

Atomic-scale Structure of Rutile (110)-Water Interface by Using High-resolution X-ray Reflectivity

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Introduction

The electrical double layer (EDL), formed at the oxide-water interface, plays an important role in many natural and industrial processes [1]. The concept of the EDL was introduced more than a century ago. Many models of the EDL structure have been developed. Few direct measurements of the EDL structure at atomic level have been made to date, however, and little is known about even the most basic aspects of the EDL structure.

High-energy, high-brilliance x-ray sources allow powerful new tools to probe the oxide-water interface structure. Previously, we successfully located the divalent ion (Sr^{2+} and Zn^{2+}) heights at the rutile (110)-water interface referenced to the crystal diffraction plane [2, 3] by using the x-ray standing wave (XSW) method. These XSW results, however, do not reveal the ion location with respect to the surface plane, nor the surface relaxations of the rutile crystal. To obtain this interface-specific information, we used high-resolution x-ray reflectivity measurements.

Methods and Materials

Rutile (110) single crystals (Princeton Scientific Corp., $10 \times 10 \times 1 \text{ mm}^3$) were baked and hydrothermally treated to remove surface defects and impurities prior to the experiment. The crystal was loaded into the thin-film sample cell [2] and sealed in deionized water (DIW). A small negative pressure was applied to minimize the water layer thickness ($\sim 2 \mu\text{m}$) between the rutile surface and a thin ($\sim 8\text{-}\mu\text{m}$) Kapton® film. The specular reflectivity was measured to high ($< 1\text{-}\text{\AA}$) resolution, revealing crystal truncation rod (CTR) profiles. Measurements were first made for a “clean” surface and then with Sr^{2+} and Rb^+ ions at the rutile-water interface. The Sr ion adsorption measurements were performed in SrCl_2 solution ($[\text{Sr}^{2+}] = 1 \text{ mM}$) at a pH of 10.7.

Results and Discussion

The CTR data are shown in Fig. 1. The symbols show the reflectivity for the clean and Sr-adsorbed surfaces, and the solid lines are the best fits to the measured CTR. The

data show significant differences between the Bragg peaks, indicating that Sr ions are specifically adsorbed to the rutile surface.

Figure 2 shows the electron density profiles near the rutile-water interface obtained from the best fits of the CTR data shown in Fig. 1, including the finite resolution of the reflectivity data. The profile for $z < 18 \text{ \AA}$ is due to the rutile crystal, where the large peaks indicate the Ti planes. The two smaller peaks between the Ti planes are due to oxygen atoms in the lattice. The fluid water above the surface is shown as a flat line at $z > 20 \text{ \AA}$.

The interfacial region has a number of interesting features. Immediately above the surface Ti plane (at $z \sim 18 \text{ \AA}$), we see two oxygen layers above the outermost Ti plane. The lower oxygen layer corresponds to the surface oxygen atoms that bridge between Ti atoms within the surface layer. The upper oxygen layer is due to (presumably) dissociatively adsorbed OH^- groups terminally bound to surface Ti atoms. This outer oxygen layer is not found at the rutile surface prepared in ultrahigh vacuum (UHV) [4] and helps to explain the smaller surface relaxation of the rutile crystal that we

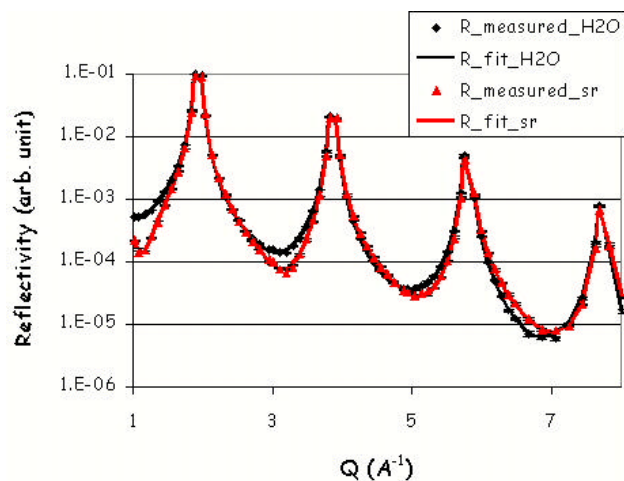


FIG. 1. CTR data from rutile-water interface.

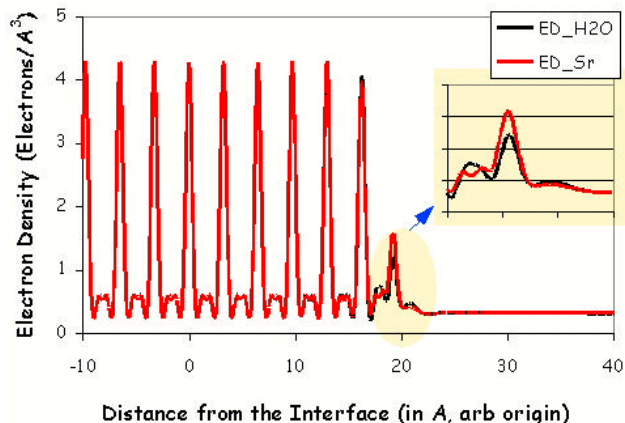


FIG. 2. Electron density profile at the rutile-water interface. Inset is the region magnified.

observe here with respect to the measurements in UHV [4].

For rutile in DIW, we find evidence for an additional unexpected electron density above the rutile surface near $19 \text{ \AA} < z < 21 \text{ \AA}$. Similar adsorbed water structures have been observed at oxide-water interfaces [5] and layered aluminosilicate-water interfaces [6]. This layered water can be interpreted as the consequence of the truncation of the bulk water by the rutile crystal and damps out rapidly away from the interface.

For rutile in contact with the Sr^{2+} solutions, we observed a significant enhancement of the electron density near $z = 19 \text{ \AA}$, which is interpreted as Sr^{2+} ions displacing the adsorbed H_2O molecules in the near-surface layer. This position of adsorbed Sr^{2+} ions agrees well with previous XSW results [3].

Additional measurements of rutile in contact with RbCl solution at alkaline pH reveals the association of Rb^+ with the rutile surface, but only at substantially elevated solution concentrations.

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