

Structure, stability, and phase transitions of the anatase TiO_2 (101) surface

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(August 23, 1999)

The (101) surface of anatase TiO_2 was studied for the first time by both secondary electron imaging and low-energy electron diffraction. We have observed a surface phase transition in real space from tetragonal anatase to face-centered cubic titanium monoxide TiO , caused by mild sputtering with 500-eV Ne^+ ions. Subsequent annealing at 900 K restores the anatase structure at the surface, which is found to be bulk terminated. These observations demonstrate the remarkable thermodynamic stability of anatase compared to its more common polymorph rutile and opens thus the way to investigate clean surfaces of this technologically important form of TiO_2 .

PACS: 68.35.Bs, 81.05.Je, 81.65.Cf, 61.14.-x, 61.50.Ks

The wide-bandgap semiconductor TiO_2 mainly exists in two polymorphic phases, anatase and rutile, which crystallize both in a tetragonal lattice. Their structure can be described in terms of chains of TiO_6 octahedra which are more distorted and differently interconnected in anatase than in rutile [1], resulting in significantly different unit cells and different physical and chemical behavior [2]. So far, only surface properties of rutile are investigated [3], because it is considered to be the thermodynamically stable form of TiO_2 . It is anatase, however, that plays a crucial role in a number of charge-separating devices, like dye-sensitized solar cells [4] or rocking-chair lithium batteries [5]. These devices are based on highly porous films with very large surface areas that consist of nano-crystalline anatase mainly exhibiting the (101) face. Although they show a remarkable performance, fundamental understanding of surface processes, like dye adsorption or charge transfer, is still deficient. Anatase is considered to be stable in pure form only for nanometer-sized crystallites [6], and due to the lack of suitably large and pure single crystals, investigations on specific surfaces are missing [7]. The different behavior of anatase surfaces compared to that of rutile, e.g., in terms of molecular adsorption [8], could hence only be deduced making the assumption of a perfect surface termination of the bulk anatase lattice.

In this Letter, we report the first successful imaging of the surface lattice of TiO_2 single crystals in the anatase structure by secondary-electron imaging (SEI) and low-energy electron diffraction (LEED), respectively. The measurements were done on samples prepared in mm size by a chemical transport reaction [9]. We have observed a structural transition from tetragonal anatase to face-centered cubic (fcc) titanium monoxide induced by preferential sputtering of oxygen as a result of bombardment of the (101) surface with Ne^+ ions (500 eV; 10^{-7} A/mm²) during 5 minutes. Subsequent annealing at 900 K restored the tetragonal anatase structure owing to a bulk-assisted reoxidation of the surface [10]. This cycle can be

repeated reproducibly, demonstrating the extraordinary stability of the anatase structure even after its complete destruction. After the sputtering-annealing process, very sharp LEED patterns of a bulk-terminated (101) surface can be observed, which are, to our knowledge, the first ever obtained for anatase TiO_2 . Earlier attempts to investigate naturally-grown anatase using LEED have failed due to surface contaminations [11].

SEI uses the same experimental setup as the LEED technique, the main difference being the energy of the primary electrons [12]. It records the backscattered (secondary) electrons generated with primary electrons having an energy near 2 keV. It is a method for obtaining real-space information about the local geometric arrangement of atoms near a surface and is therefore complementary to the reciprocal-space information accessible in LEED. Direct-projection imaging of the interatomic directions, produced by the forward-focusing effect in electron-atom scattering, is responsible for the formation of the SEI pattern. Images can be recorded while the sample is rotated, which provides three-dimensional views of the structure. For a structural transition, as reported here, SEI allows the correspondence of the high-symmetry axes of these structures to be identified, from which the relative orientation of the initial and final structures can readily be determined [13]. While LEED is extremely sensitive to changes in the surface atomic structure owing to the short mean free path of the 30-400-eV electrons, SEI furnishes information on the first 10-20 atomic layers of the surface. Thus successful imaging is possible with SEI even when the surface atomic layer is disordered or contaminated [11].

