Insulator–metal transition on heavily reduced TiO$_2$(1 1 0) surface studied by high temperature-scanning tunnelling spectroscopy (HT-STS)

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Abstract

Scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS) were used to study the electronic structure of the reduced TiO$_2$(1 1 0) surface. At the occupied part of the spectra some states at energies of about 1.1 and 0.6 eV below the Fermi level were found. At the unoccupied part of the spectra, the presence of a surface state at an energy of about 0.6 eV above the Fermi level was observed. Their presence has been ascribed to the appearance of Ti$_2$O$_3$ regions on the TiO$_2$(1 1 0) surface. High temperature spectroscopy measurements indicated smooth insulator–metal transition (I–M) caused by bands overlap in Ti$_2$O$_3$, which takes place at elevated temperatures.
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1. Introduction

During last years, increasing experimental and theoretical efforts have been made to understand the electronic conduction in oxides ([1] and references therein]. In contrast to metals, the electric properties of oxides show many characteristic features. One of these is the insulator–metal transition (I–M) marked by a change from the insulating behaviour to the metallic behaviour at certain temperatures [1,2]. The mechanism of the I–M transition is complex and is still not well understood. The complexity of this phenomenon is a result of the many electron–phonon interactions in oxides. As a result, theories for many body problems in strongly coupled electron–phonon systems must be considered to explain this phenomenon [1,2].

Until now the I–M transition, which takes place at temperatures higher than room temperature, has been mainly studied using electron spectroscopy (UPS, XPS) and resistivity measurement of a sample as a

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function of temperature [1]. However, these techniques do not allow extracting local information on the spatial distribution of electron density of states on the investigated surface, i.e. local density of states of the surface (LDOS (E, x, y)). Thus, a technique that provides local spectroscopic information at the atomic level is required. The high temperature-scanning tunnelling spectroscopy (HT-STS) technique enables us to obtain spectroscopic information from the tunnelling current characteristics by showing spectral features in agreement with other surface sensitive techniques [3]. The advantage of these methods is that they offer the possibility of examining both occupied and unoccupied electronic states with atomic selectivity and high-energy resolution. Recently, HT-STS has been successfully used to in situ studies of the effect of temperature on the electronic structure of $Ni_xMn_3O_{3-x}O_{3-\delta}$ thin films [4].

In this paper, we focus on the measurements of electron density of states as a function of temperature on heavily reduced $TiO_2(1\,1\,0)$ surface. In stoichiometric TiO_2 crystal, the metal atom is in $3d^0$ (Ti^{4+}) electronic configuration; however, the surface can be reduced by ion sputtering or heat treatment to create Ti_2O_3 regions on $TiO_2(1\,1\,0)$ surface in which metal atom is in $3d^1$ (Ti^{3+}) configuration [5,6]. At about $T_c = 450$ K, Ti_2O_3 exhibits a smooth insulator–metal transition with increasing temperature [1,2,7–10]. Below T_c, Ti_2O_3 indicates the presence of a small energy gap $E_g = 0.1$ eV between the occupied a_{1g} band and the unoccupied $e_g^\pi + e_g^{\pi*}$ band [10]. As was established the change in the conductivity of Ti_2O_3 above T_c is accompanied by an increase in the c-axis lattice parameter and a decrease in the a-axis lattice parameter with no change in lattice symmetry leading to a broad crossover between a_{1g} and $e_g^\pi + e_g^{\pi*}$ bands [1,2,7–10].

The identification of the I–M transition on heavily reduced $TiO_2(1\,1\,0)$ density of states on HT-STS data is of great importance not only from the fundamental point of view but also in the studies of early stages of high temperature oxidation of alloys, especially TiAl. Although, the scanning tunnelling microscopy (STM) results for reduced $TiO_2(1\,1\,0)$ surface have been presented previously ([11] and references therein), no experimental results for high temperature tunnelling spectroscopy have been published yet. The goal of this paper is to bridge this existing gap.

