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Hydrophilicity transition of the clean rutile TiO_2 (1 1 0) surface

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Abstract

We present contact angle measurements of water on single-crystal rutile TiO_2 (1 1 0) surfaces, exposed to ambient air, or protected in dry air. Our measurements indicate that the surfaces exposed to ambient air are hydrophobic, with a contact angle of $\theta = 61(5)^\circ$. However, the well-protected dry surface also exhibits some hydrophobic tendency, with $\theta = 32(5)^\circ$. It is known that UV irradiation transforms both surfaces superhydrophilic, with $\theta = 0^\circ$ [R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Nature 388 (1997) 431–432]. We also present preliminary X-ray crystal truncation rod measurements on the hydrophobic TiO_2 (1 1 0) surface, and of the effect of UV illumination on the surface.
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Keywords: Contact angle measurement; Surface X-ray scattering; Crystal truncation rod; UV irradiation; Hydrophobic hydrophilic surfaces

1. Introduction

Titanium dioxide is an important photocatalyst [1] used in a large and growing range of applications [2]. The TiO_2–water interface has generated a great deal of interest for, among other reasons, its ultraviolet-induced hydrophilicity conversion [3]. There is a large body of literature on TiO_2–H_2O interfaces in vacuum [4–17], much of which concentrates on the rutile (1 1 0) surface. The structure of adsorbed water on rutile (1 1 0) in air has been studied [18–20], but there is disagreement on if and how this structure changes in response to UV irradiation to produce a hydrophilic surface. The literature can be loosely classified into two groups. Several papers hypothesize the hydrophilic surface is produced by the photocatalytic removal of contaminants [21–23]. Others have proposed photo-induced surface modification mechanisms [24–28]. It has been shown that the former explanation cannot be solely responsible for the effect [27–29]. UV irradiation creates a surface nanostructure that has been ascribed to the formation of hydrophilic and hydrophobic domains [3]. It is known that the presence of O_2 is necessary for the hydrophilicity conversion to occur [30], and there is evidence the presence of water is also required [28].

The rutile (1 1 0) surface is expected to be unreconstructed in air at room temperature [31]. We define our unit cell as in Fig. 1, with the $\hat{x}$ axis along the short axis of the conventional bulk unit cell, and the $\hat{z}$ axis normal to our surface. The lattice constants in this set of coordinates are 2.958, 6.495, and 6.495 Å. The surface in air has bridging oxygen (BO) atoms coordinated to alternate rows of Ti atoms, and terminal oxygen (TO) atoms coordinated to the remaining surface Ti atoms.

While contact angle measurement provides a macroscopic measure of hydrophilicity, X-ray crystal truncation rod (CTR) measurement is a surface-sensitive technique that has been used to solve the structure of similar oxide–water systems [32]. We will combine these two techniques to learn the macroscopic behavior and molecular structure of rutile surfaces in humid conditions and in water.

2. Experimental

Experiments were carried out using rutile TiO_2 single-crystal wafers with (1 1 0) surface orientation. Samples were prepared by sonicating in acetone, etching in HF, and annealing in dry air at 600 °C for 1 h. Previous work has shown this preparation

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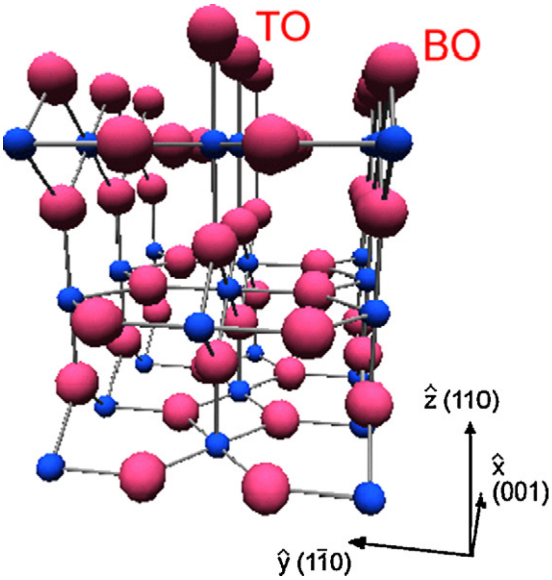

Fig. 1. The ideal, TO-terminated rutile (1 1 0) surface. Ti atoms are blue; O atoms are red. Bridging and terminating oxygen rows are labeled. Our coordinate convention is marked.

