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A SCANNING TUNNELING MICROSCOPY STUDY OF VANADIUM OXIDE

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Abstract

Atomic resolution images of the (010) surface of a divanadium pentoxide (V_2O_5) single crystal were successfully obtained by the use of a scanning tunneling microscope (STM).

The images of the filled states at sample bias voltage, $V_s = -2$ V and the empty states at $V_s = +2$ V correspond to oxygen and vanadium ions, respectively.

As for the vanadium ion sites, an additional peak of the electronic states at the conduction band edge due to the defects of vanadyl oxygen ions was found in the normalized conductance spectrum through the tunneling spectroscopy (TS) measurement.

Key Words: Divanadium pentoxide (V_2O_5), scanning tunneling microscopy, tunneling spectroscopy, atomic image, atomic scale, ultrahigh vacuum, surface states, defects, vanadyl oxygen.

Introduction

The vanadium oxides are very interesting materials with a rich variety of crystal structures, chemical characteristics and physical properties. Every compound consists of vanadium ions with different valencies which vary from two to five. The variety of the d electron states of vanadium oxides causes the complicated electron energy structures which give rise to their interesting properties. Recently, the surface structures of several transition metal oxides such as TiO_2 , ZnO and VO_2 were observed in real space with atomic resolution by the use of scanning tunneling microscopy (STM) [2, 6, 7].

In this experiment, a single crystal of divanadium pentoxide (V_2O_5), a material widely used as a catalyst [1], is studied microscopically by STM and tunneling spectroscopy (TS). Physical properties such as the surface structure and the energy structure were investigated. The images of oxygen ion rows were observed in the surface of V_2O_5 for the first time. Vanadyl oxygen ion rows on vanadium ions in a (010) surface and also vanadium ion rows were observed distinctively by applying the positive and negative sample bias voltages, respectively.

The energy structures of the density of states at the oxygen sites as well as the vanadium sites were measured by TS and a slight difference between them was found.

Experimental

This study of V_2O_5 by the use of STM was carried out in an ultrahigh vacuum (UHV) at a pressure less than 2×10^{-10} Torr. The tip was formed by electrochemically etching a 0.5 mm diameter tungsten wire. A multi-programmer (Hewlett Packard Model 7041) and a computer system (Hewlett Packard Model 332) were used for the data acquisition and the control of the STM. A tunneling current versus sample bias voltage (I-V) spectrum was obtained at each of the 64 x 64 pixels in a topographic image. The sample bias voltage was scanned in 10 ms. One step of voltage scanning was 1/50 of a full voltage range from -4 V to +4 V.

The samples of V_2O_5 used were prepared as follows: The powder of V_2O_5 was heated slightly above the