2. Experimental

The STM/STS/current imaging tunnelling spectroscopy (CITS) experiments were performed at elevated temperatures with a commercial VT-STM/AFM system in UHV condition (Omicron, GmbH, Germany) equipped with LEED/Auger spectrometer (SPECTA-LEED) and a sputtering gun (ISE 5). The $TiO_2(1\,1\,0)$ (Pi-Kem, UK) surface was prepared by repeated cycles of Ar^+ ion sputtering (typically 30 min, 1 keV, current 4 μA) and annealing (typically 1050 K, 1 h).

During the STM/STS measurements performed, the base pressure was 2×10^{-10} mbar. The tips used were prepared by mechanical cutting from the 90% Pt–10% Ir alloy wires (Goodfellow). In current imaging tunnelling spectroscopy mode, the I/V curves were recorded simultaneously with a constant current image by the interrupted-feed-back-loop technique.

The experimental parameters chosen for the CITS measurements were +2.5 V for the sample bias and 1 nA for the tunnelling current set point and the energy range of the spectroscopy was ±2 eV. Based on these measurements, the first derivative of the tunnelling current with respect to voltage (dI/dV) was calculated. The dI/dV spectra were normalised using the method proposed by Feenstra et al. [12] where the differential conductance is divided by the total conductance—(dI/dV)/(I/V). The (dI/dV)/(I/V) quantity is a measure of local density of states of the surface [12]. The divergence problem in the case of (dI/dV)/(I/V) was overcome by applying some amount of broadening (ΔV) to the I/V values [13]. In all our cases, $\Delta V = 1$ V value was chosen.

3. Scanning tunnelling microscopy results

The development of terraces, which occurred after many cycles of heating and sputtering at various temperatures of the $TiO_2(1\,1\,0)$ surface is demonstrated in Fig. 1. Atomic layer steps of 0.32 nm as expected from geometric structure separate the terraces.

Further annealing produced the (1×1) superstructure on the $TiO_2(1\,1\,0)$ surface (blue colour of the sample). The (1×1) superstructure contains two types of oxygen atoms, i.e. atoms at the bridging and in-plane positions, and two types of titanium atoms which are five- and six-fold co-ordinated. Oxygen atoms bridging
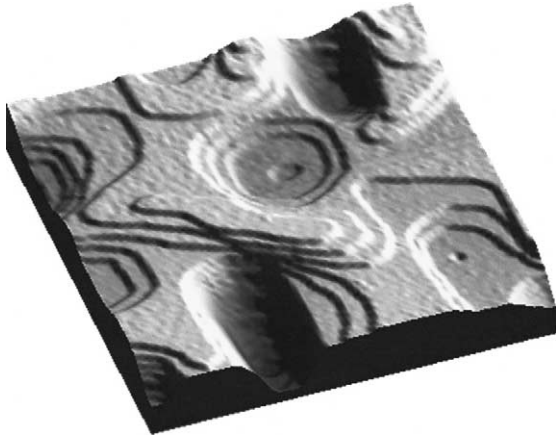
Fig. 1. The 30 nm² STM image of lightly reduced TiO₂(1 1 0) surface (blue colour of the sample). The height of the terraces is 0.32 nm.

and covering the six-fold co-ordinated Ti atoms form ridges along the [0 0 1] axis. The five-fold co-ordinated Ti atoms are exposed to the surface. Thus, the (1 × 1)

superstructure consists of alternative rows of the exposed Ti atoms and the bridging O ridges. The O ridges and Ti rows are aligned with a 0.65 nm separation, respectively (see Fig. 2).

