Thus, an accurate value of the depletion layer capacitance cannot be estimated from the C_p vs. $\omega/2\pi$ plots. In Fig. 5, the capacitance relaxation signal S and G_p/ω

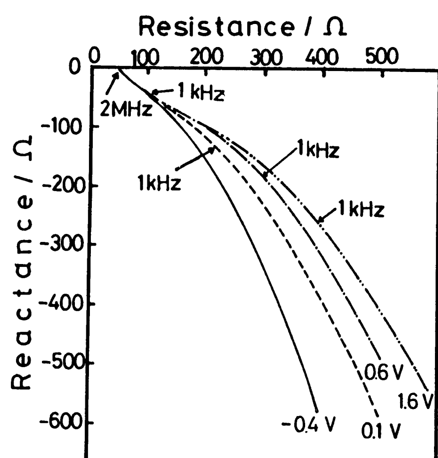

Fig. 3. Complex impedance plots of the TiO_2/H_2O interface.

of the TiO_2/H_2O interface are plotted as a function of frequency. The plots of G_p/ω vs. $\omega/2\pi$ exhibit peaks, and the peak frequency is shifted toward lower values as the electrode potential is decreased. The shift of the peak frequency is not ascribed to the electrode potential dependence of the relaxation time of surface states, because the peak frequency of surface states given by $(2\pi\tau_s)^{-1}$ is drastically decreased with the increase in the electrode potential. This shift is probably caused by the change in the background of a. c. conductance. On the other hand, the plots of S vs. $\omega/2\pi$ exhibit marked peaks at 400 Hz, and the peak frequency is independent of the electrode potential. The relaxation time of bulk trapping states τ_t is independent of the electrode potential. Thus, the capacitance relaxation spectra in Fig. 5 are attributable to bulk trapping states. The trap density of 2×10^{19} cm^{-3} is estimated from the peak values in the S vs. $\omega/2\pi$ plots. The peak frequency in the S vs. $\omega/2\pi$ plots is not affected by the leakage current. Owing to this advantage, the capacitance relaxation method can provide information about the electrode potential dependence of the relaxation time of surface(bulk trapping) states even if the leakage current flows at the S-L junction. In addition, this method has higher sensitivity. For instance, in the case of $C_{sc} = 10^{-7}$ F cm^{-2}, one can detect surface states of the state density N_{ss}>5 10^9 $cm^{-2}eV^{-1}$, and of the relaxation time τ_s < 32×10^{-3} s. Therefore, the capacitance relaxation method is very useful for studying the electronic structure of the S-L junction.

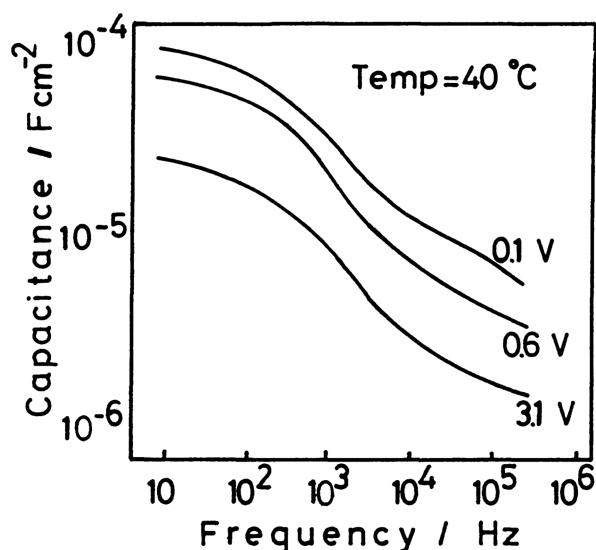

Fig. 4. Frequency dependence of C_p.

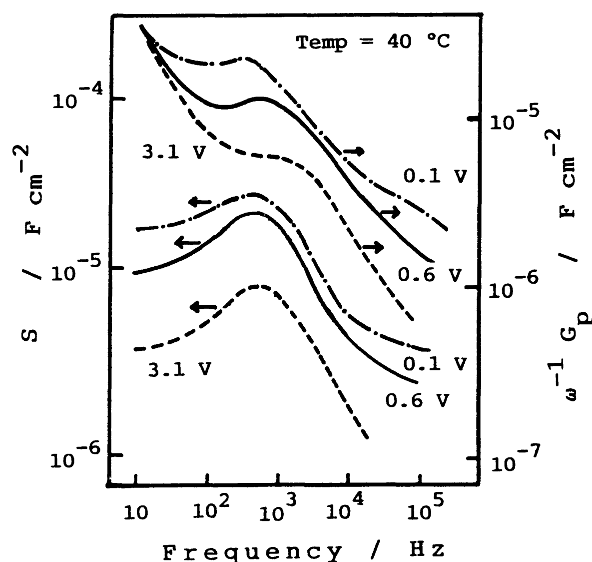

Fig. 5. Plots of S vs. $\omega/2\pi$ and plots of $\omega^{-1}G_p$ vs. $\omega/2\pi$.

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