Scanning tunnelling microscopy and current imaging tunnelling spectroscopy were used to study the topographic and electronic structure of a reduced TiO$_2$(100) surface. The STM results showed that the TiO$_2$(100) surface is capable to form (1×7) reconstruction which can transform to (1×3) reconstruction due to reoxidation of the surface. The CITS results showed that the (1×7) reconstruction is much more metallic in compared to the (1×3) reconstruction showing pronounced surface states at energy 1.3 eV and 0.8 eV below the Fermi level and at energy 1.0–1.2 eV above the Fermi level.

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**Abstract**

Scanning tunnelling microscopy and current imaging tunnelling spectroscopy were used to study the topographic and electronic structure of a reduced TiO$_2$(100) surface. The STM results showed that the TiO$_2$(100) surface is capable to form (1×7) reconstruction which can transform to (1×3) reconstruction due to reoxidation of the surface. The CITS results showed that the (1×7) reconstruction is much more metallic in compared to the (1×3) reconstruction showing pronounced surface states at energy 1.3 eV and 0.8 eV below the Fermi level and at energy 1.0–1.2 eV above the Fermi level.

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**Keywords:** Scanning tunnelling microscopy; Scanning tunnelling spectroscopy; Surface states; Titanium oxide

1. Introduction

It is widely recognized that the investigation of the rutile TiO$_2$(100) surface has received significantly less theoretical and experimental attention compared to that of the TiO$_2$(110) surface [1]. The structural investigations of TiO$_2$(100) plane were mainly focused on the description of the TiO$_2$(100)-(1×3) reconstruction based on the missing row model [2], the microfacet model [3], microfacet relaxed models [4,5], and the model with transition between the (1×1) and (1×3) terminations, considered in terms of the existence of the intermediate (1×3)-α and (1×3)-β microfacet phases [6–8]. Even though, grazing incidence X-ray diffraction (GIXD) [3], scanning tunnelling microscopy (STM) [7–11], non-contact atomic force microscopy (NC-AFM) [6] and electron-stimulated desorption ion angular distribution (ESDIAD) [12] results pointed to the applicability of the microfacet models, it is still uncertain which particular model describes the exact surface geometry. Furthermore, the application of the ‘direct methods’ to the GIXD data led to a much different atomistic model of the TiO$_2$(100)-(1×3) reconstruction than that predicted by the microfacet models [13]. In this context some LEED observations [14,15] show that unlike the TiO$_2$(110) plane, the TiO$_2$(100) surface is capable to form higher i.e. (1×5) and (1×7) reconstructions. However, as has been pointed out the observed LEED patterns could be misinterpreted as (1×5) and (1×7) reconstructions, due to the presence of steps on the vicinal TiO$_2$(100) surface [2,11].

This brief literature review presented, clearly shows that the TiO$_2$(100) surface requires further theoretical and experimental studies. The goal of this study was to use scanning tunnelling microscopy to obtain topographic information from real space on the surface subjected to different preparation treatments in order to answer the question whether TiO$_2$(100) surface is capable of forming reconstructions higher than (1×3). Furthermore we are interested in identifying the electronic structure of the
observed reconstructions (if they exist) in terms of the electron local density of states (LDOS) using current imaging tunnelling spectroscopy (CITS). The results obtained will lead to a better understanding of the morphology and electronic structure of the reduced TiO\(_2\)(100) surface.

2. Experimental

The STM/CITS experiments were performed with a commercial VT-STM/AFM system in UHV condition (Omicron GmbH, Germany). The scanner in the \(X\) and \(Y\) directions was calibrated using Si(111)-(7 \(\times\) 7) and HOPG(0001) samples. Au(111) surface with steps and HOPG(0001) surfaces with thermally etched [16] and hydrogen etched [17] monolayer pits were used to calibrate the \(Z\)-scale of the scanner. The tips used were prepared by mechanical cutting from the 90\%Pt–10\%Ir alloy wires (Goodfellow) and electrochemical etching of the W wires (Goodfellow). In CITS mode, the \(I/V\) curves were recorded simultaneously with a constant current image by the use of a interrupted-feed-back-loop technique. 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 where the differential conductance is divided by the total conductance—\((dI/dV)/(I/V)\). The divergence problem in the case of \((dI/dV)/(I/V)\) was overcome by applying some amount of broadening \((\Delta V)\) to the \(I/V\) values [18]. In all our cases \(\Delta V = 2\) V value was chosen. The reduced TiO\(_2\)(100) surface (Pi-Kem, UK) was prepared using repeated cycles of Ar\(^+\) ion sputtering and annealing.

