# Thermal Desorption of Commensurate Water from Ruthenium Dioxide (110)

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## Introduction

The interaction of water with oxide surfaces is both scientifically and commercially important, though not in general well understood. A great number of important chemical processes occur at the interface between oxide surfaces and aqueous solutions. In particular, ruthenium dioxide has been widely investigated as a candidate oxide material for ultracapacitors. In this report, we discuss the preparation of a commensurate water layer on the $RuO_2$ (110) surface by electrochemical means and the subsequent desorption of this water layer in vacuum.

## Methods and Materials

Single crystals of $RuO_2$ were grown in a multizone furnace under oxygen flow. Crystals with large (2 mm x 4 mm) (110) facets were selected for surface scattering experiments. After formation of the commensurate water layer by electrochemical processing in a glass cell, the crystal was mounted within a custom vacuum chamber that was designed to mount on a Huber diffractometer.

The vacuum chamber features 0.5-mm-thick beryllium entrance and exit windows allowing 240 degrees azimuthal access. The chamber mounts directly to the Huber $\chi$-cradle, with azimuthal sample rotation driven by the Huber $\phi$-stage and coupled through a differentially pumped rotary feedthrough. Other rotations of the sample are obtained by rotating the chamber on the diffractometer. The use of six-circle diffractometry[1] allows access of a large region of reciprocal space with minimal movement of the vacuum chamber. The chamber is additionally equipped with instrumentation for residual gas analysis, dosing with high-purity $O_2$, and $Ar^+$ ion sputtering. In addition, the sample can be heated radiatively by a tungsten filament placed immediately behind the sample. Temperature measurement and control is provided by a type-K thermocouple attached to the sample mount.

## Results

Bulk $RuO_2$ crystallizes in the rutile structure. The (110) surface of $RuO_2$ features a rectangular unit cell with dimensions 3.11 x 6.36 Å. For surface diffraction, we adopt a set of coordinates for which the in-plane bulk coordinates $(001)_{bulk}$ and $(1\text{-}10)_{bulk}$ become (100) and (010), respectively. The surface normal becomes (001) in these coordinates. The Ru atoms lie on a centered rectangular surface lattice. A consequence of the symmetry of the Ru sublattice is that scattering from Ru cancels for reflections with $(H + K)_{surf}$ = odd. Cancellation of scattering from Ru atoms allows the measurement of "oxygen truncation rods"–crystal truncation rods that contain no bulk Ru component. By measurement of these "oxygen rods," surface oxygen positions can be inferred much more reliably than would otherwise be possible (due to the low scattering power of oxygen).

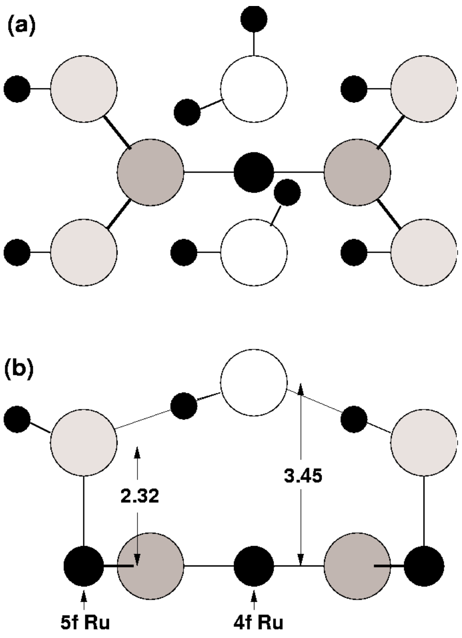

*FIG. 1. Structure of commensurate water layer obtained by complete in situ structure determination in solution. (a) Top view along $(001)_{surf}$, (b) side view along $(100)_{surf}$. Large dark-gray circles represent O atoms in the mixed Ru-O plane, light-gray circles represent O atoms as hydroxides, and white circles represent O atoms in water molecules. Larger black circles are surface Ru atoms, while small black circles represent (conjectured) positions of hydrogen atoms.*

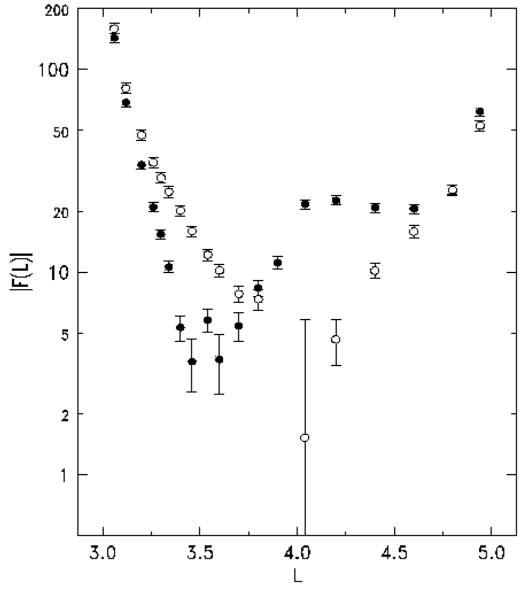

*FIG. 2. Segment of (01L) truncation rod. Filled circles represent measurement of the water layer, open circles show measurements following desorption. The water layer is evidenced by the feature at L = 4.*

Previous surface diffraction studies using an *in situ* electrochemical cell have established the existence of a commensurate water layer on the $RuO_2$ (110) surface.[2] This layer is formed by site-specific oxidation and reduction processes driven by the electrochemical potential. The structure of the layer is shown in Fig. 1. Terminal hydroxides sit directly above the 5f Ru atoms at a distance of 2.32(2) Å, and oxygen atoms in water molecules bridge the 4f Ru atoms along the (100) direction. These O atoms sit 3.45(2) Å above the mixed Ru-O plane and are laterally stabilized in a hydrogen-bonded network with the terminal hydroxides that sit atop the 5f Ru atoms.

The existence of the commensurate water monolayer in the vacuum environment was verified by measurement of the (01L) oxygen truncation rod. Based on our previous *in situ* study of the $RuO_2$ (110) surface under potential control, we identify the peak at $L = 4$ with the commensurate water overlayer. This feature was found to be stable in vacuum during exposure for several hours to the undulator beam. In fact, no variation of the structure with exposure to the synchrotron beam has been observed in our experiments.

To investigate the thermal desorption of the water layer, the intensity at the (014) point of reciprocal space was monitored as the temperature was raised. A dramatic decrease in the intensity at (014) was observed at $T = 485K$. The sample was then allowed to cool and the (01L) rod was remeasured. The rod before and after desorption is shown in Fig. 2.

## Discussion

Vacuum measurement following electrochemical preparation demonstrates the stability of the hydrogen-bonded network of water molecules in the commensurate overlayer. This study demonstrates the unique advantages of synchrotron x-ray scattering over conventional (charged-particle) surface science techniques, which are generally more destructive. The stability of the overlayer outside of the solution environment will further allow characterization by techniques, such as infrared spectroscopy, that can further probe intermolecular bonding in the surface layer. Such a measurement would not be possible with the sample immersed in solution. Future work involving the surface scattering chamber will include a mass-spectrometer-based thermal desorption study in ultrahigh vacuum, in addition to structural modeling of the surface following desorption of the water layer.

## Acknowledgments

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## References

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