The STM image showing (1 × 1) superstructure of TiO₂(1 1 0) surface exhibiting bright atomic rows parallel to the [0 0 1] direction and separated by about 0.7 nm is presented in Fig. 3. The image was recorded at a positive sample bias of 1 V (1 eV above the Fermi level), i.e. the lower conductance band of the TiO₂ was probed. From band electronic structure of the TiO₂ (see Fig. 4), it is clear that the lower conductance band consists of Ti d_{xy} orbitals contributing to the metal–metal interactions due to the σ bonding of the Ti t_{2g}–Ti t_{2g} states. These states are localised on the five-fold co-ordinated Ti atoms exposed to the surface. As a result, Ti atoms were imaged by STM as bright rows, thought the Ti atoms are located 0.11 nm below the bridging oxygen atoms. It confirms the well-known fact that STM does not show an atomic structure of the surface
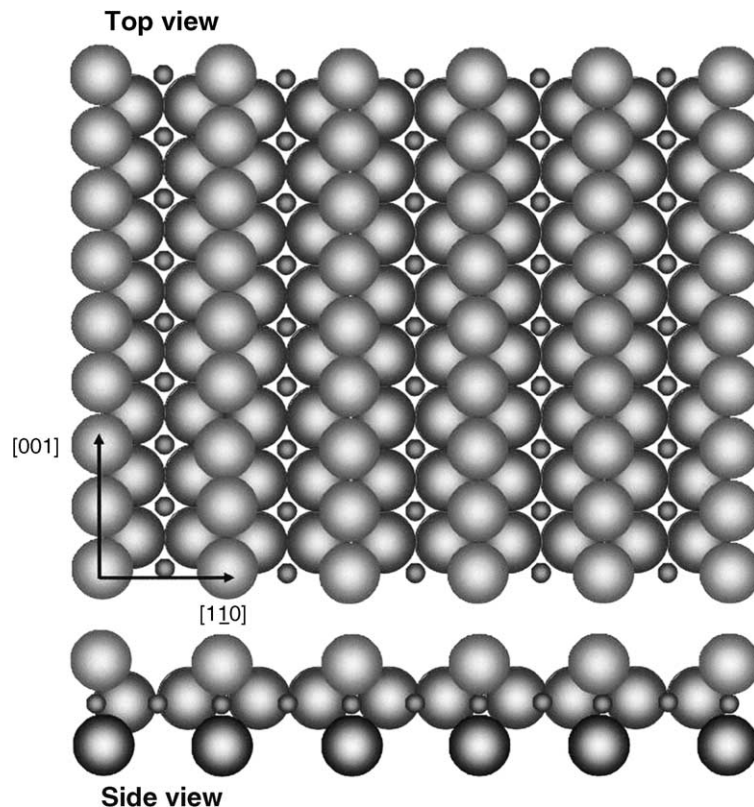

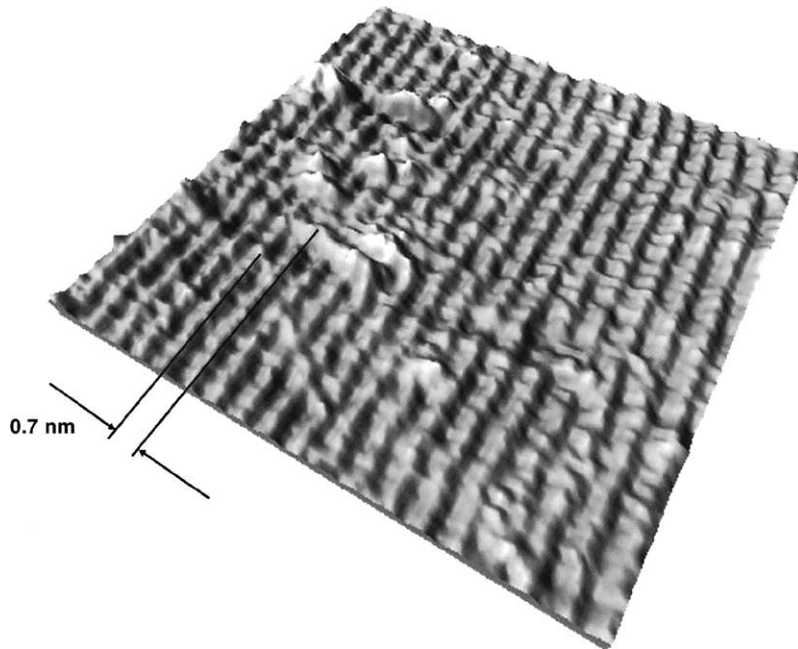Fig. 2. Atomistic model of the (1 × 1) superstructure on TiO₂(1 1 0) surface.

