Semiconductor Electrodes

XLIX. Evidence for Fermi Level Pinning and Surface-State Distributions from Impedance Measurements in Acetonitrile Solutions with Various Redox Couples

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ABSTRACT

Capacitance-voltage (C-V) measurements were made for the single crystal semiconductors n-TiO₂, n-CdS, n-InP, p-Si, p-GaAs, n- and p-WSe₂, and n-MoSe₂ in acetonitrile containing a number of redox couples whose potentials (V_redox) spanned a potential regime much wider than the bandgaps. The flatband potential (V_FB) evaluated from capacitance-potential (C-V) measurements (Mott-Schottky plots) exhibited three types of behavior with varying solution redox potentials: (i) V_FB varied monotonically with V_redox for p-Si, p-GaAs, and n-InP; (ii) for n-TiO₂ and n-CdS, V_FB did not shift for couples located negative of the midgap potential, but varied monotonically for couples positive of this value; (iii) for the layer-type, compounds (MoSe₂, WSe₂), V_FB was almost independent of V_redox. These differences were ascribed to differences in surface-state densities. For n-TiO₂ crystals, (001) face etched with molten KHSO₄ and reduced, evidence for surface states at two different potentials was obtained from the in-phase component of the total admittance. Tentative assignment of these states is to lattice defects. The shape of the photocurrent vs. applied bias curve can be used as a measure of efficiency of a PEC cell; the precipitous increase in photocurrent near V_FB for n-TiO₂ etched in a special way with simmering H₂SO₄ was taken as a sign of improvement (11). Such a sharp rise to the saturation value has been attributed to the presence of electron/photocarrier trapping states in the semiconductor material. A discussion of this paper will appear in the June 1984 Discussion Section to be published in the June 1984 JOURNAL. All discussions for the June 1984 Discussion Section should be submitted by Feb. 1, 1984.

Key words: capacitance, flatband potential, conductance.

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has been attributed to the absence of a high density of surface states. Further, the absence of surface states is sometimes assumed when frequency independent Schottky-Mott (S-M) plots (plots of $C^{-2}$ vs. $V$, where $C$ is capacitance) are found. However, we (14) and others (15-17) have shown that with small bandgap semiconductors, the in-phase ($0^\circ$, conductance) component of the total admittance is more sensitive to the presence of surface states than the quadrature ($90^\circ$, capacitance) component (see Appendix).

We report here a-c impedance studies of several single-crystal semiconductors in MeCN and show that $V_{FB}$ shifts with $V_{redox}$ occur with several of these. The effect of pretreatment of TiO$_2$ on its impedance behavior and investigation of surface states by conductance measurements are also discussed.

**Experimental**

The single crystals employed were n-TiO$_2$, n-InP, n-CdS, n- and p-WSe$_2$, n-MoSe$_2$, p-Si, and p-GaAs. The procedures for polishing and mounting the semiconductor electrodes have been described elsewhere (18-24) and the etching procedures are given in Table I. Two different types of TiO$_2$ crystals were employed. The undoped TiO$_2$ single crystal (Nakazumi Earth Crystals, Japan) is denoted crystal A and the Nb-doped TiO$_2$ crystal, obtained from H. S. Jarrett, du Pont, is denoted crystal B. Both were orientated with the (001) face exposed to solution, as ascertained by x-ray diffraction (ASTM Card No. 23-1486). Some crystals were treated by a procedure recommended by Jarrett to produce a smooth surface (treatment 1). These were polished in succession with 0.3 µm alumina and 1 µm diamond paste to produce a mirror-like surface. This surface was then etched with molten KHSO$_4$ in a Pt crucible (625°C for 2 hr). An SEM photograph (Fig. 2) shows a very smooth surface. Since the crystals had a straw-colored appearance after the molten KHSO$_4$ etch, implying that they were oxidized, they were subjected to a reduction pretreatment before use. The Nb-doped crystals were reduced in flowing CO at 700°C for 1 hr, the undoped crystals were reduced in an H$_2$ atmosphere at 625°C for 20 min. These were mounted as electrodes and used without further treatment. In treatment 2, the undoped TiO$_2$ crystals were not etched with KHSO$_4$, but instead were only reduced in H$_2$ (625°C for 20 min) directly after polishing with Al$_2$O$_3$ and diamond paste. The methods of purification of the solvent acetonitrile (MeCN) and sources of redox couples are given elsewhere (18).