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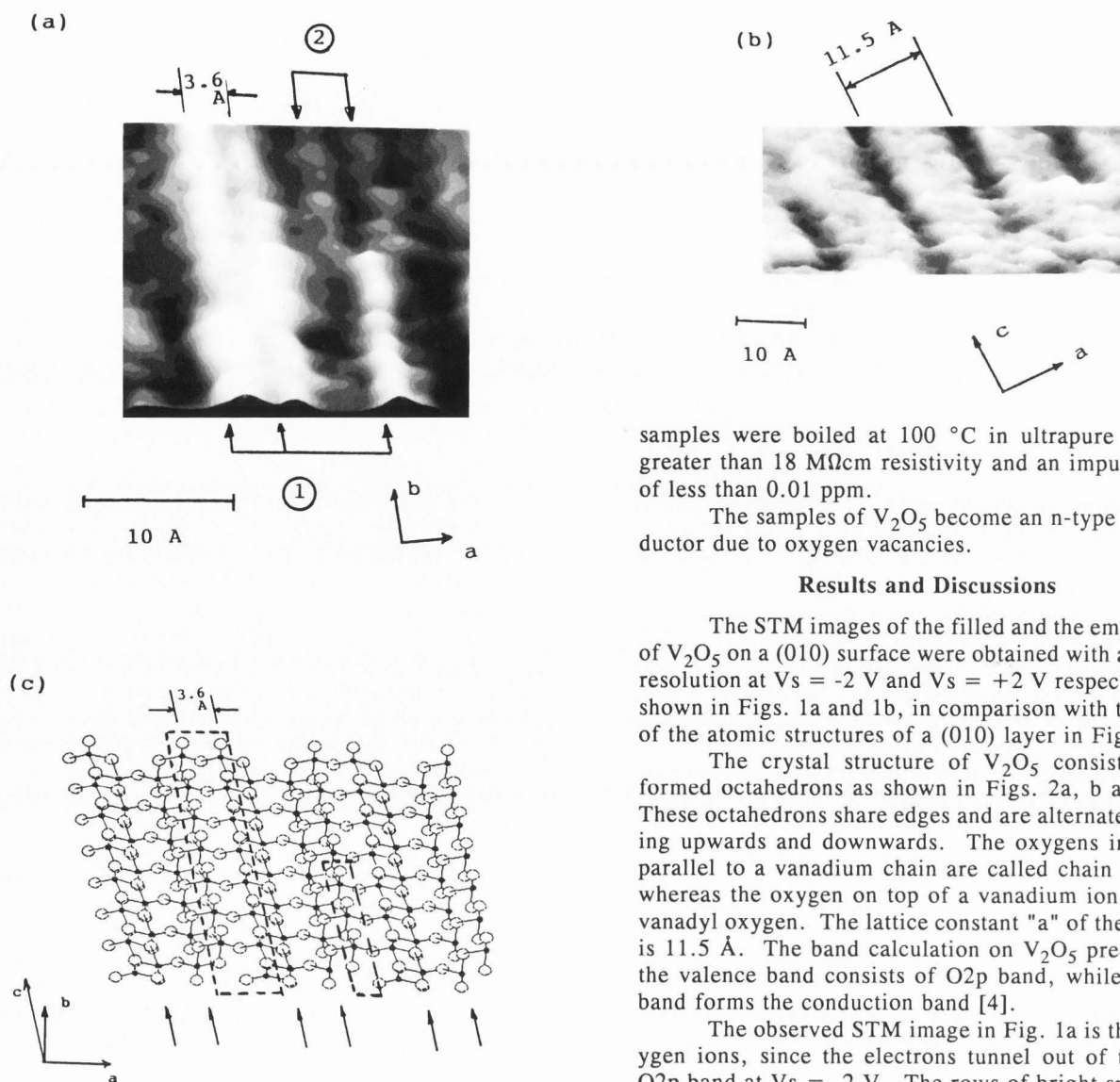


Figure 1. (a) STM image of the filled states of V_2O_5 on a (010) surface at $V_s = -2$ V. The ion rows "1" and "2" correspond to vanadyl oxygens and chain oxygens, respectively. (b) STM image of the empty states on a (010) surface at $V_s = +2$ V. (c) The schematic structure of one layer of V_2O_5 . Open circles indicate oxygen ions and black dots indicate vanadium ions. A pair of arrows indicates vanadium ion rows under which vanadyl oxygen ions are located. Vanadyl oxygens in the rectangles defined by dotted lines correspond to the bright rows "1" in the image of the filled states.

melting point of 690°C for about 24 hours in the atmosphere. Then, it was slowly cooled down to grow crystals of V_2O_5 .

The samples of V_2O_5 were cleaved to provide a specular surface parallel to a (010) layer. The cleaved

samples were boiled at 100°C in ultrapure water of greater than $18\text{ M}\Omega\text{cm}$ resistivity and an impurity level of less than 0.01 ppm.

The samples of V_2O_5 become an n-type semiconductor due to oxygen vacancies.

Results and Discussions

The STM images of the filled and the empty states of V_2O_5 on a (010) surface were obtained with an atomic resolution at $V_s = -2$ V and $V_s = +2$ V respectively, as shown in Figs. 1a and 1b, in comparison with the model of the atomic structures of a (010) layer in Fig. 1(c).

The crystal structure of V_2O_5 consists of deformed octahedrons as shown in Figs. 2a, b and c [4]. These octahedrons share edges and are alternately pointing upwards and downwards. The oxygens in a chain parallel to a vanadium chain are called chain oxygens, whereas the oxygen on top of a vanadium ion is called vanadyl oxygen. The lattice constant "a" of the unit cell is 11.5 \AA . The band calculation on V_2O_5 predicts that the valence band consists of O2p band, while the V3d band forms the conduction band [4].

The observed STM image in Fig. 1a is that of oxygen ions, since the electrons tunnel out of the filled O2p band at $V_s = -2$ V. The rows of bright spots indicated by arrows "1" in Fig. 1a are considered to be vanadyl oxygens which correspond to the oxygen ion rows shown in rectangles defined by dotted lines in Fig. 1c. The images of the nearest two vanadyl oxygen rows with a separation of 3.6 \AA and that of a row with some defects of vanadyl oxygens are clearly seen in Fig. 1a.

The two rows indicated by arrows "2" in the image are considered to be rows of chain oxygens, whereas vanadyl oxygens in the middle of two rows are desorbed.

