

Photoinduced Surface Charge Distribution on TiO₂

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The density of states at a TiO₂-electrolyte interface is measured by a photoelectrochemical technique. The Schottky barrier height for various redox couples is also obtained for the surface containing this measured density. Good agreement is obtained between the band bending calculated from the interface density of states and the measured band bending as a function of the electrolyte redox Fermi potential.

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In the simple model of a Schottky barrier at a metal-semiconductor interface, the barrier height should equal the contact potential difference.¹ This relation is almost never realized experimentally. The deviation is attributed to states that accumulate charge at the interface and reduce the magnitude of the electric field in the semiconductor.

Despite the large amount of research on surfaces, there has not been a comparison made experimentally between a measured density of interface states,²⁻⁴ N_{SS} , and the measured Schottky barrier height,⁵⁻⁷ ϕ_{SB} , of the same semiconductor surface for different work-function media in contact with the semiconductor. One reason is obvious. Surface states can arise from impurities or from any other modification of the surface. Once a metal overlay is placed on the semiconductor surface, it cannot be removed for deposition of another metal with a different work function without some alteration of the original distribution of surface states. Thus, independent measurements of ϕ_{SB} for various metals cannot be made for a given N_{SS} .

By replacement of the metal with an electrolyte containing various redox couples, such an experimental comparison can be accomplished. Use of an electrolyte has additional advantages. A standard reference electrode may be immersed into the electrolyte to provide a reference potential for *in situ* measurement of the Fermi potentials of both the semiconductor, V_F , and the redox couple, V_R , which obviates the need for an independent measurement of the contact potential. Also, the electrolyte is transparent to light of band-gap energy. Minority carrier charge may be created at the surface and the surface states can be populated in excess of that introduced only by the contact potential difference.

Nb-doped ($N_D \sim 1.9 \times 10^{19} \text{ cm}^{-3}$) single crystals of TiO₂ were made as stoichiometric as possible to minimize defect contributions from oxygen vacancies by heating 48 h at 900 °C in flowing oxygen.⁸ The impurity conductivity is 4 Ω cm at room temperature. Following the procedure of Firment,⁹ the (001) surface was polished, etched at 600 °C in molten KHSO₄,¹⁰ and reconstructed by annealing at 700 °C in a 10⁻⁸-Torr vacuum with use of sorption and Vacion

pumps to avoid reduction.¹¹ The electrolyte was anhydrous acetonitrile containing 0.2M tetrabutyl ammonium perchlorate and, where specified, a redox couple of 0.01M to 0.03M concentration.

All capacitances were obtained at 10 kHz by a computer-controlled impedance analyzer and other peripheral devices which apply bias voltages and light pulses in a prescribed sequence. Potentials are measured with respect to a standard calomel electrode (SCE).

An energy-level diagram that depicts experimental conditions is shown in Fig. 1. When no redox couple is present in the electrolyte, interface states on the TiO₂ above E_F are charged positive by a 1-sec flash of uv light while the surface is biased to depletion at about 0.8 V (SCE). The lifetime of the charge in these states is about 15 min if a reverse bias is maintained equal to or greater than the bias at the flash. Such a long lifetime allows the surface capacity C_s to be measured before the state loses its charge by thermal equilibration.

Both before and after the flash, C_s^{-2} is a linear function of surface potential with the same slope. Only the effective flat-band potential V_{FB} has shifted anodically which indicates that a light-induced positive surface charge has narrowed the Schottky barrier region and increased the surface capacitance. During the non-equilibrium period after the flash, E_F is moved through the interface states in voltage increments ΔV_F . States below E_F repopulate while those above

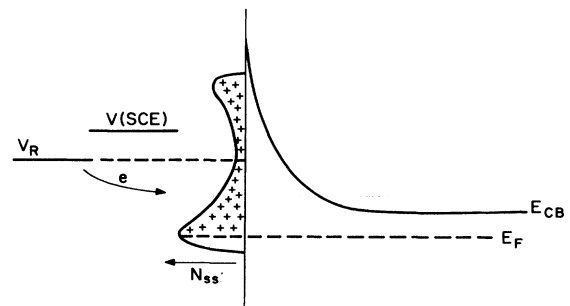


FIG. 1. Energy-level diagram at a semiconductor-electrolyte interface.