Fig. 3. The 15 nm^2 STM image of TiO$_2$(1 1 0) surface showing (1 × 1) reconstruction.
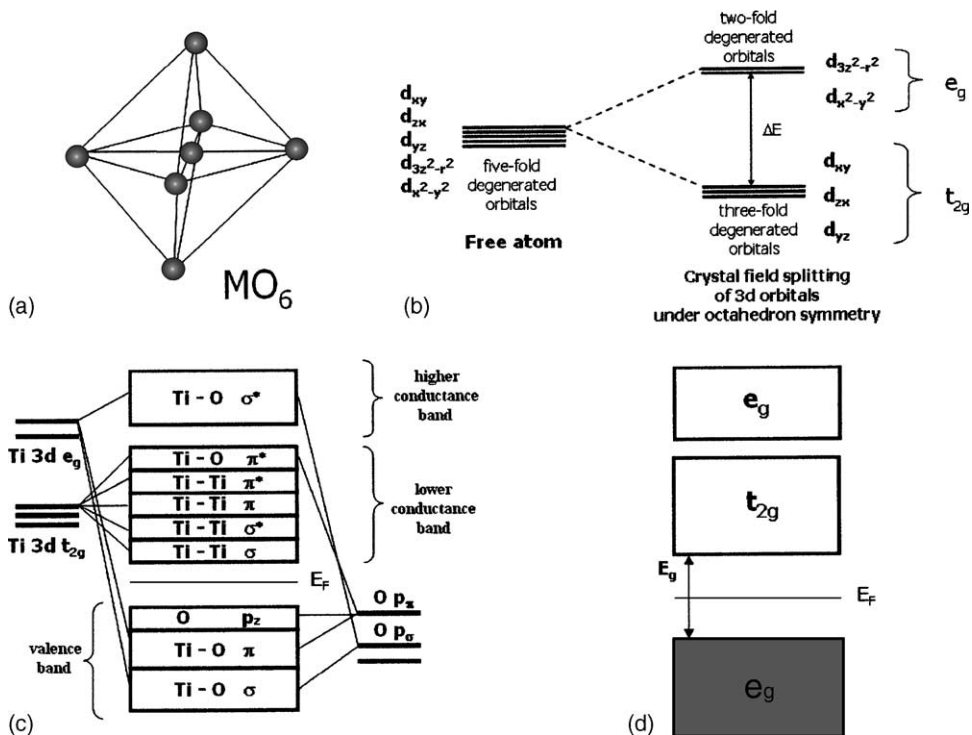

Fig. 4. (a) The basic structural unit of TiO$_2$ (octahedron—MO$_6$); (b) energy level splitting of the Ti 3d orbitals in the octahedral positions; (c) bands energy diagram for rutile TiO$_2$; and (d) simple form of bands energy diagram for rutile TiO$_2$.
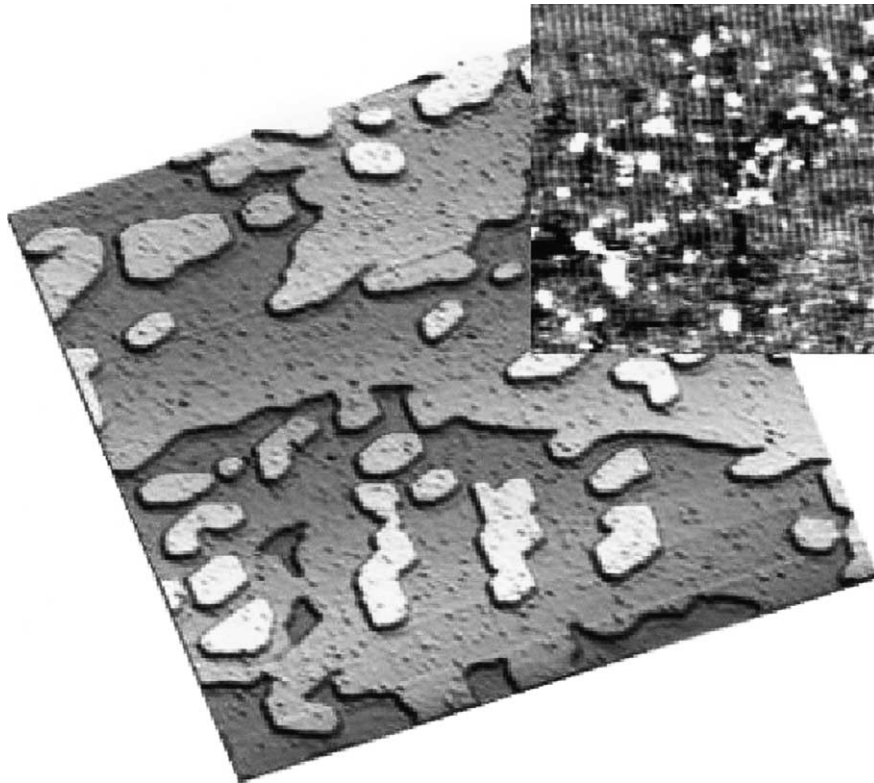
Fig. 5. The 600 nm^2 STM image of heavily reduced TiO$_2$(1 1 0) surface (black colour of the sample). The inset shows atomic resolution on the heavily reduced surface.