Abbreviations of the various redox couples employed are given in Table II. Their concentrations varied from 0.1 to 30 mM. With perylene, rubrene, chrysene, and MV(PF$_6$)$_2$ (where MV = methyl viologen) the concentrations were about 0.1 mM; for Ru(bpy)$_3$$^{2+}/^+$ and AQ$^{3+/-}$ (where bpy = bipyridine and AQ = anthraquinone) they were about 0.5 and 2 mM, respec-

<table>
<thead>
<tr>
<th>SC</th>
<th>$N_{D/A}$ / cm$^3$</th>
<th>Etching procedures</th>
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<tbody>
<tr>
<td>TiO$_2$</td>
<td>$\sim 10^{19}$</td>
<td>Conc. HNO$_3$ for 1 min followed by conc. HF for 10 sec, then rinsed with distilled water. This procedure was repeated.</td>
</tr>
<tr>
<td>Cds</td>
<td>$\sim 10^{27}$</td>
<td>Conc. HCl for 40 sec, then rinsed with distilled water.</td>
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<tr>
<td>n-WSe$_2$</td>
<td>$\sim 10^{15}$</td>
<td>6M HCl for 30 sec, then rinsed with distilled water. This procedure was repeated twice.</td>
</tr>
<tr>
<td>n-MoSe$_2$</td>
<td>$\sim 10^{15}$</td>
<td>6M HCl for 30 sec, then rinsed with distilled water.</td>
</tr>
<tr>
<td>n-InP</td>
<td>$\sim 10^{15}$</td>
<td>6M HCl for 30 sec, then rinsed with distilled water.</td>
</tr>
<tr>
<td>p-GaAs</td>
<td>$\sim 10^{15}$</td>
<td>H$_2$O$_2$%H$_2$O$_2$%H$_2$O (3:1:1 by volume) solution for 5 sec, then rinsed with distilled water.</td>
</tr>
<tr>
<td>p-Si</td>
<td>$\sim 10^{15}$</td>
<td>HNO$_3$:CH$_3$COOH:H$_2$O (1:1:1 by volume) containing a drop of H$_2$O per 50 ml for 30 sec followed by conc. HF for 5 sec, then rinsed with distilled water.</td>
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<table>
<thead>
<tr>
<th>SC</th>
<th>$V_{FB}$ (mV)</th>
<th>$V_{redox}$ (mV)</th>
<th>$V_{FB}$ vs. $V_{redox}$ (mV)</th>
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<tbody>
<tr>
<td>TiO$_2$</td>
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<tr>
<td>Cds</td>
<td></td>
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<td>n-WSe$_2$</td>
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<tr>
<td>n-MoSe$_2$</td>
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<td>n-InP</td>
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<td>p-GaAs</td>
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<tr>
<td>p-Si</td>
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Nitrobenzene used with p-Si was about 30 mM. All other couples were 10 mM. The concentrations of the electrochemically generated forms were about 20-30% of the starting material. The supporting electrolyte was electrometric grade tetra-n-butylammonium perchlorate (TBAP) (Southwestern Analytical Chemicals, Austin, Texas). This was purified by dissolving it in a minimum quantity of acetone, filtering the solution, and then recrystallizing with ether. This procedure was repeated twice. The recrystallized TBAP was dried for two days at 80 °C under vacuum (<10⁻⁵ Torr). All chemicals were stored in a helium-filled glove box (Vacuum Atmosphere Corporation, Hawthorne, California).

