Preparation and Characterization of Terraced Surfaces of Low-Index Faces of Anatase, Rutile, and Brookite

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Simple polishing and relatively low temperature annealing procedures for preparing atomically flat terraced surfaces of various single-crystal TiO₂ polymorphs are described. Anatase (101), anatase (001), rutile (100), rutile (110), and brookite (111) surfaces could all be prepared with a terraced surface structure as revealed in AFM images. The rutile (100) and (110) and anatase (101) surfaces were also shown to produce acceptable LEED patterns immediately upon insertion into a UHV system without the usual sputter and anneal cycles.

Metal oxides have many applications in catalysis, energy conversion, consumer products, and ceramics. Titanium dioxide (TiO₂) is prototypical among the metal oxides because TiO₂ can be a photocatalyst and a component of a solar cell as well as a component of sunscreen, toothpaste, and many other consumer products. Single-crystal TiO₂ surfaces have also been studied as a model for dye-sensitized solar cells and catalyst supports. Although rutile is the high-temperature polymorph of TiO₂, it is kinetically stable under ambient conditions. The anatase-to-rutile transformation occurs in the temperature range of 700–1000 °C, depending on the crystallite size and impurity content. Rutile, another polymorph of TiO₂, usually contains small amounts of Fe substituted for Ti and is converted into rutile by heating to temperatures above 700 °C.

Although there has been a lot of research on the surface structure and reactivity of TiO₂ in ultrahigh vacuum (UHV), the achievement of clean, atomically flat surfaces usually takes many cycles of sputtering and annealing, which can be time-consuming and tedious. The surfaces prepared with this method were found to be unstable after exposure to aqueous solutions. Recently, Nakato et al. reported a chemical etching method to prepare atomically flat rutile surfaces by immersing the rutile single crystals in 20% HF for 10 min, followed by washing, drying in nitrogen, and annealing at 600 °C in air. Chemical etching is a good way to prepare atomically flat surfaces for stable crystal surface planes. However, for surfaces with a higher surface energy, they can be selectively etched, forming channels or pits along certain crystallographic directions. Herein we report simple procedures for obtaining atomically flat surfaces for various surface orientations of all three common polymorphs of TiO₂ (anatase, rutile, and brookite) by polishing, ultrasonic cleaning, and annealing in air. The surfaces are characterized by atomic force microscopy (AFM) operated in air and low-energy electron diffraction (LEED) in ultrahigh vacuum (UHV).

A mechanically polished single crystal of rutile (100) was obtained from Commercial Crystal Laboratories, Ltd. The as-received polished rutile (100) showed no terraces in AFM images, and the surface roughness was measured to be about 0.32 nm. The crystal was then manually polished and soft polishi ng cloth (CHEMOMET) using 0.2 µm colloidal silica for about 3 min. After rinsing with H₂O, the sample was ultrasonically cleaned for 8 min in 18 MΩ Millipore H₂O to remove the polishing particles. To heal the polishing damage and form smooth terraces, the sample was then heated to 700 °C for 7.5 h in air in a Lindberg furnace and slowly cooled (~2 °C/min) to room temperature by turning off the power. After surface treatments, the rutile (100) surface was imaged with AFM. The images show very uniform terraces with an average width of about 50 nm corresponding to a miscut angle of 0.4° (Figure 1A). From the section analysis, the average height of a single step is shown to be 0.50 nm. It is noteworthy that the annealing step is usually required only the first time to obtain a terraced surface. If the surface becomes contaminated, the cleaning, polishing, and sonication are sufficient to maintain the terraced surface.

A LEED pattern of the rutile (100) surface was obtained after insertion into the UHV system without any additional surface treatments. Figure 1C shows a LEED pattern obtained with an electron beam energy of 46 eV. The pattern matches the rutile (100) symmetry and lattice parameters of a = 0.459 nm, b = 0.295 nm, and γ = 90°. Evaluation of the spot pattern and distances leads to the conclusion that the prepared TiO₂ (100)

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Figure 1. (A) Topographic AFM image and (B) section average of the rutile (100) surface. The average step height is 0.50 nm. (C) Observed LEED pattern (46 eV) of the as-prepared surface showing a $1 \times 3$ reconstruction. A calculated LEED pattern is given in D.

Figure 2. (A) Topographic AFM image and (B) section average of the rutile (110) surface. The average step height is 0.33 nm. (C) Observed LEED pattern (55 eV) of the as-prepared surface. A calculated LEED pattern is given in D.
surface has a $1 \times 3$ reconstruction. A schematic representation of the LEED pattern using the lattice parameters of rutile (100) with LEEDpat\(^{23}\) software is shown in Figure 1D. This reconstruction, characterized by oxygen deficiency, is usually found under UHV conditions after sputter-annealing cycles in the absence of oxygen. Muryn et al.\(^{24}\) showed that this surface is transformed into the $1 \times 1$ structure at high oxygen partial pressure. The physical and chemical reasons that our polishing and sonication procedures lead to a $1 \times 3$ reconstructed surface are still unclear. Further UHV studies to investigate this surface are in progress.

