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In-Situ Scanning Tunneling Microscopy of Semiconductor(n-TiO_2)/Liquid Interfaces. A Role of Band Bending in Semiconductors

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It is found in this study that electron tunneling from the conduction band in the semiconductor to the metal tip is possible if the electrode potential of the semiconductor is negative with respect to the flat band potential. The result clearly reveals the role of band bending in semiconductors for electron tunneling at the semiconductor/liquid interface.

Several recent investigations have opened up the possibility for STM to become a powerful new technique for electrode surface characterization in electrochemical circumstances.[1-5] It is well-known that the technique is unique in its ability to determine both the structural and the local electronic properties of semiconductors in ultra-high-vacuum(UHV).[6] However, these properties are also significant in electrochemistry; tremendous efforts have been paid during the last fifteen years for the efficient production of energy and fuels such as hydrogen at the semiconductor/liquid interface.[7,8] GaAs has been imaged in a KOH solution.[1c] An ex-situ STM has recently been described for n-TiO_2 in air.[9] Nevertheless, the in-situ STM technique will now be expected as a new appraisal method to determine the surface structure of semiconductors in solutions.

In this letter, we wish to communicate, for the first time, the dependence of tunneling currents on the electrochemical potential of the semiconductor(n-TiO_2). The microscope used was the same as reported in our previous papers.[3] The electrochemical cell and the electronic circuit built comprise a four-electrode system in which the electrode potentials of both semiconductor and tip can be simultaneously controlled with respect to the reference electrode, as described previously.[3d] This apparatus offers a new capability for the complete in-situ observation of electrode surfaces in electrolyte solutions

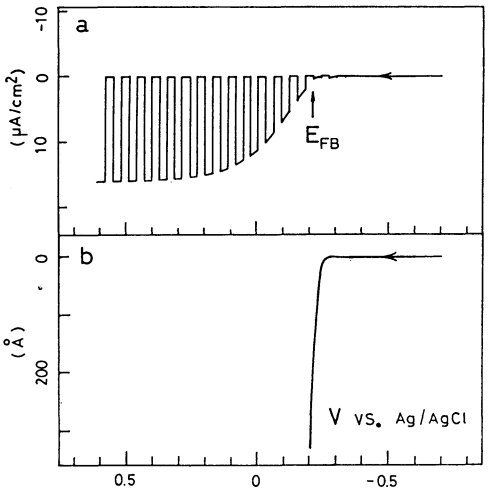

Fig. 1. a) I-V curve of n-TiO_2 in 0.1 M KCl(pH=4). b) displacement of z-axis with a tunnel current of 7 nA. The tip was 0.4 V.

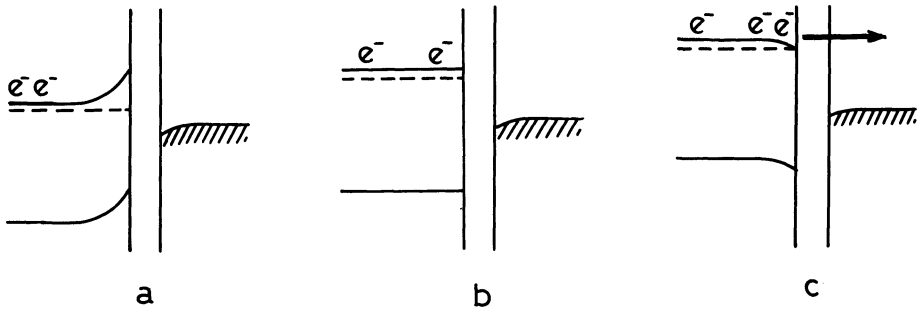

Fig. 2. Interface energetics for n-type semiconductor/liquid/metal junction. (a) $E > E_{FB}$; (b) $E = E_{FB}$; (c) $E < E_{FB}$. The electrode potential of the tip is positive with respect to E_{FB} for all cases.

under the potentiostatic condition. Similar instruments have recently been constructed in other laboratories.[4,5] A Pt wire was used as the counter electrode. Ag/AgCl was used as the reference electrodes. The tunneling tip was a glass-covered Pt electrode. The diameter of Pt wire (65 μm) used previously[3] was further reduced to 15 μm in order to suppress the residual background current(<0.1 nA). A single-crystal TiO_2 with the (001) face exposed was first mechanically polished down to 0.05 μm using alumina powder and then heated to 650 °C in vacuum at 10^{-5} Torr for 2-3 h. A donor density of about $1.0 \times 10^{18}/cm^3$ was determined from a Mott-Shottky plot. After the above heat treatment, the sample was etched for 1 h in hot, concentrated H_2SO_4 at about 200 °C.[10] An ohmic contact was made with Ga-In.