A conventional two-compartment electrochemical cell of ~25 ml capacity was used for electrochemical studies. For impedance measurements, a large area (~40 cm²) Pt-gauze immersed in the same compartment as the working electrode was used as a counter-electrode. A Pt-gauze (~10 cm²), separated from the main compartment by a medium porosity glass frit, was used as a counter-electrode for electrochemically generating radicals. An aqueous SCE with a KCl-saturated agar plug, directly introduced into the main compartment by a medium porosity glass frit, was used as a reference electrode. All the potentials are expressed against this aqueous SCE unless otherwise specified.

A PAR Model 173 potentiostat and a PAR 175 universal programmer (Princeton Applied Research Corporation, Princeton, New Jersey) equipped with a Model 2000 X-Y recorder (Houston Instruments, Austin, Texas) were used to obtain the cyclic voltammograms as well as for capacitance-voltage measurements. A Soltec (Sun Valley, California) Model 6432, X-Y recorder was used for recording both the 0° and 90° components simultaneously. In these latter experiments, a lock-in amplifier technique, which yields the in-phase and the out-of-phase components of an a-c signal superimposed on a linear sweep, was used. The frequency of 15 Hz, and the peak-to-peak amplitude of 12 mV, were used. The flatband potential vs. an aqueous SCE, V_FB, was then determined from a Schottky-Mott (S-M) plot of 1/C² vs. V

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N} (V - V_{FB} - 0.025) \tag{1}
\]

where C is the capacitance per unit area; ε, the electronic charge (1.6 × 10⁻¹⁹ C); ε₀, the semiconductor dielectric constant; ε₀, the permittivity of free space (8.85 × 10⁻¹² F/cm); and N, the acceptor (p-type) or donor (n-type) density. Although in some cases determination of V_FB from the intercept of S-M plots involves some ambiguity (25), V_FB can generally be determined to within 0.1 V, and shifts in V_FB can be readily determined from the C-V plots themselves. As shown previously (3), linear S-M plots which yield V_FB can be obtained in the presence of surface states when the frequency used to obtain the capacitance is such that the surface-state capacitance does not make an appreciable contribution. In Fig. 3, given are the S-M plots for unetched TiO₂ (crystal A, treatment 2) in supporting electrolyte alone at three different frequencies; in Fig. 4a, b, the C-V and the corresponding S-M plots, respectively, are shown for a solution containing the TMPD⁺/⁺ couple (abbreviations used are given in Table II). Although the V_FB for n-TiO₂ in the absence and presence of the TMPD⁺/⁺ couple is the same, addition of other redox couples, such as 10-MP⁺/⁺ or Per⁺/⁺, causes an appreciable shift of V_FB to more positive values. The results are summarized in Table II. Similar shifts in V_FB with V_redox are found with n-CdS and n-InP (Fig. 5 and 6). In Fig. 7, the plots of variation of V_FB with V_redox are given for p-Si, p-GaAs, p-WSe₂, and n-InP along with n-TiO₂ and n-CdS. Note however, that for the layer-type compounds n-WSe₂, n-MoSe₂, and p-WSe₂, V_FB is essentially invariant with V_redox. This finding agrees with a previous study of the C-V behavior of another layer-type compound, α-MoTe₂, where V_FB was independent of V_redox (14).

The behavior of the semiconductors which show shifts of V_FB with V_redox is consistent with FLP and the presence of surface states on the electrode surface. The density and distribution of these states can be prepared and sealed inside the glove box prior to removal for experimentation.

**Results**

C-V data.—Capacitance values were obtained for a number of single-crystal semiconductors in 0.1M TBAP MeCN solutions as a function of frequency and applied potential in the absence and presence of various redox couples spanning a wide range of V_redox. The flatband potential vs. an aqueous SCE, V_FB, was then determined from a Schottky-Mott (S-M) plot of 1/C² vs. V

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N} (V - V_{FB} - 0.025) \tag{1}
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semiconductor electrodes

1.5
0.5
-0.5
-1.0
POTENTIAL (VOLTS VS. SCE)

Fig. 4. (a) Capacitance (C) vs. potential of TiO2/MeCN containing 10 mM TMPD and 2 mM TMPD+ in 0.1M TBAP; f = 200 Hz; (b) S-M plot for the C-V curve in (a).

