

IMAGING THE ATOMIC-SCALE STRUCTURE OF MOLYBDENUM AND VANADIUM OXIDES BY SCANNING TUNNELING MICROSCOPY

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ABSTRACT

Single crystals of $\text{Na}_{0.003}\text{V}_2\text{O}_5$ and $\text{Mo}_{18}\text{O}_{52}$ were grown by chemical vapor transport and cleaved surfaces were imaged in ultrahigh vacuum using scanning tunneling microscopy (STM). Because the $\text{Mo}_{18}\text{O}_{52}$ (100) and $\text{Na}_{0.003}\text{V}_2\text{O}_5$ (010) surfaces of these layered materials have a bulk terminated structure, the atomic-scale contrast in constant current images can be directly compared to components of the bulk structure. Among the structural features identified in the STM images are the surface/crystallographic shear plane intersections, the different MoO_x coordination polyhedra on the $\text{Mo}_{18}\text{O}_{52}$ (100) surface, and the VO_5 square pyramids that make up the $\text{Na}_{0.003}\text{V}_2\text{O}_5$ (010) surface. In each of these cases, it was found that the atoms closest to the tip dominate the image contrast.

INTRODUCTION

The catalytic properties of transition metal oxides such as MoO_3 and V_2O_5 are known to be influenced by the structure of their surfaces [1,2]. Unfortunately, our ability to establish useful relationships between the surface structure and properties of these materials has been limited by our incomplete knowledge of the surface structure. It is expected that this information will soon become available through the use of the scanning tunneling microscope (STM), which allows the structure of surfaces to be visualized at micron to the angstrom length scales. However, although many transition metal oxides have already been imaged at atomic-scale resolution, correlating the contrast in an STM image of a complex binary or ternary compound surface with specific structural features remains a challenge [3-6].

Layered compounds, which have strong primary bonds between atoms within layers, but weak van der Waals bonding between the layers, are excellent models for the study of contrast in STM images because cleavage parallel to the layer breaks only the weak bonds and creates a low energy surface with little or no driving force for relaxation or reconstruction. Thus, topographic features in STM images can be correlated with bulk crystallographic data. The two compounds described here, V_2O_5 and $\text{Mo}_{18}\text{O}_{52}$ (an oxygen deficient relative of MoO_3), both have layered structures. It is the goal of this work to identify the contrast that arises from specific structural features on the surfaces of these layered compounds so that in the future, the contrast on inhomogenous or defective oxide surfaces can be identified.

The vanadium and molybdenum oxides exhibit a number of structural and chemical similarities. Both have O ions in 1-, 2-, and 3-fold coordination and both materials are very labile, with high oxygen diffusivities and easily accessed reduced valence states. The specific structural features that we wish to identify are the different coordination polyhedra (the $\text{Mo}_{18}\text{O}_{52}$ surface has both octahedral and tetrahedral groups on the surface), the orientation of the polyhedra (the V_2O_5 surface is terminated by square pyramids with opposite vertical orientations), and the surface/crystallographic shear (CS) plane intersections (the CS planes intersect the $\text{Mo}_{18}\text{O}_{52}$ surface periodically along the [010] direction).

EXPERIMENTAL

The single crystals used in this study were prepared by chemical vapor transport. The growth of $\text{Mo}_{18}\text{O}_{52}$ crystals involves heating, in a horizontal tube furnace with a small temperature gradient, at approximately 677 °C for several days, an evacuated quartz ampoule containing a stoichiometric mixture of Mo and MoO_3 together with a small amount of I_2 that acts as a transporting agent [7, 8]. Powder X-ray diffraction was used to identify platey black crystals found throughout the tube as $\text{Mo}_{18}\text{O}_{52}$.