in crystallographic sense, but rather an atomic structure of the surface, which is strongly affected by the local electronic structure.

Further sputtering and annealing of the sample make the surface more reduced (black colour of the sample). It results in loss of oxygen and rearrangements of Ti^{3+} ions leading to formation Ti$_2$O$_3$-like Ti^{3+} pairs [5,6]. When the density of pairs increases areas of Ti$_2$O$_3$ start to form on the TiO$_2$(1 1 0) surface. Typical topography of heavily reduced surface is presented in Fig. 5. Occasionally, on very small regions of the sample the (1 × 1) superstructure can be observed as presented on the inset in the Fig. 5. In this case (1 × 1), superstructure is accompanied by the presence of small bright areas, which can be attributed to early stages of Ti$_2$O$_3$ formation on TiO$_2$(1 1 0)-(1 × 1) surface. On the regions of the surface, which are completely reduced, no images with high resolutions could be collected. Even though atomic resolution
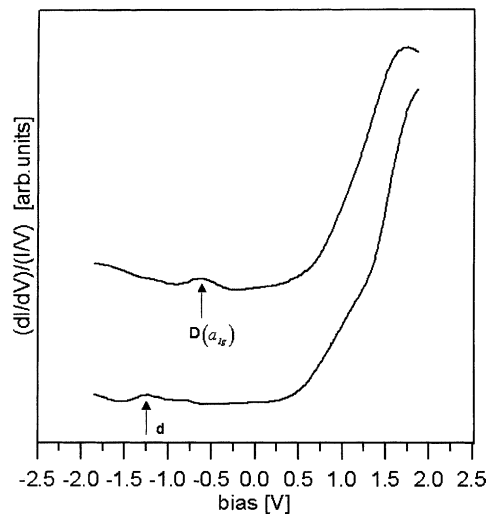

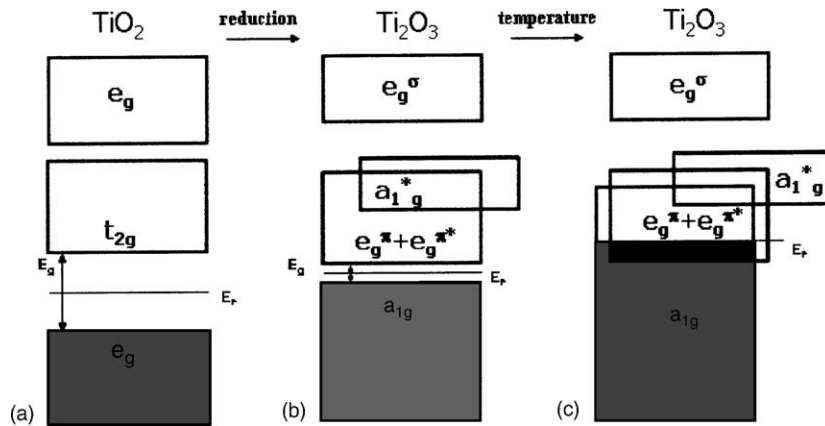Fig. 6. The (dI/dV)/(I/V) curves recorded at two different spatial positions on the lightly reduced TiO$_2$(1 1 0) surface.