E_F remain empty. Thus the space-charge region widens with decreasing semiconductor Fermi potential in increments proportional to the change in surface charge for each ΔV_F .

By application of the Maxwell boundary condition relating the discontinuity in the normal component of the displacement across the interface to the surface charge σ , the assumptions of a Schottky barrier and that C_s is comprised of the Helmholtz capacity C_H and the semiconductor space-charge-layer capacity in series give

$$C_s^{-1} = \frac{1}{2} C_H^{-1} [(1 + 4C_H/C)^{1/2} + 1], \quad (1)$$

where $C^{-1} = 2(C_H V_s - \sigma)/\epsilon N_D e$, and V_s is the potential across the interface. Differentiating the square of Eq. (1) and taking the density of states as $N_{SS} = e^{-1} \partial \sigma / \partial V_F$ gives

$$N_{SS} = \frac{1}{4} \epsilon N_D (2C_H - C_s) \partial C_s^{-2} / \partial V_F, \quad (2)$$

where capacitances are per unit area. A least-squares fit to the capacitance is made by the method of Savitzky and Golay,¹² and the smoothed derivative N_{SS} is shown in Fig. 2.

Now consider the analogy to changing the metal work function, the introduction of redox couples into the electrolyte that have a range of Fermi potentials, V_R . Nagasubramanian, Wheeler, and Bard⁶ used this technique to obtain flat-band potentials in the dark. However, to compare with the surface-state density obtained above, the band bending must be determined while the surface states are populated, i.e., during illumination. Charge created in the surface states is now distributed over the narrower potential region V_R to V_{FB} (Fig. 1). This amount of charge $\sigma(V_R)$ reduces the band bending from the unpinned case by

$$V_p = e \sigma(V_R) / 2C_H.$$

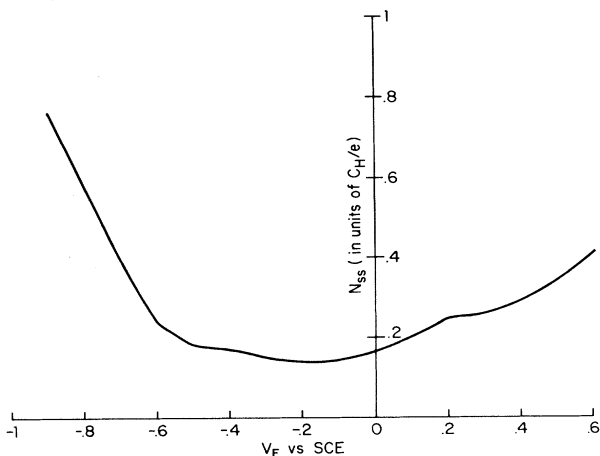


FIG. 2. Density of interface states on TiO_2 in units of C_H/e ($= 2.5 \times 10^{13} \text{ cm}^{-2} \text{ V}^{-1}$).

However, V_p is the shift in the flat-band potential and may be extracted from the data that produced Fig. 2. The calculated band bending is plotted as the solid curve in Fig. 3.

The surface potential of the semiconductor under illumination at equilibrium with the redox couple is taken as the threshold potential V_0 for oxidation current flow. This assumption is valid for semiconductors, such as TiO_2 , whose band gap is much larger than kT . The band bending ($V_R - V_0$) for four redox Fermi potentials is shown in Fig. 3 as the solid dots.