Figure 1-a shows a photocurrent-potential curve of the TiO_2 electrode obtained under chopped light illumination in a 0.1 M KCl (pH=4.0) solution. The onset of the photoanodic current was about -0.2 V vs. Ag/AgCl. Mott-Schottky plots gave a straight line with an intercept of -0.20 V indicating that the flat band potential is located near this value. Note that the TiO_2 electrode used here showed a fairly small frequency dispersion in Mott-Schottky plots, suggesting that the surface etched in hot sulfuric acid might approach the "ideal" posited by previous workers.[10]

A well-known interface energetics for an n-type semiconductor/liquid junction[7] is shown in Fig. 2 for better understanding of the tunneling process between the tip and the semiconductor electrodes. Figure 2-a shows the situation when the electrode potential of the semiconductor is positive with respect to the flat band potential(E_{FB}). A space-charge layer is now formed near the surface which is referred to as the depletion region. If the potential is equal to E_{FB}, the depletion region is diminished as shown in Fig. 2-b. Applying further negative potentials, the surface is now degenerated and is expected to behave as a metal electrode as shown in Fig. 2-c.[7]

On the basis of the energetics shown in Fig. 2, the electrode potential of the tip was set at a constant value of 0.4 V vs. Ag/AgCl which is positive with respect to the flat band potential of the semiconductor as indicated schematically in Fig. 2. In this circumstance, electron tunneling from the conduction band in the semiconductor seems to be possible if the electrode potential of the

semiconductor itself is negative with respect to the flat band potential as indicated in Fig. 2-c. Note that very stable tunneling currents were observed as long as the electrode potential of the semiconductor was set at values negative with respect to the flat band potential.

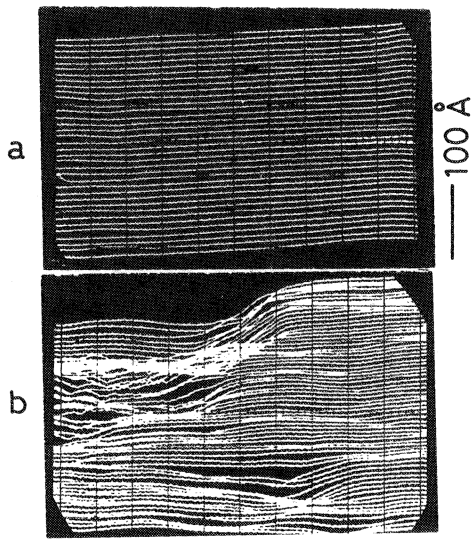

Fig. 3. STM images in 0.1 M KCl of n-TiO_2 etched in hot, H_2SO_4 (a) and in an acid mixture (b). The tunnel current was 8 nA. The x,y and z scales are the same.

Figure 3-a shows an example of the image of the TiO_2 surface observed at the potential of -0.7 V vs. Ag/AgCl. It is clearly seen for all views with different positions and magnifications that the TiO_2 surface is microscopically smooth. As well as hot, conc. H_2SO_4, the TiO_2 electrode was also etched in the most commonly employed solution of $HNO_3/HF/CH_3COOH$ (5:3:3) with a small amount of Br_2, with the etching period being changed from 15 s to 5 min. However, very irregular rough structures were consistently observed with this preparation method, as shown in Fig. 3-b. A prolonged etching in this solution did not show smooth surfaces, indicating that the above etchant cannot remove a damaged layer produced in the mechanical polishing stage. Various surface preparation methods for TiO_2 electrodes have been appraised using electrochemical techniques such as Mott-Schottky plots or photocurrent-voltage characteristics.[10] Neverthless, it seems to be clear that in-situ STM appraisal is the most direct method for evaluating the surface preparation of semiconductors.

Under the observation of STM shown in Fig.3-a, the potential of the semiconductor was scanned at 10 mV/s from -0.7 V vs. Ag/AgCl to the positive direction. As long as the electrode potential was sufficiently negative with respect to E_{FB}, microscopically flat surfaces were consistently observed. However, STM images were drastically changed when the potential approached E_{FB}; the tunneling current became unstable and started to oscillate under these conditions.

Figure 1-b shows the dependence of the output voltage for the z-piezoelectric tube on the electrode potential of the semiconductor. When scanning was undertaken with the semiconductor positive with respect to E_{FB}, the flow of the tunneling current was totally inhibited. The z-piezoelectric tube was fully expanded at this situation as shown in Fig. 1-b. Eventually the tip seemed to be plunged into the semiconductor. It is obvious that the tunneling probability from the conduction band in the semiconductor to the vacant level of the metal tip (Pt) is sharply decreased by the formation of the depletion layer in the semiconductor, as indicated in Fig. 2-a.

Note that E_{FB} measured by the Mott-Schottky plot showed a pH dependence of about 60 mV/pH unit, as expected. It is found in this study that potentials

showing a sharp decrease in the tunneling gap show a similar pH dependence. Finally, it should be pointed out that electron tunneling from the tip to the semiconductor may be possible if potentials negative with respect to E_{FB} are applied to the tip electrode, even with the existence of the depletion layer (see Fig. 2-a) However, in practice, hydrogen evolution occurred at the tip when the electrode potential of the tip was negative with respect to E_{FB}. Using other metals having larger hydrogen overpotentials or nonaqueous solutions may solve this experimental difficulty. We are currently investigating other semiconductors such as n-ZnO, p,n-Si, and p,n-GaAs. Our findings have important implications relating to the detailed electronic structures as well as the surface topography of semiconductor/liquid interfaces.[11)]

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