Fig. 7. Bands energy diagrams for (a) TiO_2; (b) Ti_2O_3; and (c) Ti_2O_3 above I–M phase transition.

was not achieved steps and terraces are well visible (Fig. 5). It helped us to record tunnelling spectra far from the step edges, which influence local electronic structure.

4. Scanning tunnelling spectroscopy results

The $(dI/dV)/(I/V)$ spectra recorded at room temperature on lightly reduced $TiO_2(1\ 1\ 0)$ surface (see Fig. 1 for topography) are presented in Fig. 6. The
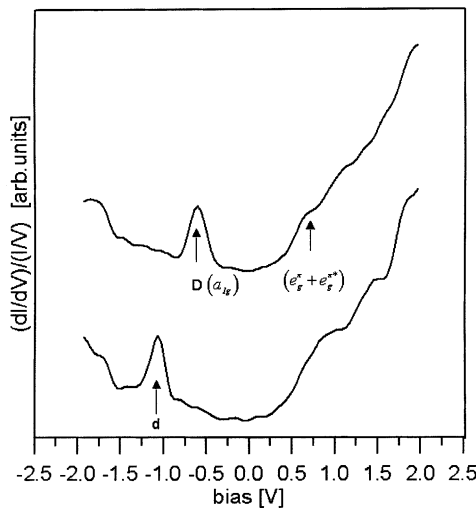
figure shows clearly two surface states located below the Fermi level, i.e. d and D surface states (herewith we use Heise and Courths [6] notation). The observed states are the extrinsic surface states caused by the presence of defects considered in terms of oxygen vacancies and formation of Ti^{3+} ions on the reduced $TiO_2(1\ 1\ 0)$ surface. As was shown in [5], the origin of the d state can be attributed to the presence of high density of Ti^{3+} ions which start to interact with each other and give rise to the formation of the Ti^{3+} pairs. This process is interpreted in terms of the surface phase transition. The D state starts to appear when the density of Ti^{3+} pairs increases, and small areas of Ti_2O_3 on the surface are formed [5,6]. The surface

Fig. 8. The $(dI/dV)/(I/V)$ curves recorded at two different spatial positions on the heavily reduced $TiO_2(1\ 1\ 0)$ surface.
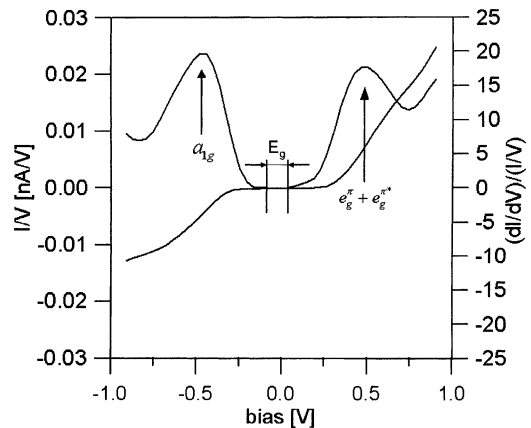

Fig. 9. The I/V curve and its normalized form $(dI/dV)/(I/V)$ recorded at low energy range.

phase transition from TiO_2 towards Ti_2O_3 is accompanied by a change in the electronic structure as presented in Fig. 7a and b.

The tunnelling spectra recorded on heavily reduced TiO_2(1 1 0) surface (see Fig. 5 for topography) are presented in Fig. 8. When comparing these spectra with the spectra recorded on lightly reduced surface (Fig. 6), we conclude that energetic positions of the d and D states agree. It is also clearly seen that the amplitudes of the d and D states on heavily reduced surface are much higher then the amplitudes measured on lightly reduced surface—it is caused by larger number of defects in this sample. Furthermore, on

heavily reduced sample, the D state was observed more frequently in comparison with d state.

