

A SCANNING TUNNELING MICROSCOPY STUDY OF SINGLE
CRYSTAL ZnO AND TiO₂ SURFACES

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ABSTRACT

The surfaces of ZnO and TiO₂ single crystals have been imaged in ultrahigh-vacuum with a scanning tunneling microscope. Constant current images of the polar ZnO faces show that single crystal surfaces cleaned by vacuum heating have numerous steps consisting mainly of (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) faces. Images of the reduced TiO₂(110) surface indicate that crystallographic shear planes in the bulk strongly influence the surface structure. Local variations in stoichiometry ranging from Ti₃O₅ to Ti₆O₁₁ have been determined by directly measuring the spacing between the periodic intersections of adjacent shear planes with the TiO₂(110) surface. The results in this paper demonstrates that it is possible to resolve atomic-scale features on the surfaces of wide bandgap semiconductors using the scanning tunneling microscope.

INTRODUCTION

The reactions at transition metal oxide surfaces which underlie complex phenomena such as heterogeneous catalysis [1] and gas sensing [2] are strongly influenced by the geometric and electronic surface structure. The application low energy electron diffraction (LEED) [3] and high resolution transmission electron microscopy [4] have provided the first insights

into the structures of these surfaces, but the current information is still rather limited and many systems have not yet been investigated. We have used a scanning tunneling microscope (STM), an instrument which has had enormous impact on the study of metal and covalently bonded semiconductor surfaces, to study the surfaces of two transition metal oxides. From topographic maps of these surfaces, we have been able to identify the types of facets which form on the ZnO polar faces and determine the influence of bulk, planar defects on the atomic structure of the TiO₂(110) surface.

EXPERIMENTAL DETAILS

The anisotropic etching of the ZnO (000 $\bar{1}$) and (0001) faces was used to determine the polarity of the single crystal. The polar faces were mechanically polished until there were no optically visible defects by sequentially reducing the size of abrasive alumina grinding media down to 0.05 micron. After heating the sample in ultrahigh-vacuum (UHV) at 600-700 °C for 2 hours, sharp LEED patterns were observed and Auger electron spectroscopy indicated that the surfaces were free of carbon contamination. Previous work has indicated that such a treatment produces steps and facets on the surface. [5] The titania surface, prepared in a similar way, was first polished and then reduced by heating in UHV at a temperature above 900 K for 36 hrs. Following this treatment, the dark grey, opaque crystal was argon ion milled and then annealed at 823 K for 30 min in 1×10^{-7} torr of O₂ in order to re-oxidize the surface and anneal out the damage produced by ion bombardment. LEED patterns indicated that this preparation method produced a well ordered, relatively defect free surface. [6] 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.

The microscope consisted of a commercial STM head [7] controlled by 'home made' feedback electronics and software of conventional design. The images were collected in the constant current mode using sample biases of -1.5 to -3.0 V and tunnel currents between 0.1 and 1.0 nA 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. Other experimental details have been described previously. [8]

RESULTS AND DISCUSSION

The constant current image of the ZnO(000 $\bar{1}$) oxygen terminated face, shown in Fig. 1, demonstrates that surfaces prepared by *in situ* annealing have a high step density. However, unannealed surfaces appeared even more disordered, presumably due to polishing damage. Atomically smooth flat areas are separated from one another by either single or multiple steps which are aligned predominantly in the either the [10 $\bar{1}$ 0] or [11 $\bar{2}$ 0] direction. This is reasonable, since these are the nonpolar faces and are known to be thermodynamically stable. [2] The height of the step which forms the large hexagonal plateau in the lower left part of the image is 5.21 Å, which agrees well with the ideal spacing between the oxygen planes along the [0001] direction which is 5.25 Å. Similar results were obtained for the (0001) surface. Spatially resolved tunneling spectroscopy has been used to detect mid-gap defect states associated with these steps, a result described in a more detailed paper. [9] In the majority of the regions imaged, the atomically smooth areas were only about 100 Å in diameter. This high density of edge sites is likely to affect the electronic properties and reactivity of this surface.

No atomic-resolution images of the ZnO surfaces have yet been recorded. However, we have examined only intrinsic (not intentionally doped) crystals with low electronic conductivities and the resolution of the images was undoubtedly space charge limited. [10] This was not the case for the reduced titania crystal which we have also examined.