method produces a smoother surface than Ar^+ sputtering [33]. Samples were cooled in the dry air flow, moved directly into a glove bag fastened to the furnace air outflow, and mounted into a sealed electrochemical cell used for X-ray measurements. CTRs were collected at beamlines 11-ID-D and 12-BM-B at the advanced photon source using 12 keV photons and a scintillation detector (Cyberstar). The samples remained in dry air flow throughout the measurements. When we wanted to introduce water to the sample environment, we bubbled the input air flow through a gently heated bottle of millipore water. To obtain a very wet surface, we flooded the cell and let it drain to below the sample level. Ultraviolet light was provided by a 500 W Hg–Xe arc lamp source (Oriel) filtered with a 240–400 nm UV-band pass filter (Edmund Optics). The hydrophobic → hydrophilic transformation was induced by illuminating the sample for typically 1 h. The intensity at the sample position was measured to be at least an order of magnitude above the quoted threshold of 20 mW/cm^2 [24]. Low-energy diffraction (LEED) measurements were made with a low-current MCP-LEED and UHV chamber with base pressure $\sim 10^{-11}$ Torr (Omicron Nanotechnology). Contact angle measurements were performed with the sessile drop method using a commercial, optical camera-based contact angle goniometer (KSV, Inc). All water used in wetting experiments comes from an ultrapure purifier (Millipore Milli-Q) and contains <5 ppb total organic carbon. Air used in the experiments is from a synthetic air cylinder (Linde Gas Inc.) and contains <2 ppm H_2O and <0.05 ppm hydrocarbons.

3. Results and discussion

The sample preparation technique was shown to produce a clean, ordered surface by transporting a sample as prepared into the UHV chamber and collecting a LEED pattern. Several hours after introduction to vacuum, the sample exhibited a clear 1 × 1 diffraction pattern (Fig. 2, left), consistent with other previous UHV studies [23]. Only a well-ordered surface without a disordered contamination layer would produce such a diffraction pattern. Photos of the as-prepared sample in ambient air, on a UHV sample manipulator and sprinkled with water droplets (Fig. 2, right), qualitatively show the hydrophobic nature of the surface.

The as-prepared sample surface, protected in dry air atmosphere, before UV illumination, is slightly more hydrophobic than reported surfaces exhibiting UV-induced hydrophilicity and a 0° contact angle [3]. We measured the contact angle of a sessile water droplet on the newly prepared surface kept in a protected environment as 32(5)° (Fig. 3, right). The uncertainty represents the standard deviation of measurements of several successive droplets. Unprepared surfaces straight out of a storage box, exposed to ambient air, exhibit much larger hydrophobic contact angles, measured at 61(5)°. In both cases, contact line pinning can affect the measured contact angle. Evap-

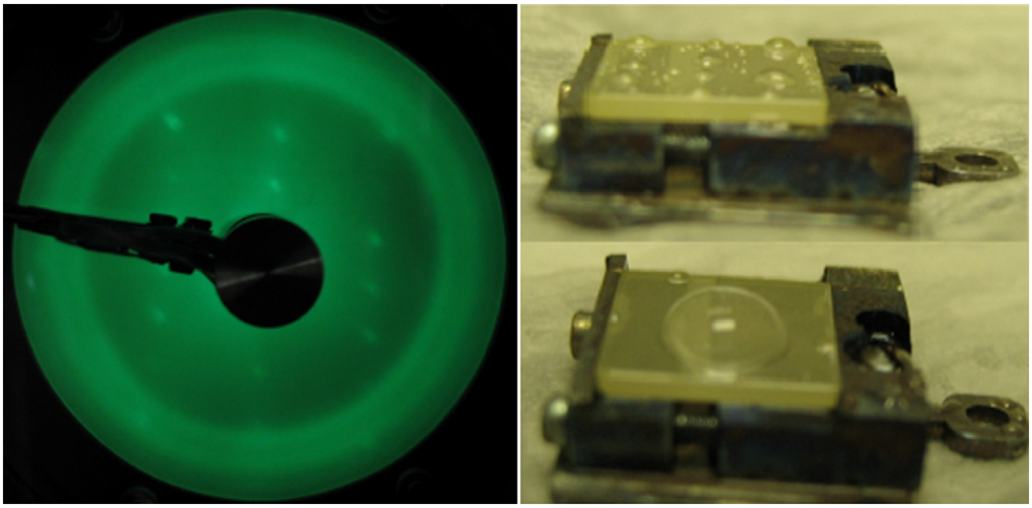

Fig. 2. (Left) A LEED pattern collected on the sample as prepared, approximately 60 min after introduction to UHV. A 1 × 1 pattern is visible. (Right) Photos showing hydrophobic surfaces of the samples as-prepared.