Rows along the "c" axis shown in the STM image of Fig. 1b indicate vanadium ions where electrons tunnel into the empty vanadium 3d band at sample bias $V_s = +2$ V.

There are two types of vanadium ions on a (010) surface. In Type 1, a vanadyl oxygen ion is located above a vanadium ion, and in Type 2, on the other hand, an oxygen is located under a vanadium ion. The electrons can hardly tunnel into the vanadium ions of the former type, since they are covered by vanadyl oxygen

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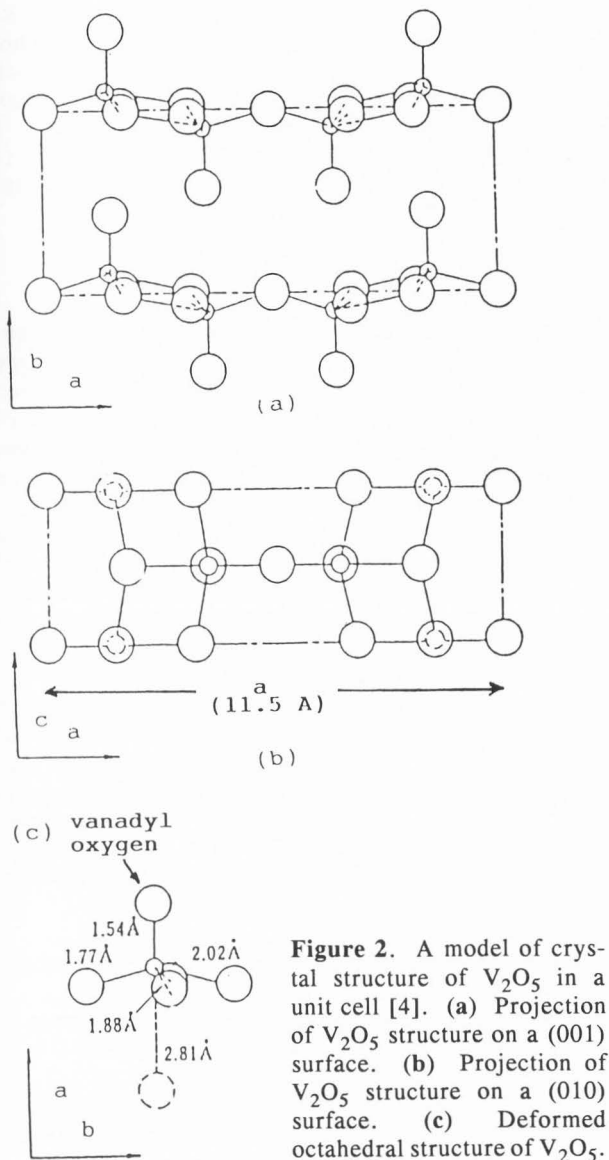


Figure 2. A model of crystal structure of V_2O_5 in a unit cell [4]. (a) Projection of V_2O_5 structure on a (001) surface. (b) Projection of V_2O_5 structure on a (010) surface. (c) Deformed octahedral structure of V_2O_5 .

ions. Therefore, the STM image in Fig. 1b shows the vanadium ion rows of the latter type at a positive sample bias voltage.

Each bright stripe in the image consists of two vanadium ion rows indicated by three pairs of arrows in Fig. 1c. This fact suggests that the conduction band is spatially spread between two vanadium ion rows across the bridge oxygen ions. The distance of 11.5 Å between the centers of two adjacent stripes agrees with the value of "a" of the unit cell shown in Fig. 1b.

Figures 3a and 3b show the tunneling I-V (current-voltage) spectra at the oxygen ion site (a) and the vanadium ion site (b), respectively. These two sites are assigned to the bright and dark positions of the STM topographic image at a negative sample bias voltage, respectively.