Fourier analysis and direct measurement of the images of the TiO₂(110) surface (see Fig. 2a) indicate that the rows oriented in the [1 $\bar{1}$ 1] direction have an 8.5 Å periodicity and a 1 Å corrugation height. The corrugation directed along the rows has a 3.4 Å periodicity and a 0.2 Å amplitude. The width of these rows seems to vary somewhat and there are also numerous "missing cells". The bulk terminated rutile lattice

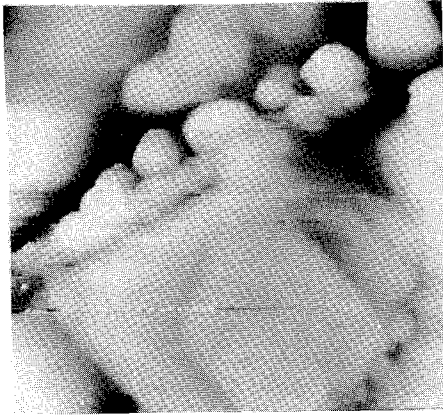


Fig. 1. Constant current image of the ZnO(0001) face. Steps are visible which form (1010) and (1120) faces. The image is 771 Å X 771 Å and was acquired at -1.5 V sample bias and 0.3 nA. The vertical resolution is 36 Å from black to white.

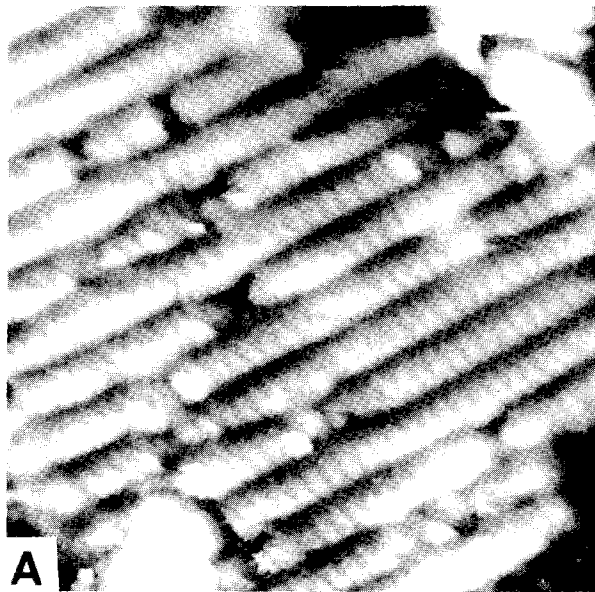
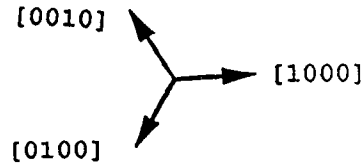
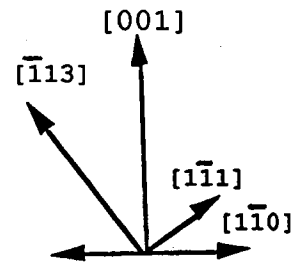


Fig. 2.a) 109 Å X 109 Å image of titania(110). acquired at -2.0 V and 0.1 nA. Vertical resolution is 2 Å from black to white and the rows are oriented in the [111] direction. b) 273 Å X 108 Å image of a different region acquired using the same conditions. The vertical resolution is 9 Å and the rows are oriented in the [113] direction.



vectors have been added for comparison. Other images of this area show ledges which occur approximately every 100 Å and some regions of the images are either disordered or covered with adsorbates. The image in Fig. 2b, acquired on another area of the surface, shows rows oriented along the [113] direction with an approximately 20 Å spacing. It is clear from these observations that the surface structure can not be

described by a simple termination of the bulk unit cell or some combination of unit cells.