Anatase single crystals were grown from the gas phase by a chemical transport reaction as described earlier [9]. The transparent and colorless crystals ordinarily have a truncated bipyramidal habitus exhibiting mainly the (101) and (001) faces as confirmed by Laue x-ray diffraction. They have surface areas between 1 and 4 mm², and atomic-force microscopy revealed that the corrugation of

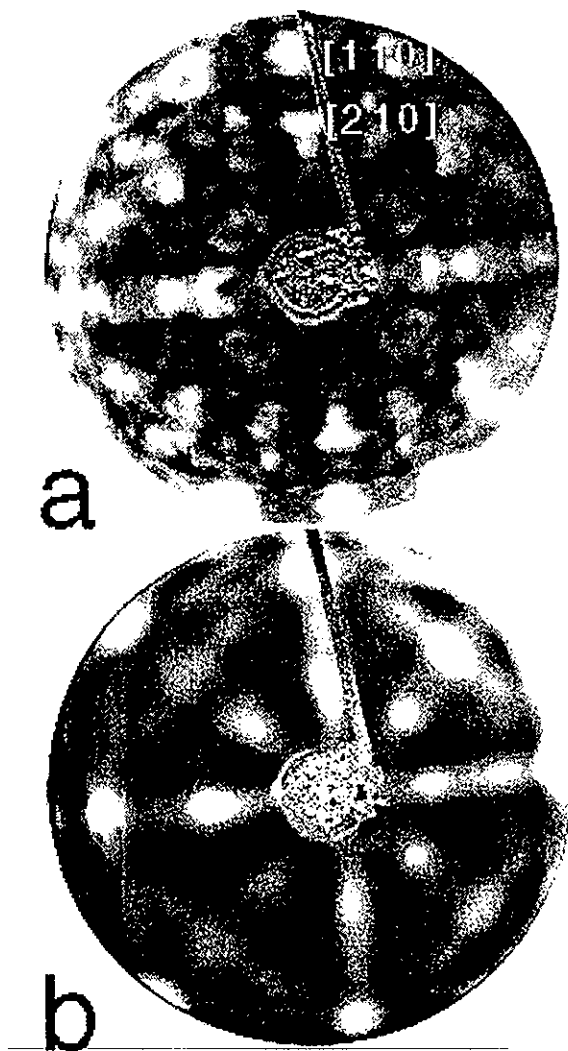


FIG. 1. Secondary-electron patterns obtained from the anatase surface. (a) before, (b) after sputtering with 500-eV Ne^+ ions. The sample is tilted by 23° so that the primary electrons are incident along the $[100]$ direction. The central portion of the pattern is covered by the shadow of the electron gun used for the excitation.

the working surfaces was typically below 1 nm. One of the crystals investigated here was reductively doped in pure hydrogen at 800 K for 24 h, another one was left undoped. Both crystals were rinsed in water, ethanol, and acetone and contacted with silver glue to a copper plate in direct contact with an oven. The experiments were performed in an ultrahigh-vacuum chamber with a total pressure in the lower 10^{-10} -Torr range. Chemical information about the surface was obtained by Auger electron spectroscopy (AES). The electron energy was 101.7 eV for the LEED data reported here, 1000 eV for AES, and 2 keV for SEI.

Fig. 1(a) shows a secondary-electron pattern of the doped anatase crystal recorded directly before any in-situ treatment of the surface [14]. The primary-electron

beam is incident along the $[100]$ direction of the crystal, which coincides with the center of the display unit. This is achieved by turning away the (101) surface normal from the display axis by 23° . The twofold symmetry of the (100) surface of the tetragonal anatase is clearly detectable. The horizontal bright band corresponds to the (010) lattice plane of the anatase structure. The central vertical band on the display contains directions in the (001) plane that are above or below the (010) plane at a distance of approximately $\pm 27^\circ$ and $\pm 45^\circ$ from $[100]$. They can be identified as belonging to $\langle 210 \rangle$ and the $\langle 110 \rangle$ directions, respectively. The bright spot, 23° to the left of the electron gun, corresponds to the (101) surface normal of the crystal. Other salient features can be assigned to different symmetry directions of the anatase lattice. These results are in good agreement with the earlier investigation [11], and imply that the positions of the atoms in a near-surface region do not deviate from the bulk values, i.e., the crystalline structure is flawless and not reconstructed within the inelastic mean free path of 2-keV electrons. Still, LEED patterns could not be observed for any of the crystals at this stage of the experiment. However, the near-perfect contrast quality of the pattern, without any cleaning process of the surface, leads to the conclusion that the structurally damaged and/or contaminated surface layer that is involved in LEED is confined to an atomically thin surface layer.