In our measurements, the D state has the same energy (0.6 eV below the Fermi level) as the energy of the valence band edge (a_{1g} in pure Ti_2O_3 [14]. Thus, the D state and a_{1g} band edge state are the same states, i.e. $D \equiv a_{1g}$ (Fig. 7b). Since, Ti_2O_3 is treated as a insulator with small energy gap between the valence and the conductance band edges then the $D \equiv a_{1g}$ state should be accompanied by the presence of a symmetrically located state at the unoccupied part of the spectra which can be ascribed to the presence of the edge of the conductance band, i.e. $e_g^{\pi} + e_g^{\pi*}$ state. This
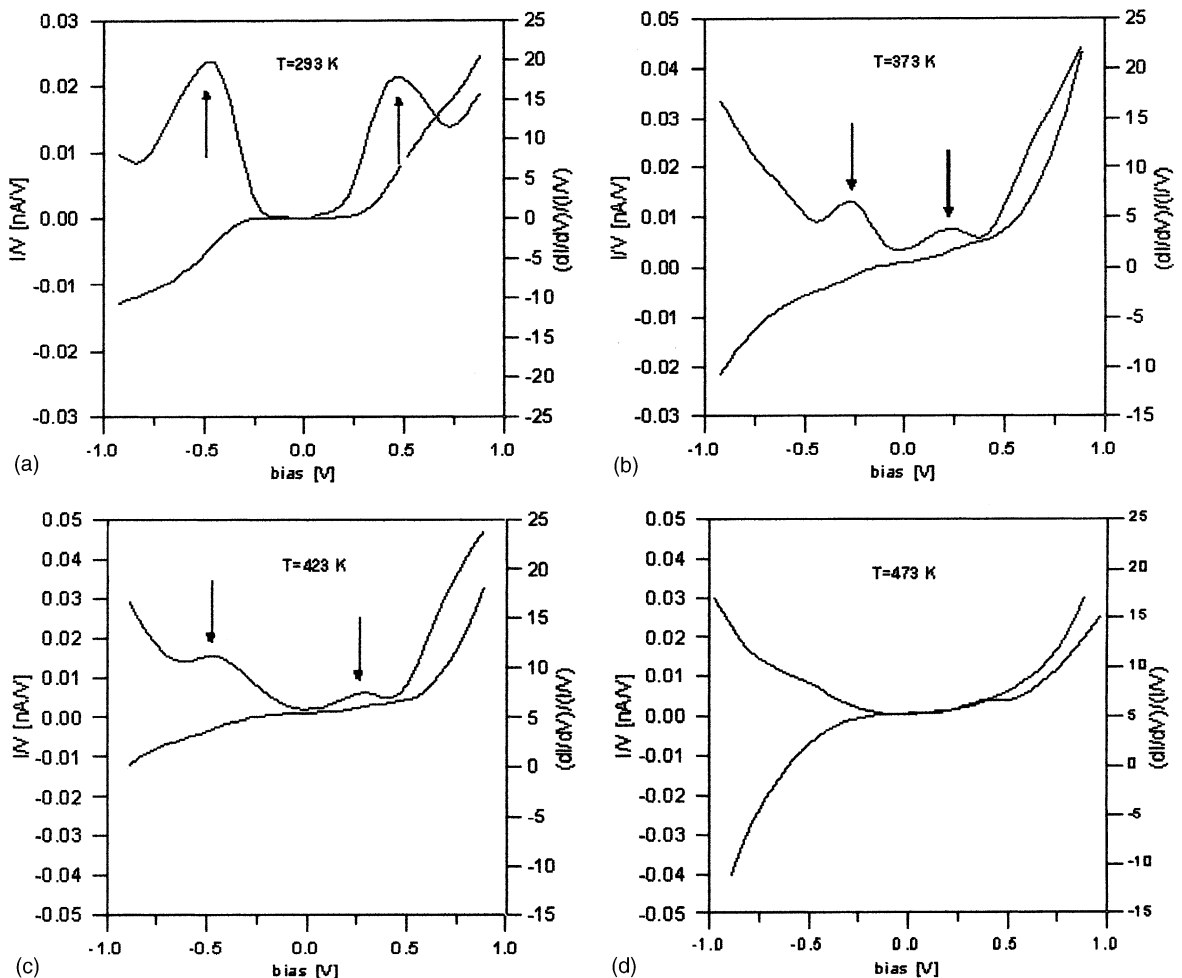

