

SURFACE SCIENCE LETTERS

SCANNING TUNNELING MICROSCOPY OF SEMICONDUCTOR  
(n-ZnO)/LIQUID INTERFACES UNDER POTENTIOSTATIC  
CONDITIONS

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The topography and the surface electronic structure of n-ZnO(001) single crystal electrodes have been examined in a 0.1M KCl aqueous solution. The tunneling current strongly depends on the electrode potential of the semiconductor at the semiconductor/liquid/metal interfaces. The probability of tunneling from the conduction band in the semiconductor is sharply decreased by the formation of the depletion layer.

The scanning tunneling microscope (STM) has proven to be a very powerful tool for studying both the structural and the local electronic properties of various semiconductors [1–3]. To date, most applications have concerned themselves with the study of clean or ideal surfaces, such as Si(111)7 × 7, prepared in ultra-high vacuum (UHV). However, several recent efforts have opened up the possibility for STM to become a powerful new technique for electrode surface characterization in electrochemical circumstances [4–10]. In-situ STM investigations have been carried out for Pt [4,5], Au [6], Ni [7], Ag [8], and electrochemically deposited metal particles on highly oriented pyrolytic graphite (HOPG) [5,9,10].

It is well known in the field of photoelectrochemistry that both the structural and the electronic properties are significant for understanding electrochemical reactions occurring at the semiconductor/liquid interface [11]. Although ex-situ STM studies can be used, as described for n-TiO<sub>2</sub> in air [12] and for p-Si and n-Si in an inert atmosphere [13], the in-situ STM technique can now become a new critical method to determine the surface structure of semiconductors in solutions. The surface topographic images of semiconductors immersed in aqueous solutions have recently been reported for GaAs(001) by Sonnenfeld et al. [14]. Lin et al. have demonstrated a photoelectrochemical etching of n-GaAs in aqueous alkali solutions by means of STM [15].

Here we will describe the semiconductor topography and the surface electronic structure of n-ZnO(001) single crystal in a 0.1M KCl aqueous solution. Oxide semiconductors such as ZnO and TiO<sub>2</sub> seem to be suitable

materials for the present study, because these semiconductors are very stable even in aqueous solutions and cannot be further oxidized, at least in the dark [11,16]. Our results clearly reveal the role of band bending in the semiconductor for electron tunneling to occur at the semiconductor/liquid interface.

The in-situ STM apparatus used here has recently been described in detail [5,10]. The electrochemical potentials of the tunneling tip and the semiconductor can be controlled simultaneously with respect to a reference electrode. It has been shown that the apparatus mentioned above offers a new capability for comprehensive in-situ observation of electrode surfaces in electrolyte solutions, under potentiostatic conditions [10]. Note that similar apparatuses have recently been constructed in other laboratories [6,15]. The electrochemical cell for the STM measurement has a four-electrode configuration. Pt and Ag/AgCl wires were used as the counter and the reference electrodes, respectively. The tunneling tip was a glass-coated Pt wire whose diameter was 15  $\mu\text{m}$ . A ZnO single-crystal with the (001) face exposed was first mechanically polished down to 0.05  $\mu\text{m}$  using alumina polishing powder and then etched in a concentrated HCl solution for 15 s at room temperature. Ohmic contact was made with Ga-Hg alloy.

Fig. 1a shows current-potential curves of the ZnO electrode obtained in the dark and under illumination in 0.1M KCl (pH = 4.0). The anodic current observed under illumination is due to the photo-anodic dissolution of ZnO to give  $\text{Zn}^{2+}$  and oxygen according to the following reaction [16]:



However, the anodic current is extremely small in the dark, indicating that ZnO cannot be oxidized electrochemically without illumination. The cathodic current first observable at about  $-0.9$  V versus Ag/AgCl is due to hydrogen evolution including reduction of ZnO to metallic zinc. Fig. 1b shows Mott-Schottky plots measured at different frequencies. It can be seen in fig. 1b that these plots give straight lines with a small frequency dispersion. The intercept of these lines was about  $-0.3$  V versus Ag/AgCl. As shown in fig. 1a, the photoanodic current became observable at about the same potential, suggesting that the flat-band potential of n-ZnO in this media is about  $-0.3$  V versus Ag/AgCl, which agrees well with a literature value [16]. From the slope of Mott-Schottky plots the donor density of n-ZnO was calculated as  $N_d = 1.73 \times 10^{17} \text{ cm}^{-3}$ .