Because crystals of pure V_2O_5 are too insulating to permit high resolution STM measurements, we increased the conductivity by intercalating them with a small amount of Na [9]. In order to insure uniformity, the Na was added during the crystal growth. The single crystals of $\text{Na}_{0.003}\text{V}_2\text{O}_5$ were prepared by sealing $\text{Na}_x\text{V}_2\text{O}_5$ (prepared by treating V_2O_5 in an aqueous $\text{Na}_2\text{S}_2\text{O}_4$ solution) in a quartz ampoule with a small amount of TeCl_4 to act as a transporting agent. The ampoule was then heated in a 30 °C temperature gradient (530 °C to 500 °C) for seven days after which crystals were harvested from the cooler end of the tube. Powder X-ray diffraction was used to show that the structure of these crystals was essentially identical to that of pure V_2O_5 , with no extra peaks. Analysis of the sodium content by flame emission spectroscopy indicated a chemical composition of $\text{Na}_{0.003}\text{V}_2\text{O}_5$. The electronic conductivity, determined using a four-point probe method, is $0.04 \Omega^{-1}\text{-cm}^{-1}$. These structural, chemical, and electrical measurements are all consistent with the model that the single crystals grown by chemical vapor transport are essentially V_2O_5 with a small amount of sodium intercalated into the interlayer spaces that increases the electronic conductivity by donating electrons to the V_2O_5 framework, but does not significantly alter the structure.

STM imaging was carried out in ultrahigh vacuum (UHV) on cleaved surfaces. Surfaces of $\text{Na}_{0.003}\text{V}_2\text{O}_5$ were prepared either by cleavage in the vacuum chamber, or by cleavage in a N_2 filled glove bag connected to the chamber's load-lock. $\text{Mo}_{18}\text{O}_{52}$ surfaces were cleaved in air immediately before transferring them to the UHV environment. Constant current images were obtained using current levels between 0.6 and 1.0 nA. Images of $\text{Mo}_{18}\text{O}_{52}$ were recorded at -1.6 V sample bias (tunneling from filled states) using a clipped Pt-Ir tip. Images of $\text{Na}_{0.003}\text{V}_2\text{O}_5$ were recorded in the range of 2 to 3 V sample bias (tunneling to empty states) using a similar tip. The images presented here are representative of many observations on several crystals.

RESULTS

Topographic STM images showed that the cleavage surfaces of $\text{Mo}_{18}\text{O}_{52}$ (100) and $\text{Na}_{0.003}\text{V}_2\text{O}_5$ (010) are flat over hundreds to thousands of angstroms in each direction. For each material, higher resolution images reveal contrast that has, within the errors caused by thermal drift, the periodicity of the planar repeat unit of the bulk structure.

A characteristic image from a $50 \times 50 \text{ \AA}$ area of the $\text{Na}_{0.003}\text{V}_2\text{O}_5$ (010) surface is shown in Fig. 1c. The primary contrast in this image is due to the elevated (white) areas oriented along [100] separated by approximately 11 Å. The height of this corrugation is 2 Å. There is additional contrast along these rows with an approximately 3.7 Å period. The primary contrast in images of the $\text{Mo}_{18}\text{O}_{52}$ (100) surface (see Fig. 2a) is caused by a series of steps and terraces oriented along the [010] direction with a 26 Å period. Typically, the steps were very straight and evenly spaced, but occasional curves and variations in terrace width were observed. There is a series of bright features at the edge of each step which has an 11.8 Å average frequency along the direction of the step. The topographic variation over these features is less than 1.0 Å. There is also a series of rows within each step which have a periodicity of 3.8 Å and a corrugation height of 0.4 Å. Any additional features within these rows are incompletely resolved.