Cleaning of transition-metal oxide surfaces by ion bombardment is known to lead to the preferential removal of oxygen and, therefore, to a modification of the surface composition [15]. Attempts to produce atomically flat and clean surfaces on naturally-grown anatase by sputtering (500-eV He^+ ions for 15 minutes) failed in a previous experiment due to the destruction of the surface atomic order [11]. The SEI patterns smeared out and could not be restored even after a heat treatment at 500 K and exposure of the surface to oxygen up to 1000 Langmuirs (1 Langmuir $\equiv 10^{-6}$ Torr-s). A similar problem was encountered with our vapor-phase grown anatase already after sputtering for only 30 s with 500-eV Ne^+ ions. The SEI pattern became diffuse, but still showed twofold symmetry around the (010) plane. However, after continuing the sputtering for 5 minutes, this symmetry changed to fourfold (*cf.* Fig. 1(b)). Viewed along the $[100]$ direction one recognizes a highly symmetrical cross with the horizontal band still being the (010) and the vertical band the (001) plane. In the middle of these two bands, other bands corresponding to the (011) and $(0\bar{1}1)$ planes can be identified. Tilting the crystal around the $[010]$ direction, one detects bright patches at angles of 45° and 90° to the $[100]$ direction, signalling the $[101]$ and $[001]$ directions, respectively. All these features are characteristic of a cubic crystal. Calculations of the central projection for an fcc crystal sustain this conclusion. The only cubic phase in the binary titanium-oxygen

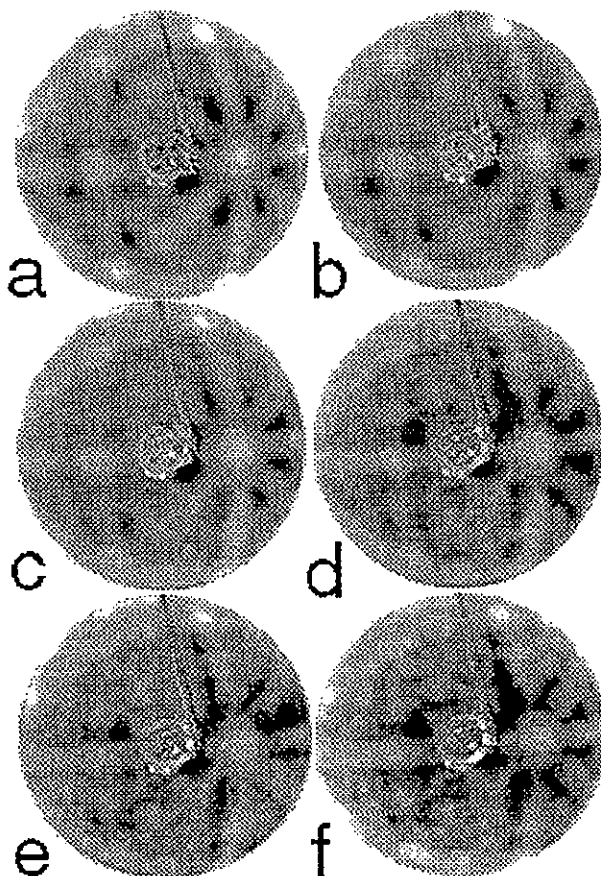


FIG. 2. Secondary-electron patterns of the ion-bombarded (101) surface with electrons incidence normal to the (101) surface of anatase. Image (a) was taken before annealing, (b)–(e) during annealing at 900 K at subsequent 2-min intervals and (f) after annealing and cooling down of the sample.

system is titanium(II)-monoxide, which has a defective rocksalt structure with up to 15% random Ti and O vacancies [16]. Apparently, the preferential sputtering is so effective that it leads to a phase transformation into this epitaxial fcc structure, which is still remarkably well ordered. AES confirmed this conclusion by showing a significant decrease of the oxygen signal. For rutile, this effect is less pronounced. In contrast to our findings, even prolonged sputtering of this polymorph with 500-eV Ar^+ results only in a transformation to titanium(III)-oxide, Ti_2O_3 [15]. A photoemission investigation revealed that intense sputtering of rutile partially changes the chemical state of the titanium atoms from Ti(IV) to Ti(III) or to Ti(II), but even after bombardment with 10-keV Ar^+ , the fraction of Ti(II) is only about one third [17].