Two typical STM images of the n-ZnO surface prepared by the method described above are shown in fig. 2. It is noteworthy that the electrode potentials of the n-ZnO and the tip electrodes were set at  $-0.6$  V and  $0.2$  V versus Ag/AgCl, respectively. It is found in this study that the electrode potential of n-ZnO should be set at values far negative with respect to  $E_{\text{FB}}$  in order to obtain actual surface STM images. Fairly stable tunneling currents from the semiconductor to the tip were observed under these conditions.

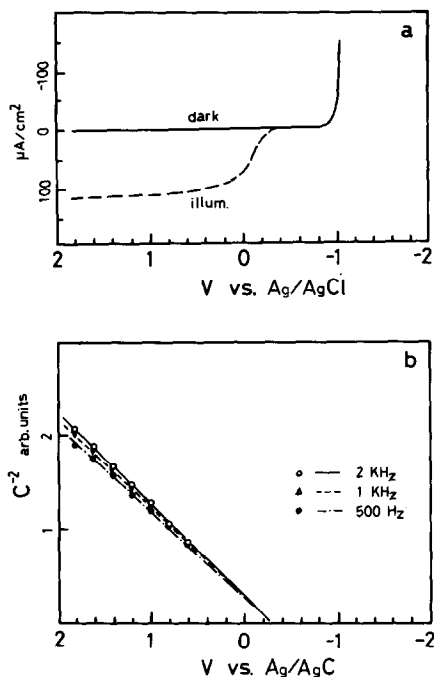


Fig. 1. (a) Current-potential curves of n-ZnO obtained in the dark (—) and under illumination (---) in a 0.1M KCl (pH = 4.0) solution. The scan rate of the electrode potential of n-ZnO was 20 mV/s. (b) Mott-Schottky plots as a function of the frequency for n-ZnO.

As shown in fig. 2, a rolling hill topography characteristic was consistently observed for the surfaces in different positions, although there were also many atomically flat regions on a scale in the order of a few hundred ångströms. No

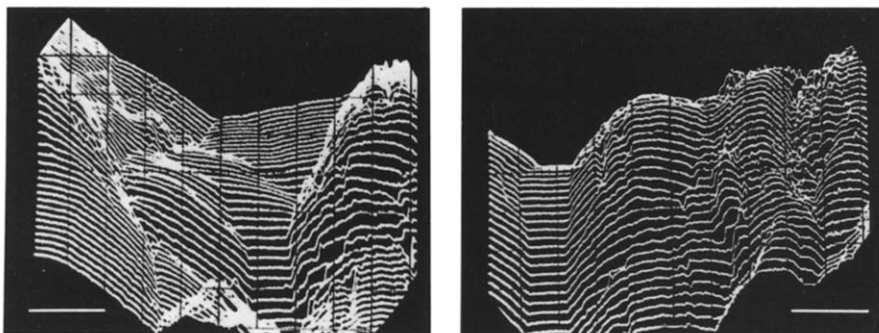


Fig. 2. Two typical STM images of n-ZnO obtained in 0.1M KCl. The electrode potentials of the semiconductor and the tip were set at  $-0.6$  V and  $0.2$  V versus  $\text{Ag}/\text{AgCl}$ , respectively. The tunnel current was 4 nA. The scale of the  $x$ ,  $y$ , and  $z$  axes is the same, marker indicates 500 Å.

improvement in the flatness of the surface was evident from the STM images when the etching period was increased from 15 s to 5 min. This result suggests that alternative etching methods must be found for the preparation of more smooth surfaces. However, these results also demonstrate clearly that in-situ STM appraisal is the most direct method for the evaluation of the surface treatment of semiconductors.

