

A SCANNING TUNNELING MICROSCOPY STUDY OF THE REDUCED TiO₂(110) SURFACE

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ABSTRACT

The scanning tunneling microscope has been used to image a reduced TiO₂(110) surface in ultrahigh vacuum. Structural units with periodicities ranging from 21 Å to 3.4 Å have been clearly imaged and the observed surface structures can be explained by a model involving ordered arrangements of two dimensional defects known as crystallographic shear planes. An electronic state 0.5 eV below the conduction band edge, detected in tunneling spectra, has been assigned to reduced Ti cations which reside along the crystallographic shear planes. This state appears to be empty at the surface, possibly due to a small amount of band bending. The results indicate that the topography of nonstoichiometric oxide surfaces can be rather complex and that the tunneling microscope provides an effective tool for studying the atomic scale surface features of wide band gap semiconductors.

INTRODUCTION

In order to understand the atomistic mechanisms behind the reactions that occur at the surfaces of transition metal oxides, such as titania, it is first necessary to acquire detailed structural information. In the past, such information has been derived from the results of surface electronic diffraction and spectroscopic experiments [1,2] as well as the application of certain high resolution transmission electron microscopy techniques [3]. However, in the last several years, the scanning tunneling microscope (STM) has been used to determine atomic-level structural information from oxide surfaces. Notable successes among the STM analyses of oxides include the atomic or near-atomic resolution imaging of several different metallic oxide surfaces [4-7] and the imaging of atomic scale features on the surface of the semiconducting oxide, Rb_{0.05}WO₃ [8]. The STM has also been used by several groups to study the titania surface and images have revealed some atomic scale features, despite the fact that they were acquired in air [9-13]. We have recently examined a clean TiO_{2-x} surface in ultrahigh vacuum (UHV) and have obtained detailed images of the surface structure [14]. In this paper, we present some of these images and discuss the relationship of tunneling spectroscopy results with the observed surface structure.

EXPERIMENTAL

A rutile single crystal was oriented, cut, and polished by standard techniques and then reduced in UHV by annealing in a resistively heated tantalum boat at a

temperature above 900 K (based upon color) for 36 hours. The crystal was ion milled and then annealed at 823 K for 30 min in 1×10^{-7} torr of oxygen in order to re-oxidize the surface and anneal out the damage produced by ion bombardment. Low energy electron diffraction (LEED) patterns indicated that this preparation method produced a well ordered, relatively defect free surface [15]. The crystal was then exposed to air for several days before being introduced into the UHV STM chamber, where it was heated at approximately 673 K for 2 min and then 'flushed' at approximately 973 K for 5 sec. Following this treatment, a (1X1) LEED pattern was found, identical to that observed following the initial preparation.

Images and tunneling spectra were produced using a commercial STM head [16] controlled by 'home made' feedback electronics and software of conventional design. The mechanically formed Pt tip was 'sharpened' *in situ* by applying a 90 V potential between the sample and tip and passing 1 μ A of current for several minutes. The dependence of the tunneling current on sample-tip separation was used to gauge the integrity of the vacuum gap. Using the standard vacuum tunneling equation, computed values of the effective barrier height were between 4.2 eV and 5.0 eV [17]. All images presented here were collected in the constant current mode at a 2.0 V sample bias with respect to the tip and a 0.1 nA tunneling current and are presented after the subtraction of a background plane which eliminates the tilt of the sample that would otherwise overwhelm small variations and make atomic features undetectable. Tunneling spectra were recorded during the imaging process using methods described in ref. 17. Measurements of the current were disregarded when they fell below the level of 1 pA, which is near the detection limit of the sensor, and a straight, dashed line is substituted for the spectral data.

RESULTS

Several well ordered regions were found on the surface, examples of which are shown in Fig. 1. Fourier analysis and direct measurement of the image in Fig. 1a indicates that the rows oriented in the $[1\bar{1}1]$ direction have an 8.5 Å periodicity and an approximately 1 Å corrugation height (see Fig. 1b). The corrugation directed along the rows has a 3.4 Å periodicity and a 0.2 Å amplitude. The bulk terminated rutile lattice vectors have been added for comparison. The image in Fig. 1c shows a different ordered structure found on another part of the surface. In this area, the major rows are oriented in the $[\bar{1}13]$ direction and are approximately 20 Å wide. Each row is apparently composed of three discrete and inequivalent subunits, which are roughly the dimension of the bulk unit cell. The rounded unit on the right of each row is clearly larger than the other two subunits.