Since the structural order in the near-surface region of the crystal was obviously disturbed by sputtering, broad bands rather than distinct sharp patches appeared on the SEI pattern. To restore structural perfection, the crystal was heated up to 900 K. The effect of this subsequent annealing of the ion-bombarded surface is shown by the sequence of secondary-electron patterns in Fig. 2. The

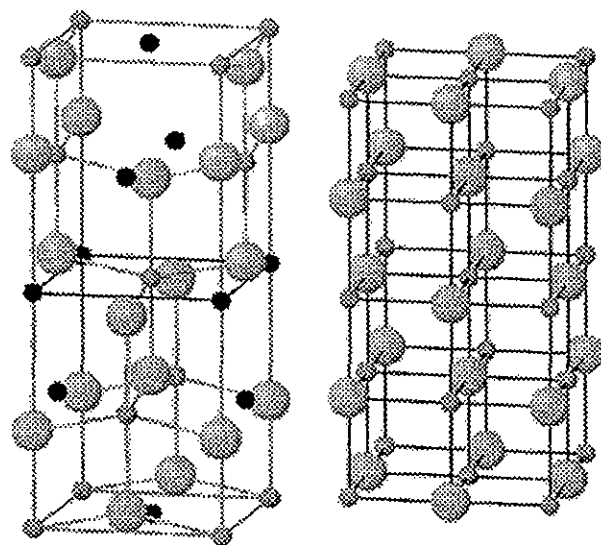


FIG. 3. (a) The unit cell of anatase TiO_2 with octahedral interstitial sites indicated in black and (b) twice the unit cell of titanium monoxide TiO . Titanium: small spheres; oxygen: large spheres.

crystal is tilted by approximately 23° with respect to its position in Fig. 1, so that the primary-electron beam is now incident perpendicular to the sample surface. The pattern in Fig. 2(a) was taken directly after sputtering. Each successive pattern was obtained after annealing for additional 2-min increments. The differences between successive patterns are quite small, but one can still recognize the change of the fourfold symmetry around the [100] axis (located at the right-hand side of the display center) to the more complex pattern possessing twofold symmetry of the original anatase. More clearly detectable is the transition by observing the disappearance of the symmetric [101] pattern of the cubic crystal approximately 22° to the left of the center in Fig. 2(a). The surface of the crystal eventually coincides again with a (101) face of anatase. Upon completing the annealing, AES shows that the chemical composition of the surface is restored. Recent experiments on rutile indicate that reoxidation of the surface layers proceeds via diffusion of Ti cations from the surface to the bulk at elevated temperatures [10].

A comparison of the anatase and the rocksalt structure of titanium monoxide is shown in Fig. 3. The structure of anatase is conceivable as a closed packing of large oxygen atoms with titanium atoms in every second octahedral interstitial site in a zig-zag alignment. Every titanium atom is thus surrounded by an oxygen octahedron. The atoms have pronounced ionic character, resulting in a strong crystal field that distorts the octahedra [1]. The resulting structure of the unit cell is shown in Fig. 3(a). Removal of every second oxygen atom or, equivalently, filling every interstitial site with a titanium atom leads directly to the structure shown in Fig. 3(b). Again, each

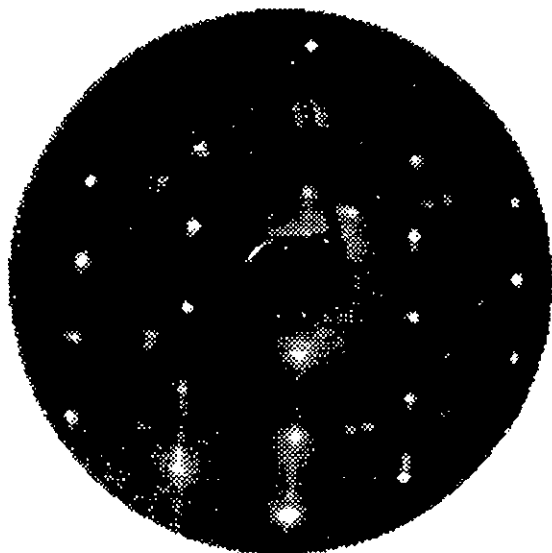


FIG. 4. LEED pattern of the sputtered and annealed (101) surface of anatase, recorded at 101.7 eV.

titanium atom is surrounded by an oxygen octahedron, but in this case, because of the highly symmetric distribution of titanium atoms, no distortion takes place. This leads to an fcc lattice. There is a slight change in the interatomic distances during this transition. The value for the a axis is 3.78 Å for anatase and 4.17 Å for titanium monoxide, the latter value decreasing with increasing oxygen content, i.e., with the stoichiometry closer to anatase [18]. For the c axis, which corresponds to twice the a axis in the cubic lattice, the values are 9.51 Å and $2 \times 4.17 = 8.34$ Å, respectively. Although not apparent at first glance, this shows the close similarity between the two structures that facilitates the transition.