3. Results and discussion

The originally reduced TiO\(_2\)(100) surface (deep blue colour of the sample) was sputtered with Ar\(^+\) ions at room temperature (energy = 1.5 keV, \(t = 15\) min, current 12 \(\mu\)A, angle between surface and ions beam = 30\(^\circ\)) and subjected to subsequent heating for 30 min at 1073 K. After 2–3 sputtering/heating cycles the surface revealed the presence of well-ordered bright rows separated by an average distance of 3.16 nm and parallel to the [001] direction as presented in Fig. 1a. The height of the observed rows varies from 0.19 nm up to 0.52 nm as measured from the STM profile. The STM image was recorded at a positive sample bias of 2 V (tunnelling current set point 1 nA) i.e. the lower

![Fig. 1. (a) 69 nm \(\times\) 69 nm STM image of TiO\(_2\)(100)-(1 \(\times\) 7) surface, (b) 68 nm \(\times\) 68 nm STM image of TiO\(_2\)(100) surface where (1 \(\times\) 7) and (1 \(\times\) 3) reconstructions coexist, (c) 68 nm \(\times\) 68 nm STM image of TiO\(_2\)(100)-(1 \(\times\) 3) surface, (d) the \(I/V\) curves recorded over (1 \(\times\) 7) and (1 \(\times\) 3) reconstructions.](image-url)
conductance band of the TiO$_2$ was probed. However, it should be mentioned that STM images were also reproducible for the positive sample bias much less than 1 V. The measured average distance of 3.16 nm between the bright rows shown in Fig. 1a is very close to the theoretical larger side of the 1×7 unit cell of the TiO$_2$(100) surface which equals 3.21 nm. We ascribe the observed topography to the occurrence of (1×7) reconstruction on the TiO$_2$(100) surface. On the surface with the (1×7) reconstruction it was sporadically possible to observe bright rows separated by the average distance of 1.48 nm—see Fig. 1b. These rows are ascribed to early stages of formation of the (1×3) reconstruction—the theoretical larger side of the 1×3 unit cell of the TiO$_2$(100) surface equals 1.38 nm.

In Fig. 1c we present a typical STM image recorded after a long-term (7 h) heat treatment in UHV conditions at 1073 K. The image shows bright rows parallel to the [001] direction running along the terraces. The average distance between the rows equals 1.34 nm, which is typical for the (1×3) reconstruction. No bright rows with periodicity higher than 1.34 nm were observed. The height of the observed rows varies from 0.15 nm up to 0.27 nm as measured from the STM profile. Further heating of the sample for another 7 h at 1073 K made the surface smoother and well ordered—similar STM results were presented elsewhere [9–11].

The average $I/V$ curve obtained from several spectra recorded over the TiO$_2$(100)-(1×7) region is presented in Fig. 1d and shows a slightly asymmetric shape; the tunneling current being higher for the positive polarization of the sample than for the negative voltage of the same value. The $I/V$ curve recorded over the TiO$_2$(100)-(1×3) region is also presented in Fig. 1d. It is clearly observed that the curve shows distinct suppression of the tunneling current at negative bias, which is typical for n-type semiconducting materials.

An illustrative way of presenting spatially resolved spectroscopy data is to plot $(dI/dV)/(I/V)$ quantity as function of bias voltage and position along the surface. In Fig. 2 we show normalized conductance maps measured along the lines perpendicular to the rows on the surfaces with the (1×7) and (1×3) reconstructions together with appropriate topography cross-section profiles. It is easy to observe that in the case of (1×7) reconstruction, the conductance map shows distinct asymmetry between the occupied and the unoccupied states. At the occupied part we observe pronounced periodic maxima of LDOS (energy around 1.2 eV below the Fermi level) located on every second wall of the reconstruction. The presence of these periodic maxima means that the energy gap is not homogenous and strongly depends on position on the surface. In the case of (1×3) reconstruction pronounced periodic maxima of LDOS were not observed.