The rutile (110) crystal was also commercially grown and was polished in an identical fashion to the (100) surface. The topographic AFM image of this surface is shown in Figure 2A and revealed an average terrace height of 0.33 nm (shown in Figure 2B), matching the calculated single TiO\(_2\) layer step height of 0.325 nm. The LEED pattern obtained at 55 eV indicated an unreconstructed $1 \times 1$ surface (Figure 2C) identical to the simulated pattern shown in Figure 2D.

The anatase samples were naturally occurring mineral crystals that were mined in Hargvidda, Tyssedal in Norway. These bipyramidal crystals exhibited low-energy growth surfaces with large wedge-shaped (101) faces and (001) end caps. The (101) crystal faces were dark-gray metallic and shiny. They were cut along the (101) plane using a low-speed diamond saw, or the entire crystals were used. The natural anatase (101) surfaces were initially quite rough, so the crystal face was first ground flat with fine (600 grit) sand paper for 30 s, followed by successive polishing steps with 0.3 and 0.05 $\mu$m alumina each for 3 min. The next step was polishing with 0.02 $\mu$m colloidal silica for 2 to 5 min followed by ultrasonic cleaning for 8 min. The surface was then characterized with tapping-mode AFM. After about four cycles of polishing and ultrasonic agitation (total polishing time about 11 min), the AFM images indicated that the surfaces were very flat (rms roughness of 0.17 nm) but no distinct terrace structures were evident. The anatase (101) was then gently annealed in the furnace at 350 °C for 2 h, and the surfaces were given a final polish for about 5 min with 0.02 $\mu$m colloidal silica, followed again by ultrasonic cleaning. Figure 3A and B show the surface topography and section analysis of the anatase (101) surface prepared in this manner. Unlike the commercial rutile single crystal, the AFM images of the natural anatase single crystal show that the entire surface has terraces with irregular widths and edges. Section analysis of the image gives an average step height of 0.36 nm matching a one-monolayer step height (0.35 nm). The LEED pattern of this sample was obtained at 100 eV (Figure 3C) and showed both first- and second-order spots. The measured reflection distances and angles are in good agreement with the known parameters of the anatase (101) surface (centered rectangular: $a = 1.02$ nm, $b = 0.378$ nm, and $\alpha = 90^\circ$). A simulated LEED pattern for this surface is shown in Figure 3D.

The anatase (001) surface was polished in an identical fashion to the anatase (101) surface. After the series of surface treatments and annealing at 275 °C for 10 h, AFM images revealed low terraces with an average step height of about 0.28 nm, corresponding to $1/4$ of a unit cell height along the [001] direction.

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(23) http://w3.rz-berlin.mpg.de/~hermann/LEEDpat/
Parts A and B of Figure 4 show the topographic image and section analysis for this surface, respectively.

The brookite (111) crystal is also a natural mineral crystal from Magnet Hill in Arkansas. The natural brookite (111) surface was the roughest of the crystals that we studied, so extensive polishing was necessary. The polishing procedures used for anatase, from sand paper to 0.02 μm colloidal silica, were also applied to the brookite crystal. The polishing revealed some inclusions in the crystal, so the entire surface could not be polished to as smooth a finish as the surfaces of the other polymorphs. After a total polishing time of about 15 min, the crystal was gently annealed in the furnace in air at 250 °C for 16 h. It was then given a final polish for 5 min with 0.02 μm colloidal silica followed by ultrasonic cleaning as described above. Figure 5A shows the topographic image of a typical area of the brookite (111) surface. Irregular terraces are observed. The corresponding section analysis is shown in Figure 5B. The average terrace height is calculated to be 0.31 nm, close to the single unit cell step height along the [111] direction in brookite (0.35 nm). Because of the small size of the anatase (001) and brookite (111) crystal sections, we were unable to mount them onto a UHV sample holder, so no LEED patterns were obtained.

In summary, we have shown that surfaces with atomically flat terraces can be obtained for five low-index surfaces of three TiO2 polymorphs using simple physical polishing and low-temperature annealing in air. The LEED patterns demonstrate that the surfaces have long-range order and the flat terraces with defined steps, observed with AFM, are not selected areas of unusual order. We have used these procedures, coupled with a final ultraviolet photooxidation step to remove any organic contaminants, to prepare reproducible surfaces for studying the dye sensitization of these oxide semiconductors.\(^{25}\) Greatly improved dye coverages were obtained when compared to previous work where the surface pretreatments were not done.\(^{6}\) We anticipate that performing these procedures prior to inserting these oxide crystals into the UHV system will substantially reduce the sputter and annealing times and cycles usually necessary to produce such well-terraced surfaces because, on the three surfaces where LEED was measured, acceptable LEED patterns were obtained immediately after inserting them into the UHV system.

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