In order to investigate the spectroscopic properties of semiconductor/liquid interfaces, we have measured the voltage applied to the z-piezo-electric element as a function of electrode potential of the semiconductor for a constant tunneling current of 4 nA. The electrode potential of the semiconductor was first set at  $-0.7$  V versus Ag/AgCl, i.e., far negative with respect to the flat-band potential and then was scanned in the positive direction from  $-0.7$  V versus Ag/AgCl at a scan rate of 100 mV/s under a constant current STM mode. As long as the electrode potential was sufficiently negative with respect to the flat-band potential, the change in the voltage applied to the z-piezo-electric element was very small. The displacement of the tip was only in the order of a few ångströms in the potential range between  $-0.7$  and  $-0.5$  V versus Ag/AgCl. However, when the electrode potential was approaching the flat-band potential, the voltage applied to the z-piezo-element gradually increased. The z-piezo-electric element was almost fully expanded near the flat-band potential. When scanning of the electrode potential was undertaken with the semiconductor positive with respect to  $E_{FB}$ , the flow of electrons from the semiconductor to the tip was totally inhibited. Under this condition, the tip seemed to be plunged into the semiconductor or to be point-contacted to the surface of the semiconductor. The above result clearly indicates that the tunneling current strongly depends on the electrode potential of the semiconductor at the semiconductor/liquid interface. In our recent investigation of n-TiO<sub>2</sub> materials, exactly the same potential dependence for the electron tunneling has been found in aqueous solutions [19].

Fig. 3 shows three typical schematic views of the energy diagram for an n-type semiconductor/liquid/metal junction using a well-known formulation

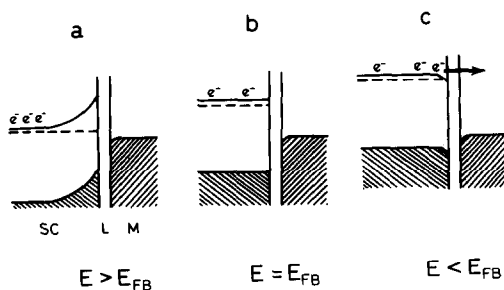


Fig. 3. Energetics for n-type semiconductor(SC)/liquid(L)/metal tip(M) interfaces.  $E$  and  $E_{FB}$  are the electrode potential of the semiconductor and the flat-band potential, respectively.

for semiconductor/liquid interfaces [11]. In ideal n-type semiconductor/liquid systems, the flat-band potential can be found at a certain value with respect to a reference electrode and the semiconductor band edges are then fixed at the electrolyte interface. Positive potentials applied to the semiconductor electrode only appear across the semiconductor space charge layer. Fig. 3a shows the interface energetics when the electrode potential of the semiconductor is positive with respect to the flat-band potential. A space-charge layer is formed near the surface of the semiconductor. If the electrode potential of the semiconductor is equal to  $E_{FB}$ , the depletion region in the semiconductor diminishes (fig. 3b). When a negative potential with respect to  $E_{FB}$  is applied to the semiconductor, the surface is degenerated and it is expected to behave as a metal electrode. This is shown in fig. 3c.

On the basis of the energy diagram (fig. 3), electron tunneling from the conduction band in the semiconductor to the vacant levels in the metal tip seems to be possible if the semiconductor electrode is negatively biased with respect to the  $E_{FB}$  as shown in fig. 3c. However, as shown in fig. 3a, it is expected that the probability of tunneling from the conduction band in the semiconductor is sharply decreased by the formation of the depletion layer in the semiconductor.

The expansion of the *z*-piezo-element near the flat-band potential, as described above, may now be qualitatively understood by band bending in the semiconductor. It must be pointed out that there is a remarkable difference between the semiconductor/liquid and the semiconductor/vacuum interfaces. In the latter case, the applied voltage between the semiconductor and the tip has to be divided into two voltage drops, which occur in the semiconductor and across the vacuum, respectively [18].

Feenstra et al. have extensively investigated the tunneling spectroscopy of GaAs, Si, Ge, etc. in UHV [2,18]. In these studies, a sequence of tunneling current-voltage (*I-V*) curves at various tip-sample separations has been measured. The differential conductivity  $dI/dV$  can yield a measure of the surface density of states. Similar experimental quantities are of interest to determine detailed electronic properties of the semiconductor/liquid/metal system.

We are currently investigating other semiconductors such as p- and n-silicon in aqueous solutions. We have found that the surfaces of silicon remain stable even in aqueous solutions [20].

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