Fig. 5. S-M plot for n-CdS contacting MeCN, 0.1M TBAP containing various redox couples; f = 2 kHz blank (-); 10-MP/ + ( ); Th/ + ( ) (For abbreviations, see Table II).

probed by conductance measurements (14). If a surface-state level is assumed with a time constant, τ, independent of potential, the measured overall in-phase (0°) component, \( G_p \), of a semiconductor in contact with a liquid electrolyte can be related, under certain conditions (see Appendix), to the surface-state capacitance, \( C_{ss} \), and its time constant (τ) by the following equation (14)

\[
\frac{G_p}{\omega} = \frac{G_{ss}}{\omega} + \frac{G_D}{\omega} = \frac{C_{ss} \omega^2}{1 + \omega^2 \tau^2} + \frac{G_D}{\omega}
\]  

where \( G_D \) is the depletion layer conductance, \( C_{ss} \) is the surface-state capacitance, and \( \omega \) is the angular frequency. Then a plot of \( G_p/\omega \) vs. \( \omega \) at a given potential will go through a maximum when \( \omega = 1 \). The reciprocal of this peak angular frequency will yield a time constant \( \tau \) which represents a weighted average of the time constants associated with the surface states located around that potential. For the layer-type compound, n-MoSe2, a plot of \( G_p/\omega \) vs. \( \omega \) at +0.25V vs. SCE, in MeCN, 0.1M TBAP, containing 10-MP is given in Fig. 8a. The time constant, \( \tau \), corresponding to the peak frequency evaluated from this plot, is around \( 1.14 \times 10^{-4} \) sec. This value of \( \tau \) is in good agreement with that obtained by Kautek and Gerischer for MoSe2 (26). Notice also that the peaks of the \( G_p/\omega \) vs. \( \omega \) plots (Fig. 8a) occur at about the same frequency for different applied potentials in the region where the peak is observed in the \( G_p \) vs. \( V \) plots; this suggests that \( \tau \) is relatively independent of potential. With this value of \( \tau \), the surface-state density as a function of potential (\( N_{ss} \) in cm\(^{-2} \) eV\(^{-1} \)) can be calculated from the equation

\[
N_{ss} = \frac{2G_{ss}}{e} \cdot \tau
\]  

where \( e \) is the electronic charge. The procedure used to determine \( G_{ss} \) is given in the Appendix. A typical plot of \( N_{ss} \) (cm\(^{-2} \) eV\(^{-1} \)) vs. \( V \) is shown for n-MoSe2 over the potential range +0.1-0.45V vs. SCE in Fig. 8b. The integrated value of the curve in Fig. 8b when multiplied by \( \tau/e \) yields the value of \( N_{ss} \) (cm\(^{-2} \)). Thus for n-MoSe2, the surface-state density in the +0.1-0.45V regime is estimated as about \( 1.4 \times 10^{10} \) cm\(^{-2} \). This value of the density of surface states is comparable to that obtained with a-MoTe2 (14) which is \( 10^{10} \) cm\(^{-2} \). Similar values for \( \tau \) and \( N_{ss} \) were obtained for n- and p-WSe2. In Fig. 9a, b are shown the plots of \( G_p/\omega \) vs. \( \omega \) at −0.1V and \( N_{ss} \) vs. \( V \), respectively, for p-Si.
probe the effects of these two different treatments on the properties of surface states such as time constant, energy, and density distribution, the \( \varphi \) component was measured both as a function of potential and frequency for two undoped (crystal A) and Nb-doped (crystal B) TiO\(_2\) crystals. In Fig. 10 are shown the \( G_p \) vs. \( V \) curves in MeCN, 0.1M TBAP containing 10 mM 10-MP\(^{0+/+}\) for crystal A (treatment 1). For crystal A (treatment 2) such plots are shown in Fig. 11. For Nb-doped TiO\(_2\)

Following the method described above for n-MoSe\(_2\), the \( \tau \) and \( N_{ss} \) are about \( 4 \times 10^{-5} \) sec and \( 10^{15} \) cm\(^{-2}\), respectively.