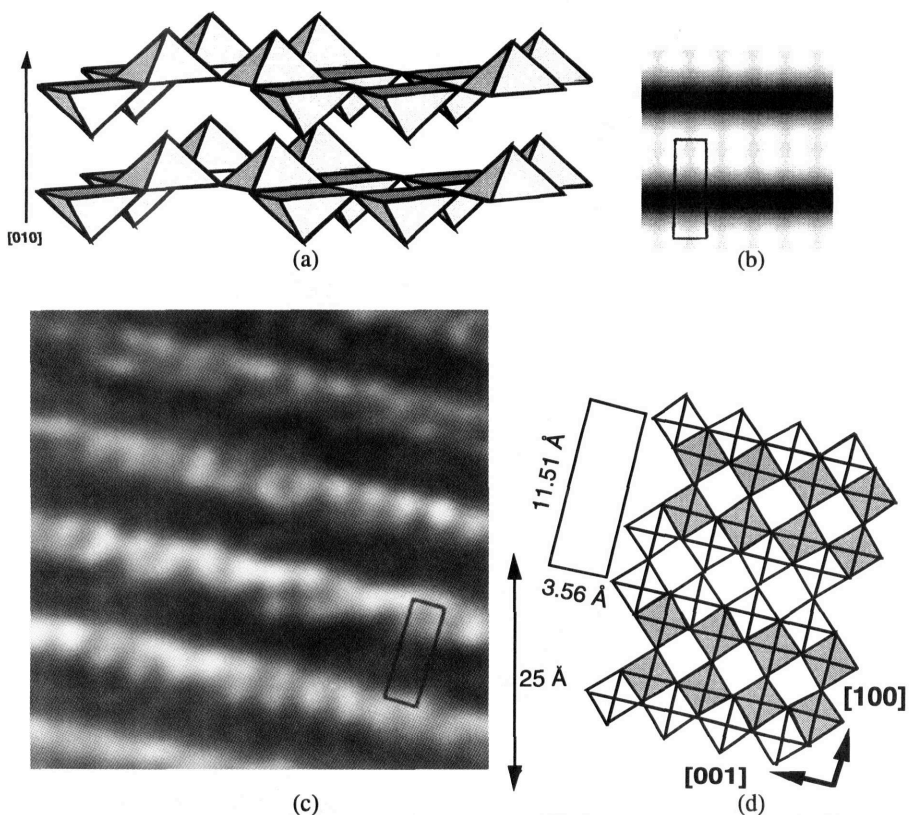


Figure 1. (a) A 3-dimensional rendering of the idealized V_2O_5 structure, composed of layers of edge- and corner-sharing square pyramids in up and down orientations. (b) A simulated constant current image of the V_2O_5 surface, $23 \text{ \AA} \times 21 \text{ \AA}$. The rectangle marks the unit cell, as in c & d. (c) A $50 \text{ \AA} \times 50 \text{ \AA}$ constant current image of the $Na_{0.003}V_2O_5$ (010) surface. The vertical resolution from black-to-white is 2 \AA . (d) A projection of the structure along $[010]$ (not to scale). Lighter pyramids have the upward orientation, darker ones point downward.

DISCUSSION

Contrast in an STM image is determined by a convolution of the geometric positions of atoms on the surface and lateral variations in the surface density of states. Although the atomic positions are known on the basis of bulk crystallographic data, our knowledge of the electronic structure of the surface is incomplete. We can, however, assume that in both cases images were formed using electrons coming from (in the case of $Mo_{18}O_{52}$) or going to (in the case of $Na_{0.003}V_2O_5$) states in a partially filled conduction band formed by the overlap of metal d and O 2p orbitals. Considering the polarity of these materials, this band should be predominantly "d" in character and, therefore, we might expect the metal atoms to represent the bright contrast. However, we find that in each case the geometric structure of the surface is important for a consistent interpretation.