The orientation and spacing of the rows on the crystal surface suggest that they are caused by the intersection of crystallographic shear (CS) planes with the (110) surface. The (121) family of planes are among those along which the CS displacements can occur. [11] The (121) plane intersects the (110) surface along the $[\bar{1}\bar{1}1]$ direction, the same direction that the rows in Fig. 2a are oriented. The intersection of the $(\bar{1}\bar{2}1)$ plane and the (110) surface is in the direction $[\bar{1}13]$, the direction in which rows in Fig. 2b are aligned. Because the CS displacement is always of the type $\frac{1}{2}[0\bar{1}1]$, adjacent sections of the crystal are vertically displaced 1.6 \AA 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. The spacing of the rows in Fig. 2a suggests that every sixth anion (121) plane is a CS plane and that the local composition in this area is Ti_3O_5 , while the spacing of the rows in Fig. 2b suggests that CS occurs at every twelfth anion $(\bar{1}\bar{2}1)$ plane and that the local composition is Ti_6O_{11} . The 0.2 \AA corrugations within the rows of Fig. 2a have a 3.4 \AA spacing which is very close to the spacing of titanium atoms (3.5 \AA) along this same direction in the ideal rutile unit cell.

It should also be noted that the presence of excess titanium along the CS planes should result in an electronic density of states corrugation which is opposite to the geometric effect. However, corrugations in the electronic density of states are usually some tenths of angstroms, so this effect should not be able to cancel the larger geometric effect. In fact, the observation that the corrugations in Fig. 2a are about 1 \AA , less than the expected value of 1.6 \AA , suggests that the presence of excess titanium in these positions compensates somewhat for the geometric effect. Although previous models of the reduced $\text{TiO}_2(110)$ surface have not considered the possible existence of CS planes or their effect on the titania surface structure [12], the existence of these planar defects has been proposed by Firment et al. [13] to explain angle-resolved UPS data

from the reduced MoO₃(010) surface, another transition metal oxide which forms a variety of CS structures.

CONCLUSION

This work demonstrates that the STM is capable of determining the surface structure of ionic materials, such as TiO₂ and ZnO, and that these oxides have unusual surface structures which undoubtedly play a role in determining their activity as catalysts and sensors.

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DISCUSSION

J. Nowotny: In the Max Planck Institute for Solid State Research in Stuttgart, there has been research on the electrical properties of titanium oxide involving measurements of electrical conductivity as a bulk property and work function as a surface property under the same conditions. What has been observed is that the same material, under the same conditions is n-type in the bulk and is p-type at the surface. So we have p-type conditions coming from the bulk to the surface. Is it known how the surface might become the type as you have mentioned?

G. S. Rohrer: Yes, under some circumstances I think it's quite possible for there to be an accumulation layer at the surface that could actually transform the material from one type to the other. However, that did not appear to be the case during these measurements.

D. Cahen: Could it be possible that when you try to compare the results from UPS, XPS and STM, you see problems that are associated with desorption and adsorption of oxygen? Because unless you work consistently at very low pressures you will get oxygen very quickly, on most of these surfaces.

G. S. Rohrer: I have to say that's always a possibility, because I don't know exactly the chemistry of the edge sites. But I'd also have to point out that these surfaces stay very clean in the UHV pressure range. In fact, they only interact weakly with most gases, so that once you clean them off they are very stable. These experiments were carried out in roughly the 5×10^{-10} torr pressure range.

R. Newnham: What are the prospects of using STM for real ceramics?

G. S. Rohrer: For nonconductive ceramics, the prospects are very poor right now. We've made preliminary efforts to do this at Penn, by photo-exciting surfaces. Another approach is to dope an insulating surface and make it conductive, but then, of course, you might change the chemical properties of the surface.

We've already put out some papers on polycrystalline zinc oxide ceramics and there is a lot of promise for probing grain-boundary interactions. But the key thing right now is that the crystal has to have some kind of conductivity.

D. Cahen: I'm a little bit concerned about your remark that you have clean surfaces, because in all papers which I know there's always a question of oxygen and water absorption. How do you know that you have clean surfaces?

G. S. Rohrer: Well, with respect to oxygen and water absorption, it's difficult to say absolutely. However, I followed instructions from the literature for cleaning procedures which produced one-by-one surfaces as determined by LEED.

As far as the chemistry and possible absorption at the edge sites, I have to try to deduce that from the experimental results. However with respect to carbon-containing species, my experiments indicate that once I cleaned the surfaces, they stayed clean in UHV.