**Effect of pretreatment on TiO\(_2\) behavior.**—For TiO\(_2\), the etching procedures documented in literature span a wide regime of chemical activity—from such caustic mixtures as H\(_2\)SO\(_4\)/(NH\(_4\))\(_2\)SO\(_4\) (1:1) (27) and molten NaOH (28, 29) to solutions that probably only clean the surface, such as dilute acids (30–32). Molten bisulfates have been shown to dissolve TiO\(_2\) at high temperatures, and KHSO\(_4\) as an etchant has been shown to be specific for the TiO\(_2\) (001) face (33). We report below the effects of two different pretreatment procedures (treatment 1 and 2, see Experimental) on the properties of surface states on n-TiO\(_2\) (001). To

**Fig. 8.** (a) \( G_p/\omega \) vs. \( f \) (where \( G_p \) is the measured equivalent parallel conductance and \( f \) is the frequency) for n-MoSe\(_2\) in MeCN, 0.1M TBAP, 18 mM 10-MP at different potentials; (b) \( N_{ss} \) vs. \( V \) for n-MoSe\(_2\) in MeCN, 0.1M TBAP containing 18 mM 10-MP.

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**Fig. 9.** (a) \( G_p/\omega \) vs. \( f \) for p-Si in MeCN, 0.1M TBAP at a potential of 0.1V vs. SCE; (b) \( N_{ss} \) vs. \( V \) for p-Si in MeCN, 0.1M TBAP.

**Fig. 10.** \( G_p \) and \( C_p \) vs. \( V \) for TiO\(_2\) (crystal A, treatment 1) in MeCN, 0.1M TBAP containing 10 mM 10-MP\(^{0+/+}\); (a) \( f = 25 \) Hz; (b) \( f = 50 \) Hz.
crystals (treatment 1), G_p vs. V plots are given in Fig. 12. The frequencies employed and the concentrations of the redox couples used are given in the respective figure captions. For crystal B, the S-M plots in the presence of different redox couples are shown in Fig. 13. A typical G_p/\omega vs. \omega plot is given for crystal B in Fig. 14. Following the arguments given for n-MoS_2, the time constant, \tau, and the density of surface states located around 0V vs. SCE are around 8 \times 10^{-5} sec and 10^{10} cm^{-2}, respectively. Similar values of \tau and N_{ss} were obtained for crystal A.