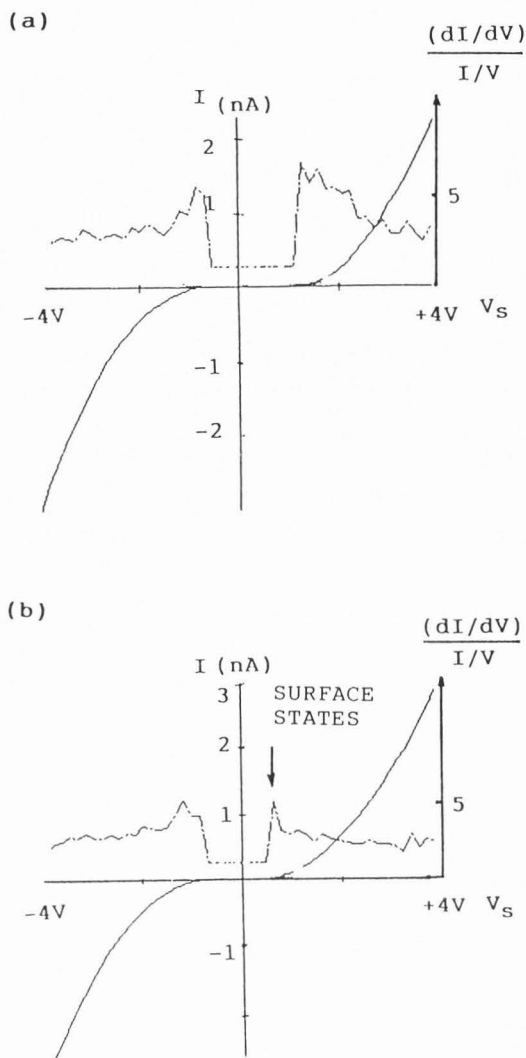


Figure 3. The tunneling I-V spectra (solid lines) and their normalized conductance spectra (broken lines) at oxygen ion sites and those at vanadium ion sites are shown in (a) and (b), respectively. Here, each curve is averaged over measurements at 10 different positions of each ion site. The arrow in (b) indicates additional gap states.

To improve the signal to noise (S/N) ratio of tunneling spectra, the I-V curves at oxygen ion and vanadium ion sites are averaged over the measurements on 10 bright sites and 10 dark sites, respectively. Their normalized derivative conductance curves, $(dI/dV)/(I/V)$, indicating the characteristics of density of state are also shown in Figure 3.

The energy gap at the oxygen site on the surface is measured to be about 2.0 eV from the normalized conductance spectrum in Fig. 3(a), the value of which agrees with the data of the optical band gap 2.1 eV [8].

At several vanadium ion sites, on the other hand, a peak of the additional electronic states appears in the

band gap just below the conduction band edge as indicated by an arrow in Fig. 3b.

It is likely that these additional states originated from dangling bonds and lattice distortion due to defects of vanadyl oxygen.

Conclusions

The structure and the electronic states of the surfaces of V_2O_5 were studied by the use of STM and TS. The atomic images of oxygen ions and vanadium ions on the surface (010) were observed distinctively by changing the polarity of sample bias voltages corresponding to the valence band states consisting of O2p and the conduction band states consisting of V3d.

In the TS measurement, a comparison of I-V spectrum at vanadium ion sites with that on oxygen sites indicates that surface states just below the conduction band are seen only on vanadium ion sites. This fact suggests that the surface states are affected by dangling bonds and lattice distortion due to defects of vanadyl oxygen.

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Discussion with Reviewers

Reviewer III: Is merely citing the polarity of the tunneling process sufficient to conclude that one image shows the vanadium ions while the other depicts oxygen ions? STM images show the spatial arrangement of electron states which are not necessarily localized to the atom cores (for instance see a number of publication interpreting the tunneling images on Si(001) surfaces).

Authors: Interpretations of STM images of the surface of an ionic crystal of V_2O_5 are different from those of covalent bonding type surfaces such as Si(001). Feenstra *et al.* [3] showed in the STM image of GaAs (a partially ionic crystal), that the occupied state corresponding to valence electrons are localized around the anions and the unoccupied states are localized around cations. In the case of V_2O_5 , the occupied density of states of O2p is one order of magnitude larger than that of vanadium atoms [5]. The electrons in the O2p band are naturally localized at oxygen ion sites in the case of strongly ionic oxides like V_2O_5 . Therefore, it is appropriate that cation and anion rows can be distinguished by citing the polarity of the tunneling process.

O. Marti: How is the reproducibility of the images and spectra?

Authors: The reproducibility in this experiment is fairly good.

O. Marti: The +2 V and -2 V images are measured one after the other. The orientation of the sample is different. Are the samples also different?

Authors: Those images were obtained on the same sample but at two different grain positions having the same structure.

O. Marti: Why boil the samples in water? Why not cleave in UHV?

Authors: The surface condition of V_2O_5 in UHV is quite delicate. It is found to be rather difficult to obtain a flat surface in an atomic scale by cleaving in UHV. Moreover, oxygen atoms on the surface of V_2O_5 are easily desorbed by annealing the crystal. It was discovered that a flat silicon surface at the nanometer level can be obtained by boiling [9]. We found this method is valid also in the case of V_2O_5 . We could obtain a flat surface by this method.