

Defects at the $\text{TiO}_2(100)$ surface probed by resonant photoelectron diffraction

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Available online 12 April 2007

Abstract

We report photoelectron diffraction (PED) experiments of weakly sub-stoichiometric $\text{TiO}_2(100)$ rutile surfaces. Apart from standard core-level PED from the Ti-2p_{3/2} line, we have studied valence band PED from the defect induced Ti-3d states in the insulating band gap. For maximum yield, the latter were resonantly excited at the Ti-2p absorption edge. The PED patterns have been analyzed within the forward scattering approximation as well as by comparison with simulated PED patterns obtained in multiple scattering calculations. The analysis shows that the defect induced Ti-3d charge is mainly located on the second layer Ti atoms.

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Keywords: Titanium dioxide; Surface defects; Photoelectron diffraction; Resonant photoemission

1. Introduction

The (110) surface of rutile TiO_2 is often considered as a model system for oxide surfaces and has been studied extensively [1]. The (100) surface is much less well understood. Upon reduction of TiO_2 a peak appears in the band gap of the valence band photoemission (PE) spectrum. This defect peak is due to the filling of Ti-3d states and thus a signature of Ti^{3+} ions [1]. The peak intensity can be used to monitor the surface defect concentration. For the present sample, the defect peak was below noise level in a *non-resonant* PE experiment. From this, an upper bound of about 4% can be given for the surface defect concentration.

Photoelectron diffraction (PED) from core-levels is a powerful technique for determining structural properties of single crystal surfaces. Hardman et al. reported an extensive core-level PED study on $\text{TiO}_2(100)$ and found that the PED patterns are “insensitive to the details of the surface

structure” [3]. The main purpose of this work is to gain some insight into the electronic structure of the defect states. Since the defect state is the HOMO of the surface, it plays an important role in the surface chemistry. While the defect state at the $\text{TiO}_2(110)$ surface has received much attention recently [2], very little is known in the case of the (100) surface. In order to probe the defect states directly, we have performed *valence band* PED from the defect state. In off-resonance conditions, the photocurrent from this state is, however, too low for PED. Therefore, we have performed a *resonant* PED experiment using synchrotron radiation. The photon energy was tuned to the Ti $L_{2,3}$ absorption edges. This enhances the defect peak intensity by up to two orders of magnitude [4]. From the analysis of the PED patterns we conclude that the defect charge is mainly located on second layer Ti atoms.

2. Experimental

The experiments were carried out at the ALOISA beamline [5] of the Elettra Synchrotron Light Source in Trieste,

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Italy. The radiation was impinging in grazing incidence ($\sim 6^\circ$). Rotations of both the electron analyzer and the sample allow sweeping the electron emission direction with an angular resolution of 1° both in polar angle θ and azimuthal angle ϕ . We define ϕ with respect to the [001] direction. The PED patterns were taken by scanning ϕ over 120° including both symmetry directions [001] and [010]. The polar angle was varied from -2° to 65° . The step size was 2° for both θ and ϕ . The PED patterns were then folded according to the C_{2v} point symmetry of the $\text{TiO}_2(100)$ surface. They are reported as χ -functions, where $\chi(\theta, \phi) = (I(\theta, \phi) - I_0(\theta))/I_0(\theta)$. Here, $I(\theta, \phi)$ is the absolute intensity of the photocurrent and $I_0(\theta)$ a smooth background obtained by polynomial fitting of the azimuthal average of $I(\theta, \phi)$. The photon energy for Ti 2p detection ($h\nu = 920$ eV) was chosen such that the photoelectrons have nearly the same kinetic energy (460 eV) as the electrons coming from the defect peak in the Ti 2p–3d resonant PED experiment. The kinetic energy of the Ti-3d electrons is fixed by the resonance condition which is fulfilled, at the L2-edge, for a photon energy around 458 eV [4]. Since the kinetic energy is the same in both experiments, the escape depth is the same (about 1 nm) and the two PED patterns can be compared directly. The $\text{TiO}_2(100)$ crystal was cleaned by ion bombardment. The PED patterns recorded directly after the sputtering show little structuring which indicates a high degree of disorder. The sample was then annealed in several cycles under UHV. After annealing at 400°C , the patterns have developed clear structures, i.e. ordering of the surface has taken place. Subsequent annealings to 500 and 600°C hardly changed the PED results.