From the conductance maps it is also possible to extract individual $(dI/dV)/(I/V)$ curves as presented in Fig. 3 for positions denoted by lines #1–#8. In the case of (1×7) reconstruction the $(dI/dV)/(I/V)$ curves show an asymmetric shape and a small energy gap. However for the curve denoted by #5 it is easy to observe that LDOS around the Fermi level shows a rather parabolic shape with very small gap. Similar LDOS profiles have been recorded on semimetals like graphite [17]. Furthermore we observe the occurrence of surface states at energy of about 0.8 eV and 1.3 eV below the Fermi level. The observed states are ascribed to extrinsic surface states caused by the presence of defects considered in terms of oxygen vacancies and the formation of Ti$^{3+}$ ions on the reduced TiO$_2$(100) surface. The states with similar energy were observed previously by STS technique on the reduced TiO$_2$(100)
In the case of (1\times3) reconstruction the \((dI/dV)/(I/V)\) curves also show asymmetric shape, however energy gap is much higher. In this case we also observe a surface state at energy about 0.8 eV below the Fermi level, however the amplitude of this state is much lower in comparison with the amplitude observed for the (1\times7) reconstruction. At the unoccupied part of the spectra a pronounced state was observed at energy about 1.0–1.2 eV above the Fermi level for both (1\times3) and (1\times7) reconstructions. This state is also well seen on the conductance maps, especially for the (1\times3) reconstruction. In our interpretation the observed state can be ascribed to the presence of the edge of the conductance band in TiO₂.

Summing up, the spectroscopic results showed that the (1\times7) region is much more metallic in comparison with the (1\times3) region i.e. TiO₂(1\,0\,0) surface seems to be much more reduced when the (1\times7) reconstruction appears. In our experiments the highly reduced state of the surface changed towards the less reduced state by long-term annealing in vacuum (in our case at least 7 h at 1073 K). This was accompanied by a change of the surface reconstruction from (1\times7) to (1\times3) as observed by STM. We believe that reoxidation process [21,22] involving diffusion of the titanium cations in reduced oxidation state from the surface to the bulk can be responsible for phase change. However, it should be stressed that this assumption must be treated tentatively because further experimental evidences which link reoxidation process with phase change are required. Further experiments are in progress.

Unfortunately in the present paper we are not able to propose a comprehensive atomistic model of the (1\times7) reconstruction, which combines STM and CITS results. The simplest approach is to extend the existing microfacet model for (1\times3) reconstruction to the description of (1\times7) reconstruction. In this extended model the distance between the rows of the (1\times7) reconstruction should be

Fig. 3. (left): The \((dI/dV)/(I/V)\) curves for the (1\times7) reconstruction selected at different positions (#1–#8). The # positions are shown in Fig. 2. (right): The \((dI/dV)/(I/V)\) curves for the (1\times3) reconstructions selected at different positions (#1–#8). The # positions are shown in Fig. 2.
equal 3.216 nm, while the height of the observed rows equals 1.61 nm. In our STM experiments the distance between rows equals 3.16 nm, which is in good agreement with the extended microfacet model. Thus we can assume that we are dealing with (1 × 7) reconstruction. Unfortunately, the height of the observed rows varies from 0.19 nm up to 0.52 nm, which is far from the theoretical value of 1.61 nm. However it should be remembered that in contrast to the relaxed microfacet models \cite{6,7} all the microfacet models \cite{3,6–8} tend to overestimate the height of the rows in the case of (1 × 3) reconstruction where the measured value was much lower than the theoretical value predicted by the microfacet model \cite{9,11}. Also in our present measurements the height of the rows in the case of (1 × 3) reconstruction is much lower than predicted by the microfacet model, even though the distance between rows is close to the theoretical value. As a result it seems that only the fully relaxed microfacet model of (1 × 3) reconstruction can be extended to the (1 × 7) reconstruction to provide the ultimate answer about height of the observed rows. Furthermore based on the extended relaxed microfacet model theoretical simulation of the STM image is required to allow a full comparison with the experimental data. This is because STM does not show atomic structure in crystallographic sense; hence estimation of the height of the observed rows is strongly affected by their electronic structure. Much research needs to be done to clarify the influence of local electronic structure on the height measurements in STM technique, particularly in the case of (1 × 3) and (1 × 7) reconstructions on the TiO$_2$(100) surface.

4. Conclusions

In summary, we have studied the topographic and electronic structure of the reduced TiO$_2$(100) surface by STM/CITS. We found that heating of the sample for 30 min at 1073 K created (1 × 7) reconstruction on the surface. Father heating at least for 7 h at 1073 K changed (1 × 7) reconstruction towards (1 × 3) reconstruction. Reoxidation process has been taken tentatively into consideration to explain the observed phase change. It is proved that (1 × 7) reconstruction is much more metallic in comparison with the (1 × 3) reconstruction and shows pronounced surface states at 1.3 eV and 0.8 eV below the Fermi level. The observed states are ascribed to existence extrinsic surface states caused by formation of Ti$^{3+}$ ions on the reduced TiO$_2$(100) surface. The observed state at energy about 1.0–1.2 eV above the Fermi level is ascribed to the edge of the conductance band in TiO$_2$.

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