The definition of contrast in Fig. 2 improves continuously, indicating the gradual healing of structural defects. In fact, after the complete sputtering-annealing cycle, the entire surface, including the top layer, was so perfect and clean that LEED patterns could be generated from the anatase surface. Images with extremely sharp spots, as shown in Fig. 4, were taken from the undoped anatase crystal. Besides the definition of the spots, their symmetry shows that the surface structure is bulk terminated, i.e., the surface is not reconstructed. The surface lattice constants, calculated from the LEED pattern, equal the bulk values within an error limit of $\leq 1\%$. The (101) surface, the most stable face of anatase [19], is thus undistorted, similar to (110), the most stable face of rutile [20]. Speculations about the adsorption mechanism of molecules on the anatase (101) surface [21] can now be supported by this experimental finding.

In conclusion, we have observed a structural transition on an anatase (101) surface to titanium monoxide. This transformation is reversible and hence confirms the thermodynamical stability of anatase. More important, it presents for the first time the possibility to obtain clean

and structurally perfect anatase surfaces, thus opening the way for surface-specific investigations of adsorption and charge-transfer processes on anatase. This is demonstrated by LEED measurements, which showed a highly ordered and unreconstructed (101) surface.

This work was financially supported in part by the Swiss National Science Foundation.

- [1] A. Fahmi, C. Minot, B. Silvi, and M. Causa, *Phys. Rev. B* 47, 11 717 (1993).
- [2] M. Grätzel and F. P. Rotzinger, *Chem. Phys. Lett.* 118, 474 (1985); J. Augustynski, *J. Electrochim. Acta* 38, 43 (1993).
- [3] V. E. Henrich and P. A. Cox, *The surface science of metal oxides* (Cambridge University Press, Cambridge, 1994); D. A. Bonnell, *Prog. Surf. Sci.* 57, 187 (1998) and references therein.
- [4] B. O'Regan and M. Grätzel, *Nature* 353, 737 (1991).
- [5] S. Y. Huang, L. Kavan, I. Exnar, and M. Grätzel, *J. Electrochem. Soc.* 142, L142 (1995).
- [6] H. Zhang and J. F. Banfield, *J. Mater. Chem.* 8, 2073 (1998).
- [7] H. O. Finklea, *Semiconductor Electrodes* (Elsevier, Amsterdam, 1988).
- [8] A. Vittadini, A. Selloni, F. Rotzinger, and M. Grätzel, *Phys. Rev. Lett.* 81, 2954 (1998).
- [9] L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz, and H. J. Scheel, *J. Am. Chem. Soc.* 118, 6716 (1996).
- [10] M. A. Henderson, *Surf. Sci.* 419, 174 (1999).
- [11] V. Shklover *et al.*, *J. Sol. Stat. Chem.* 132, 60 (1997).
- [12] M. Erbudak, M. Hochstrasser, E. Wetli, and M. Zurkirch, *Surf. Rev. Lett.* 4, 179 (1997).
- [13] B. Bolliger, M. Erbudak, D. D. Vvedensky, M. Zurkirch, and A. R. Kortan, *Phys. Rev. Lett.* 80, 5369 (1998); *ibid.* 82, 763 (1999).
- [14] The undoped crystal produced identical patterns. Due to the high electron mobility in the conduction band, anatase samples obviously need not to be doped in order to prevent electrostatic charging of the samples.
- [15] V. Henrich, G. Dresselhaus, and H. J. Zeiger, *Phys. Rev. Lett.* 36, 1335 (1976).
- [16] A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1975).
- [17] D. Leinen, A. Fernandez, J. P. Espinos, and A. R. Gonzales-Elipe, *Appl. Phys. A* 63, 237 (1996).
- [18] J. Whitehead, *Encyclopedia of Chemical Technology* (John Wiley & Sons, New York, 1983) Vol 23, p.137.
- [19] P. Oliver, G. Watson, E. Kelsey, and S. Parker, *J. Mater. Chem.* 7, 563 (1997).
- [20] Y. W. Chung, W. J. Lo, and G. A. Somorjai, *Surf. Sci.* 64, 588 (1977).
- [21] V. Shklover, Y. E. Ovchinnikov, L. S. Brabinsky, S. M. Zakeeruddin, and M. Grätzel, *Chem. Mater.* 10, 2533 (1998).