3. Results and discussion

Figs. 2 and 3 show the PED patterns for Ti-2p3/2 and resonant Ti-3d emission, respectively, obtained after annealing to 500°C . The Ti-2p3/2 PED compares well with the Ti $L_3M_{23}M_{23}$ Auger electron diffraction pattern reported by Hardman et al. [3] with a kinetic energy of 375 eV. The main difference is that the patterns in Ref. [3] are sharper, in particular in the small polar angle region ($\theta < 20^\circ$). This suggests that our sample had a somewhat higher degree of disorder than the sample in Ref. [3].

3.1. Forward scattering analysis

At sufficiently high kinetic energy (typically 1 keV) the intensity peaks on PED patterns are found around the near neighbor forward scattering directions. As shown in Ref. [3], this also holds for Ti-2p PED of $\text{TiO}_2(100)$ with a kinetic energy of 787 eV. As the kinetic energy decreases, the PED peaks deviate more and more from the forward scattering directions, since the focussing effect of the individual scattering events is reduced and multiple scattering becomes more important. When keeping in mind its limitations, the forward scattering analysis is valuable as a first qualitative approach even for rather low kinetic energies

such as used here (460 eV). The first few relevant near neighbor Ti–Ti and Ti–O directions are listed in Table 1. They are given for the bulk terminated surface as well as taking into account atomic relaxation as predicted by first principle calculations [6]. For the labeling of the atoms, see Fig. 1. The relaxed directions are marked as crosses in Figs. 2 and 3.

Looking first at the Ti-2p PED pattern, it can be seen that the directions 1, 2' and 5 agree well the observed intensity peaks (bright spots). There is still a fair agreement for directions 3 and 4 or 4'. For the direction marked as N, no assignment was found. Direction No 2 (first near neighbor pair Ti–O1) fits well to the spot at 2' if the unrelaxed direction is used (see Table 1). This can be understood by the fact that all but the surface layer Ti–O pairs are virtually unrelaxed. Although the agreement between forward scattering directions and observed PED is far from perfect, this simple analysis allowed us to assign most bright spots to near neighbor forward scattering events.

The resonant Ti-3d PED pattern is shown in Fig. 3. It has a much simpler structure than the Ti-2p pattern, but many features are similar. In particular, three out of the five main spots of the Ti-2p PED, namely the spots found near 1, 2' and 4' are also found on the Ti-3d PED. The agreement of these spots with the forward scattering direc-

Table 1
Relevant interatomic directions from Ti atoms in the first three surface layers

Atoms	R	θ	ϕ	θ_r	ϕ_r	Label
Ti2–Ti1	3.57	49.9	57.2			1
Ti1–O1	1.95	62.6	31.2	57.4	17.8	2
Ti2–Ti1'	5.50	65.3	27.4			2'
Ti3–Ti1'	5.46	32.8	0.	33.0	2.1	3
Ti2–O2	1.98	45.0	90.	42.2	90.	4
Ti2–O1	3.49	23.7	90.	27.8	90.	4'
Ti2–O2'	3.49	66.3	90.			5

R is the bond length in Å, angles are given in degree. R , θ and ϕ correspond to the bulk-terminated surface, and θ_r and ϕ_r to the relaxed surface [6]. Where θ_r and ϕ_r are not given the deviation from θ and ϕ is less than 2° for both angles.

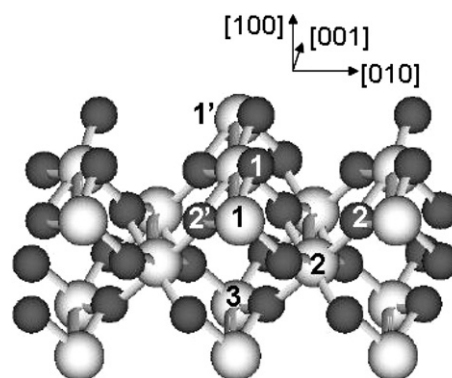


Fig. 1. Ball and stick model of the $\text{TiO}_2(100)$ surface with Ti as big bright balls and O as small dark balls.

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