Fig. 10. The I/V curve and its normalized form (dI/dV)/(I/V) recorded at (a) 293 K; (b) 393 K; (c) 423 K; and (d) 473 K on the TiO_2(1 1 0) surface.

can especially be seen from Fig. 9 in which we present the *I/V* curve and its normalized form recorded in the lower energy range where the energy gap, the valence band edge (a_{1g}), and the conductance band edge ($e_g^\pi + e_g^{\pi*}$) are well pronounced (see also Fig. 7b for bands description). Especially, it is possible to estimate the width of the band gap, which is 0.1 eV. This value agrees very well with the theoretical calculations based upon the Mott–Hubbard regime giving $E_g = 0.098$ eV for 300 K [10]. This result clearly shows that we are dealing with Ti_2O_3 regions on the reduced $TiO_2(1\,1\,0)$ surface [15]. It should be mentioned here that the tip-induced band bending effect can be neglected in our experiments. This effect is large only in the case of small number of charge carriers, which is not the case with the heavily reduced TiO_2 crystal.

Finally, in Fig. 10, we present the *I/V* curves and their normalized form (d*I*/d*V*)/(*I/V*) recorded on heavily reduced $TiO_2(1\,1\,0)$ surface at four temperatures: 293; 393; 423 and 473 K. It is clearly seen the disappearance of the energy gap accompanied by substantial decreasing of amplitude of the band edge states (a_{1g}, $e_g^\pi + e_g^{\pi*}$) with increasing temperature. It indicates smooth insulator–metal transition, which takes place on the surface. As was observed the disappearance of the energetic gap was completely reversible and it appeared when the temperature was lowered. As was shown in [8,10], the I–M transition in Ti_2O_3 can be explained by the competition between electron–electron correlation energy and electron-band entropy at elevated temperatures. As a result, the a_{1g} and $e_g^\pi + e_g^{\pi*}$ bands overlap producing smooth transition with no change in crystal symmetry. Sketch of the Ti_2O_3 bands model above the I–M transition is shown in Fig. 7c. This clearly explains the disappearance of the energetic gap on high temperature-tunnelling spectroscopy measurements presented in Fig. 10.

5. Conclusions

We have studied the electronic structure of the heavily reduced $TiO_2(1\,1\,0)$ surface by scanning tunnelling spectroscopy. At the occupied part of the spectra, we found the presence of a surface state at energy of about 1.1 eV below the Fermi level (d surface state). The presence of the d state is ascribed to the appearance of Ti^{3+} pairs. When the density of Ti^{3+} pairs increases, and small areas of Ti_2O_3 on the surface are formed a new surface state starts to appear (D surface state). The energy of the D state is about 0.6 eV below the Fermi level and is related to the presence of the valence band edge in Ti_2O_3. At the unoccupied part of the spectra, we found the presence of a surface state at energy of about 0.6 eV above the Fermi level. This state is ascribed to the conductance band edge in Ti_2O_3. The result obtained clearly shows that we are dealing with Ti_2O_3 regions on the reduced $TiO_2(1\,1\,0)$ surface.

High temperature spectroscopy measurements recorded on the $TiO_2(1\,1\,0)$ surface which contains Ti_2O_3 regions showed disappearance of the energy gap accompanied by substantial decreasing of amplitude of the band edge states with increasing temperature. It indicates smooth insulator–metal transition caused by bands overlap in Ti_2O_3, which takes place at elevated temperatures.

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