**Discussion**

Not many studies have been reported in literature pertaining to the a-c impedance measurements of semiconductors in nonaqueous solvents (34). Dutot et al. (35) and Tyagai and Kolbasov (36) have made a systematic investigation of the C-V behavior of single crystal TiO_2 and CdS in aqueous solutions. Essentially both of these studies indicate that surface states located within the bandgap influence the mechanism of the overall charge transfer occurring at the interface. For n-TiO_2 (crystal A, treatment 2), the V_{FB} was found to be frequency independent, although there was a marginal variation in the slope (Fig. 3). A similar observation was made by Kabir-ud-Din et al. (36), although the V_{FB} values in MeCN reported by them were more negative by about 0.3V than our values; values of V_{FB} closer to ours were reported earlier (3, 37). In the presence of Fe(Cp)_{2}/0/+ and TMPD_{0/+}, which are located above half of the gap, there is little variation in the V_{FB} from the blank solution. However, for couples such as Fe(Cp)_{0/+} and 10-MP_{0/+} located below half the gap, the V_{FB} varies monotonically as shown in Fig. 7. In the case of n-CdS, the variation in V_{FB} with V_{redox} is similar to that of n-TiO_2 (see Fig. 7). A similar observation was made by Frase (38) for n-CdSe in aqueous solutions. With p-Si, p-GaAs, and n-InP, the V_{FB} varies monotonically with V_{redox} (Fig. 7). In the case of n-InP, the S-M plot is linear for the entire bandgap (Fig. 6); similar observations with n-InP were made by Van Wezemall et al. (39) in aqueous solutions and by Tuck et al. (40) for solid-state Al/n-InP Schottky barriers. They observed that the S-M plot is linear over a range of 0.8V and deviates slightly thereafter implying the presence of deep donor levels about 0.8V below the conduction band. The layer-type compounds represent a different situation where there is no significant shift in V_{FB} with V_{redox} from that observed in blank solutions for couples with Eo's located within or outside of the bandgap (Fig. 7). This probably indicates that for many large and small bandgap semiconductors the role of bandgap surface states is important, for layer-type compounds the surface states have only marginal effects. The time constant associated with surface states on p-Si is around 4 \times 10^{-5} sec, and this falls in the domain of fast surface states. The N_{ss} is around 10^{13} cm^{-2}, and this is high enough for Fermi level pinning to occur.

The surface states on TiO_2 made conductive by reduction are due in part to oxygen vacancies and Ti^{4+}. Several investigators have used different techniques to deduce the presence of these states. These include (i) thermal and photoelectronic properties (41), (ii) electron spectroscopy (42), (iii) catalytic decomposition of N_2O supplemented with EPR studies (43), and (iv) low frequency capacitance-voltage method (44). However, in all the methods, the evidence for surface states was not obtained with TiO_2 in contact with an
electrolyte. Since the properties of the electrode surface dramatically change upon immersion in electrolyte (because of the large electric field in the interfacial region and interaction with solvent and electrolyte), a study of surface states in situ produces more meaningful information about the electrode surface. The low frequency C-V method, which employs the quadrature component of the a-c impedance, can be employed to study the properties of the surface states, but it suffers from the limitation (15) that the spread in the space charge capacitance values, even when the frequency is increased by one order of magnitude, is only 14%. This means large errors will be introduced in the calculation of the surface-state properties as we discussed in more detail in a recent paper (14). The conductance technique is more useful in extracting surface-state properties. In our studies on the a-c admittance characteristics of n-TiO₂ (crystals A and B, treatment 1), the in-phase component yields evidence for the presence of states at two energies (Fig. 10, 12). However, in the case of TiO₂, crystal A, treatment 2, only one peak in the Gp vs. V plot at 0.1V vs. SCE is observed (Fig. 11). Based on the evidence obtained by other investigators, we tentatively assign those closer to VFB (shallow levels) to oxygen vacancies and those around the middle of the gap (deep levels) to Ti³⁺.

The peak heights are frequency dependent as shown in Fig. 10-12. The shift in VFB's of the KHSO₄-etched TiO₂ crystals to positive values when Vredox is below half the gap (Fig. 13) is similar to that observed with crystal A (treatment 2) (see Fig. 7). In all the S-M plots, the deviation from linearity near the VFB is due to the constancy of the capacitance around VFB since at potentials negative of VFB, an n-type semiconductor behaves like a metal. For both crystals etched with KHSO₄, the peak potentials of the surface states due to Ti³⁺ are located at the same potential (0.72V vs. SCE), but those due to oxygen vacancies (shallow levels) are offset by 0.1V (crystal B) or 0.1V more negative than crystal A). Note that surface states due to Ti³⁺ ions are oxidized in this crystal or a surface layer forms to block these sites.