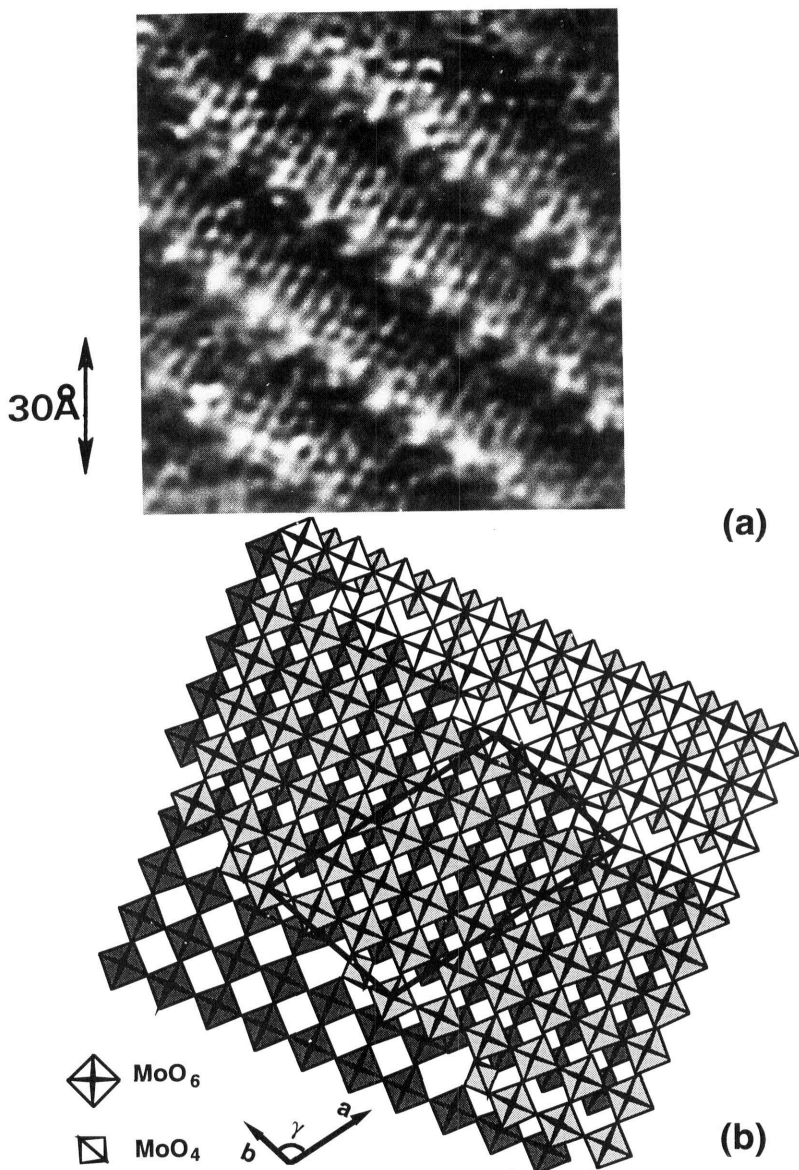


Figure 2. (a) A constant current STM image of a $110 \text{ \AA} \times 110 \text{ \AA}$ area of the $\text{Mo}_{18}\text{O}_{52}$ (100). The vertical resolution is 2.5 \AA from black-to-white, the planar repeat unit is 26 \AA along the long axis (the distance between CS planes) and 11 \AA along the short axis (the distance between tetrahedral groups at the edge of the shear step). The fine corrugations are 3.8 \AA apart, the distance between adjacent corner-sharing octahedra. (b) A structural model (not to scale) of the surface with polyhedra shaded according to their vertical height, darker ones being lower.

Considering the projection of the $\text{Na}_{0.003}\text{V}_2\text{O}_5$ (010) surface shown in Fig 1d, there are two structural features that could cause the white contrast in the image. The first are the pairs of vanadyl O that cap the square pyramids in the upward orientation. The second are the pairs of exposed V atoms at the bases of the inverted pyramids. Based only on the electronic structure, one might conclude that it is the V atoms. However, based on the facts that the O 2p states make some contribution to the conduction band, that the O ions are larger than the V ions, and that the O ions are elevated 2.5 Å above the plane of the V atoms, we expect the O ions to make a greater contribution to the tunneling current than the V. In order to quantify these suggestions, we have calculated the tunnel current as a function of the lateral and vertical position over the surface assuming that the tunnel current is given by the sum of contributions from each atom according to:

$$I = \sum_i D_i \exp(-1.025 S_i \sqrt{\phi}) \quad (1)$$

For the tunneling barrier height, ϕ , we take a characteristic value determined by measurements of the dependence of I on S_i . This variable acts as a scale factor and changes only the overall vertical corrugation of the image without effecting its appearance after normalization. S_i is defined as the distance between the surface of the tip (a sphere with radius r_{tip} = the radius of a Pt atom) and the surface of the i^{th} atom which is a hard sphere whose size is defined by the ionic radius. Although not explicitly in the equation for the tunneling current, the tip radius influences the current through its effect on the separations, S_i . Based on the polarity of the structure, D_i , the relative contribution of the i^{th} atom to the total density of electronic states in the conduction band, was taken to be 1 for V and 0.1 for O. A more complete explanation of this model appears in ref. [10]. After the current has been determined at each position, constant current images can be easily extracted and displayed as shown in Fig 1b. In this simulated image, the white contrast corresponds to the O atoms at the peaks of the square pyramids. Based on the qualitative similarity of the experimental and computed image, we conclude that the white contrast comes from pairs of incompletely resolved square pyramids in the upward orientation.

Contrast in images of the $\text{Mo}_{18}\text{O}_{52}$ surface can be interpreted based on the bulk crystal structure which has been specified by Khilborg [11]. Based on their spacing and orientation with respect to other features, we conclude that the lines of contrast with the 26 Å periodicity are the surface/CS plane intersections that define the boundaries of the unit cell. Between the CS planes the structure of $\text{Mo}_{18}\text{O}_{52}$ is nearly identical to MoO_3 . The small O deficiency of $\text{Mo}_{18}\text{O}_{52}$ with respect to MoO_3 is accommodated by these structural elements. Using the bulk structure as a model, the vertical displacement between two terraces separated by a surface/CS plane intersection should be 1.7 Å. Measured vertical displacements on the image vary from 1.5 to 2.5 Å, depending on the point of measurement.

The 3.8 Å period of the contrast within the terraces correlates with both the positions of the Mo atoms and the apical O atoms that cap the MoO_6 octahedra. Without attempting to deconvolute the competitive effects of the greater contribution of the Mo atoms to the conduction band states and closer proximity of the O atoms to the tunneling tip, we will simply assume that it is the MoO_x group as a whole that is responsible for the contrast. This interpretation is consistent with explanations of the contrast in STM images of alkali molybdate bronzes, related compounds which can also be considered as arrangements of MoO_x polyhedra [12-14]. Thus, we assign the 3.8 Å periodicity to the rows of corner sharing MoO_6 octahedra in each terrace (see Fig. 2b). This assignment leads to an explanation of the bright contrast that occurs with an 11.8 Å period at the end of every third row of octahedra. The position and frequency of these spots correspond to the only positions on the surface where MoO_4 tetrahedral units occur. One possible reason for the pronounced contrast difference between the tetrahedral and octahedral units, based solely on geometric considerations, is that while a Mo atom in the octahedral environment is well shielded from the tip by the apical oxygen, in the tetrahedral unit there is a direct line between it and the tip which might lead to

an enhanced local density of electronic states and the enhanced corrugations. In any case, the two coordination polyhedra are clearly discriminated.

CONCLUSION

The contrast in STM images of the surfaces of layered oxides such as $\text{Na}_{0.003}\text{V}_2\text{O}_5$ and $\text{Mo}_{18}\text{O}_{52}$ can be interpreted based on comparisons with the bulk structure. Through such comparisons, we have determined that square pyramids with the upward orientation (oxygen atoms) are the source of white contrast on the STM images of the $\text{Na}_{0.003}\text{V}_2\text{O}_5$ (010) surface and that the surface/CS plane intersection, octahedral MoO_6 groups, and tetrahedral MoO_4 groups can all be distinguished on the (100) surface of $\text{Mo}_{18}\text{O}_{52}$. In each of these cases, it was found that the atoms closest to the tip dominate the image contrast. The identification of contrast from the structural elements of these ordered surfaces will aid in the interpretation of contrast from images of defective surfaces.

ACKNOWLEDGMENTS

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