The band bending expected in the absence of interface states is also shown in Fig. 3 as the dashed line. Fermi-level pinning that occurs in the presence of a high density of interface states would appear as a horizontal line located at a fixed band-bending potential. It is evident that TiO_2 lies intermediate between these two cases.

The value of $C_H = 4 \mu\text{F}/\text{cm}^2$ was determined from the dark capacitance at the flat-band potential. The flat-band potential in the absence of a redox couple in the electrolyte is taken to be the potential at which surface capacitance is independent of illumination for light intensity of $100 \mu\text{W}/\text{cm}^2$. It is conventional to assume that C_H is equal to the metal-electrolyte value of $20 \mu\text{F}/\text{cm}^2$,¹³ but for the TiO_2 surfaces prepared in the manner described above, the capacitance is lower by a factor of 3 or more. In fact the surface-charging effects reported here are observable only because of the low value of C_H . A total surface charge of 10^{13} cm^{-2} is obtained, or about 1% of the average density of (001) TiO_2 surface molecules.

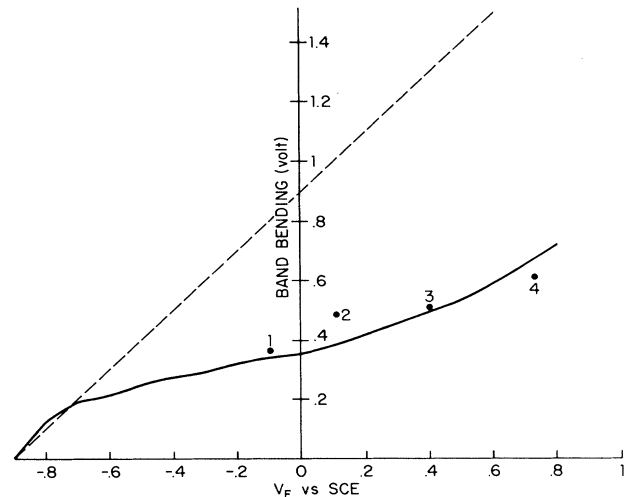


FIG. 3. Band bending as a function of redox Fermi potential. The various redox couples used in this figure are (1) bis(pentamethyl cyclopentadienyl)Fe, (2) tetramethyl para-phenylene diamine, (3) ferrocene, and (4) 10 methyl phenothiazine.

Two interface states reported in the literature were eliminated by the surface preparation. An extrinsic surface state near the flat-band potential caused by water reported by Kobayashi, Aikawa, and Sukigara¹⁴ was observed. When this extrinsic state is present, it superimposes on the state reported here and modifies the distribution. This surface state appears to be a "fast" state coupled to the bulk of the semiconductor, since it does not retain the charge as does the state reported here. The "intrinsic" surface state reported by Siripala and Tomkiewicz¹⁵ is believed to be the same as that reported by Jarrett.¹⁶ This state has also been removed from the TiO₂ surface by techniques similar to those described in Ref. 16.

The density of interface states in Fig. 2 is modified at a potential above V_R when a redox couple is present in the electrolyte, because a negative charge transfer from the redox couple to the surface state reduces the photoinduced positive charge in the state. These observations suggest that the surface state is in contact with the redox couple, but isolated from the semiconductor bulk. Thus, the state is "slow" when charge transfer across the interface is forbidden by the absence of a redox couple, but becomes "fast" when a redox couple is present in the electrolyte.

The origin of the interface state is uncertain. Surface states of the density calculated above could arise either from a defect structure, from impurities, or from intrinsic origin. The distribution of states depends on the surface preparation and on exposure to the atmosphere during sample mounting. Dependence on the contacting medium, e.g., electrolyte or the molecular structure of the redox couple, does not seem to be a factor, as has been suggested for metal-induced states at the metal-semiconductor interface.¹⁷

Stabilization of the Fermi level at a fixed surface potential was never observed. In all cases band bending was reduced in the presence of surface states, but the density was not so large that the Fermi level became pinned.

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