The tunneling spectrum shown in Fig. 2 is characteristic of those acquired from regions of the surface similar to that shown in Fig. 1a. In each case there is a wide region where the tunneling current fell below the detectable limit. We assume that this region corresponds to the surface band gap. No reliable correlation could be established between differences in the spectra recorded at positions in the center of the rows and the positions between the rows. However, judging from the resolution of the image simultaneously acquired during the spectrum measurements, the tip was more blunt than when the image in Fig. 1a was acquired. The Fermi level is at the zero bias position and the valence band edge (E_v), the conduction band edge (E_c), and a state at the top of the gap region (E_d) have been labeled on Fig. 2. The relative position of the Fermi level and the splitting between the valence and conduction bands are consistent with the fact that reduced titania is an n-type semiconductor with a 3.1 eV band gap.

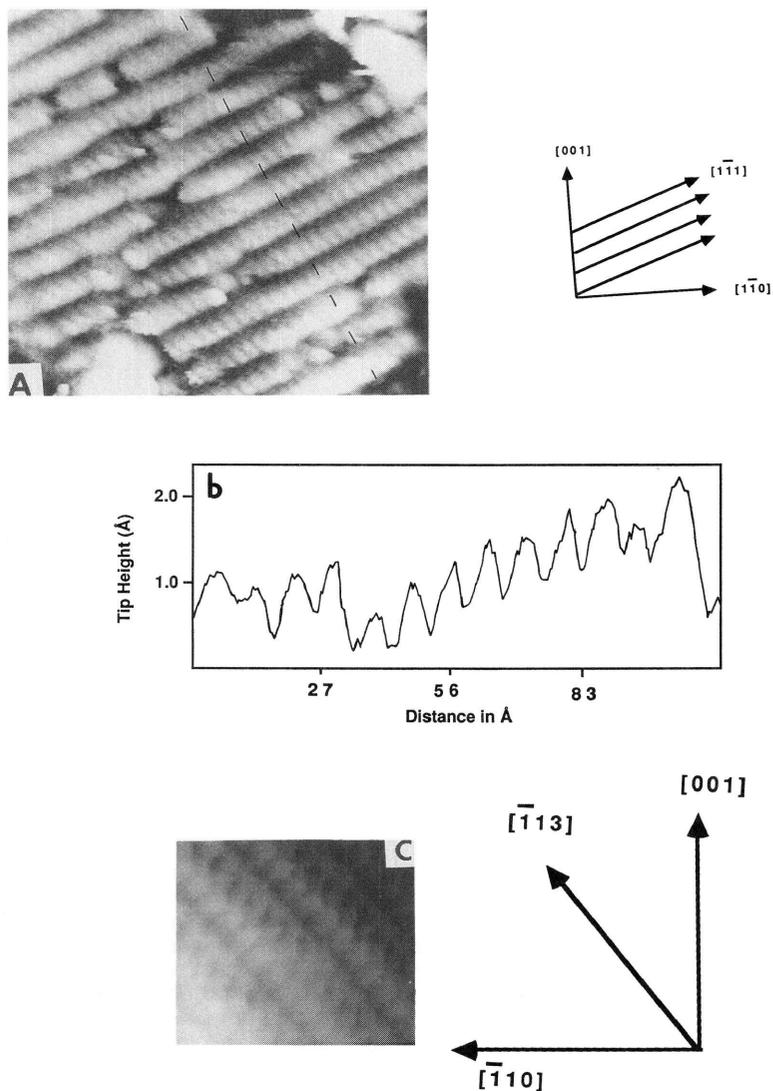


Fig. 1 a) STM image showing a $109 \text{ \AA} \times 109 \text{ \AA}$ area of the $\text{TiO}_2(110)$ surface. The vertical resolution from black to white is 2 \AA , with lighter shades corresponding to topographic peaks. b) Topographic profile measured along the dashed black line. c) A $65 \text{ \AA} \times 58 \text{ \AA}$ STM image of a different area of the surface where rows were oriented in the $[113]$ direction.

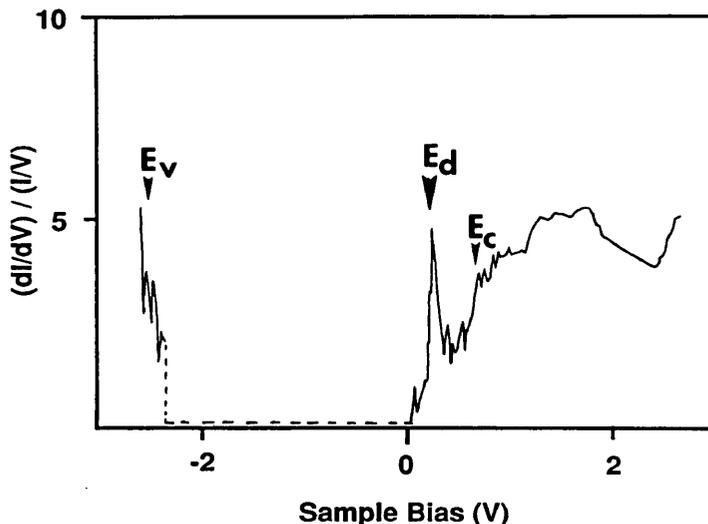


Fig. 2 Tunneling spectrum from an area of the reduced $\text{TiO}_2(110)$ surface similar to that shown in Fig. 1a.