**Conclusions**

Based on the results reported here, we can assign the semiconductors studied here into three categories: (i) Small bandgap compound and elemental semiconductors (GaAs, InP, Si) represent a situation where VFB tracks Vredox monotonically; (ii) Large bandgap semiconductors (TiO₂, CdS) where VFB remains fairly constant for couples located above half of the gap and varies monotonically for couples located below half of the gap; and (iii) Layer-type compounds (WS₂) where VFB does not vary with Vredox. Evidence for two sets of surface states on a TiO₂ surface contacting MeCN has been obtained by a-c impedance measurements of the in-phase component of the total admittance. The time constant associated with surface states on TiO₂ surfaces is equal to 8 × 10⁻⁵ sec, and the Nss for the level at 0V vs. SCE was found to be ~10¹⁹ cm⁻². The time constant and the Nss for p-Si are 4 × 10⁻⁵ sec and 10¹⁸ cm⁻², respectively. This value of Nss is sufficient for pinning the Fermi level.

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**APPENDIX**

Figure A-1 is the equivalent circuit of the semiconductor-electrolyte interface (45), neglecting the contribution from the Helmholtz layer and counter-electrode capacitance as well as the bulk resistance of the semiconductor, resistance of the electrolyte, and the Faradaic impedance. The net equivalent circuit comprises a series combination of surface-state resistance (Rss) and capacitance (Css) connected in parallel to a parallel combination of space charge layer capacitance (Cd) and resistance (Rd) respectively; these are frequency independent but voltage dependent. The total admittance of the equivalent circuit is Ys = Gs + jωC0 where the in-phase component

\[ G_p = \frac{ω^2 C_{ss}^2 R_{ss}}{1 + R_{ss}^2 ω^2 C_{ss}^2} + \frac{1}{R_d} \]  

(A-1)

![Fig. A-1. Equivalent circuit of the semiconductor/electrolyte interface in the presence of surface states.](image-url)
and the out-of-phase component

$$C_p = \frac{C_{ss}}{1 + \omega^2 \tau C_{ss}^2} + C_D \quad \text{[A-2]}$$

Equations [A-1] and [A-2] can be written as

$$G_p = \frac{\omega^2 \tau C_{ss}}{1 + \omega^2 \tau^2} + G_D = G_{ss} + G_D \quad \text{[A-3]}$$

and

$$C_p = \frac{C_{ss}}{1 + \omega^2 \tau^2} + C_D \quad \text{[A-4]}$$

where $G_{ss} = C_{ss} \omega^2 / (1 + \omega^2 \tau^2)$, $\tau = R_{ss} C_{ss}$, and $G_D = 1/R_D$. $G_p$ can be equated with $C_p$ and hence $N_{ss}$, only after considering $G_D$ (Eq. [A-3]). Therefore, Eq. [2] holds only when $G_D$ is small compared to $G_{ss}$. Since $G_D$ and $C_D$ are frequency independent, a change in the value of $G_D$ would be manifested in the $G_p/\omega$ vs. $\omega$ plot by a shift parallel to the $G_p/\omega$ axis. The $\omega$ value corresponding to the peak would not be affected by such a change. Hence, the $G_p/\omega$ vs. $\omega$ plot will always be valid for finding the value of $\tau$ independent of the relative values of $G_{ss}$ and $G_D$.

To determine $N_{ss}$, Eq. [2] can be written

$$G_p - G_D = \frac{C_{ss} \omega \tau}{1 + \omega^2 \tau^2} \quad \text{[A-5]}$$

Theoretically, the $G_p/\omega$ vs. $\omega$ plot should yield values of $G_D$ from the baseline of the plots. However, these plots do not always have flat baselines, and obtaining reliable values of $G_D$ becomes difficult. In these situations, the $G_p$ vs. $V$ curves can be more helpful. Values of $G_D$ at a particular potential can be obtained by extrapolating a smooth parabolic baseline in the regime of the peak due to surface states (Fig. A-2). This value can then be subtracted from the measured value of $G_D$ to obtain $G_{ss}$.