DISCUSSION

The images shown in Fig. 1 can not be explained by any simple termination of the bulk rutile lattice. The results can, however, be explained by a model involving the intersection of crystallographic shear (CS) planes with the surface. It is well known that titania can support a wide range of oxygen deficiency (TiO_{2-x} , $x = 0$ to 0.33) through the formation of these planar defects known as CS planes which, when numerous enough, order to form new compounds with distinct compositions and structures that are known as Magneli phases [19]. The CS displacements can occur along a variety of planes including the $\{121\}$ family of planes. The (121) plane intersects the (110) surface along the $[1\bar{1}1]$ direction, the same direction along which the rows in Fig. 1a are oriented. The intersection of the $(1\bar{2}1)$ plane the (110) surface is in the direction $[\bar{1}13]$, the same direction in which the rows in Fig. 1c are aligned. The CS displacement is always of the type $\frac{1}{2}[0\bar{1}1]$, which means that adjacent sections of the crystal are vertically displaced 1.6 Å with respect to one another along the line normal to the (110) surface. Because the plane subtraction applied to each image removes any global slope, a stepped structure appears saw-toothed, so that the intersection of each CS plane with the surface appears as a depression or dark spot on the image. This model and another involving oxygen vacancies are discussed more completely elsewhere [14].

The bonding and antibonding bands of titania are formed by the overlap of O $2p\pi$ orbitals and Ti e_{2g} orbitals, which are split from the Ti 3d orbitals by the octahedral crystal field [20]. Using the method of Pauling [21], these bonds have 63% ionic character which suggests that the antibonding (conduction) band can be thought of as deriving primarily from the Ti orbitals and the bonding (valence) band can be thought of as deriving primarily from the O orbitals. These bands are split by approximately 3.1 eV, but partial oxygen deficiency creates shallow donors that makes the reduced sample and n-type semiconductor and moves the Fermi level to the bottom of the conduction band edge.

Previous photoemission experiments [1] and theoretical studies [22] indicate that the electronic structure of perfect single crystal rutile surfaces are nearly identical to the bulk. It is generally agreed that for primarily ionic, wide band gap semiconductors, the occurrence of a surface does not necessarily result in the creation of new states in the band gap as is often the case for more covalently bonded semiconductors. The reason for this may be understood in the following way. Electrons in nonbonding surface states of covalently bonded semiconductors relax toward energy levels close to that of the hybridized orbitals (sp^3 levels for Si and Ge) which are often in the gap between the bonding and antibonding levels. However, electrons in nonbonding surface states of more ionic materials such as TiO_2 relax toward the atomic energy levels, which in the case of nonbonding O_{2p} states, generally occur as resonances in the valence band. Therefore, with the exception of these resonances, the electronic structure of the surface is expected to be the same as the bulk. The only deviation from the perfect structure which has been considered is that of vacuum annealed and electron or ion bombarded surfaces in which ultraviolet photoelectron spectroscopy (UPS) has been used to demonstrate that the most common defect is the oxygen vacancy which occupies a state 0.8 eV below the lower conduction band edge [1]. The possible existence of crystallographic shear planes on such surfaces, and influence of such defects on the surface electronic structure was not mentioned in earlier work.

The tunneling spectrum shown in Fig. 2 essentially corroborates the previous UPS findings that there is an electronic state less than one electron-volt below the conduction band edge [1]. However, based on the STM images, we assign this band not to oxygen vacancies, but rather to the Ti(III) that reside along the CS planes. The cations along these planes are closer together than those in the unperturbed bulk and, thus, can be expected to have a lower potential and form a narrow band of states (which might be localized) below the conduction band edge. We believe that the peak observed in the tunneling spectrum can be assigned to these states. However, we would also expect these states to be occupied to compensate the charge imbalance caused by the oxygen deficiency. We can only explain the fact that the states appear above the Fermi level by assuming that there is some band bending at the surface which locally empties these states. Finally, we point out here that these results do not necessarily agree with the tunneling spectra published earlier by other groups [9-13]. However, the previous results were acquired in air and likely to be subject to substantial adsorbate induced band bending effects [23].

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