REFERENCES

A Study of the Transition from Oxide Growth to $O_2$ Evolution at Pt Electrodes in Acid Solutions

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ABSTRACT

A Pt ring disk electrode was used in acid solutions to study the transition from Pt oxide growth to oxygen evolution and to distinguish the rates of these two processes. When a constant current is applied to the disk electrode, the disk potential, $V$, initially increases linearly with time, and hence with the charge density, while a negligible current is observed at the ring. In this potential region, essentially all of the applied current is used for the growth of a Pt oxide film. Following the linear $V/t$ region, $V$ continues to increase but now more slowly and nonlinearly with time, while the ring current initially increases sharply and then slowly approaches the value expected for 100% oxygen evolution at the disk electrode. Thus, the Pt oxide film continues to grow in the nonlinear $V/t$ region even when oxygen evolution becomes the major reaction. In the nonlinear $V/t$ region, $V$ again increases nearly linearly with the integrated charge density for oxide film formation or with the oxide film thickness. This $V/q$ relationship in the nonlinear $V/t$ region is different from the $V/q$ relationship in the linear $V/t$ region. However, the mechanism of Pt oxide growth and the properties of the film when the $O_2$ evolution reaction is the dominant reaction remain the same as in the initial Pt oxide growth region where $O_2$ evolution is not significant. The distribution of potentials in the oxide film and in the inner and outer Helmholtz layers is discussed.

When a constant anodic current is applied to a pre-reduced oxide-free Pt electrode starting from the rest potential in $O_2$-saturated acid or alkaline solutions, $V_R = 0.98$V vs. RHE (1), three distinct potential regions can be seen in a $V/t$ transient (2-5). Initially, the potential increases rapidly and nonlinearly with time as the first monolayer of an oxide film is formed (5-7). Following this region, the electrode potential increases fairly linearly with time (Fig. 1) with the current being used for further growth of the oxide film (8). Eventually at higher potentials, oxygen evolution begins and soon becomes the major electrode reaction (9). In Fig. 1, potential/time curves are shown for three constant current densities in a 0.2N H$_2$SO$_4$ solution. In this figure, the time axis has been scaled for each current density to represent charge density, $q = it$. At a particular potential, which depends on the applied current density and the pH, the linear increase of the potential with time, or charge density, ceases. Now, the potential increases at a rate which decreases with time while $O_2$ evolution continues to increase and soon becomes the predominant electrode reaction (9). Previous work has shown that at long times the potential changes nearly linearly with the logarithm of time of polarization and the oxide film continues to grow at a very slow rate (3, 9, 10).

In this study, a Pt ring disk electrode has been used to separate the reactions of Pt oxide growth and $O_2$ evolution. A comparative analysis of their individual rates and their dependence on the electrode potential is expected to yield information on the nature of the changes in the kinetics of oxide growth and on the potential distribution across the complex interface, comprised of the oxide film and the inner and outer Helmholtz layers, during the transition from the oxide growth to $O_2$ evolution. Such an analysis is also expected to aid in the overall understanding of the mechanism of the $O_2$ evolution reaction at oxide-covered electrodes.

Experimental

A commercially designed Pt disk-Pt ring electrode (Pine Instrument Company, disk radius 0.383 cm, ring inner radius 0.389 cm, and ring outside radius 0.422 cm) was utilized in an all-glass cell similar to that described in (11). The ring-disk electrode was polished to a mirror finish with alumina paste. In some experiments, a thin layer of gold (~1000A) was electrodeposited over the ring electrode. A saturated calomel electrode in a separate compartment served as the reference electrode, and a Luggin capillary extended upward toward the center of the disk electrode. A Pt counterelectrode was placed in the same compartment as the ring disk electrode.

Solutions were prepared from reagent grade sulfuric acid and conductivity water. No extensive purification of solutions was carried out, e.g., by pre-electrolysis. In all experiments, solutions were first purged of $O_2$ with high purity Ar. During electrochemical measurements, Ar was passed over the solution.

Prior to each series of experiments, the disk electrode was anodically oxidized and cathodically re-