

Atomic-scale Structure of the Quartz (1010)-Water and Quartz (1011)-Water Interfaces

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Introduction

Quartz is ubiquitous in the continental crust, and it plays a key role in controlling the dissolved silica concentration in aqueous systems. To better understand and model the kinetics of quartz dissolution and precipitation, an extensive knowledge of the quartz-water interface structure is desirable. In this study, we probed the structure of prismatic (1010) and pyramidal (1011) growth faces of natural quartz crystals by atomic force microscopy (AFM) and in water by high-resolution x-ray reflectivity (XRR).

Methods and Materials

Quartz slabs were sonicated in acetone, methanol, and deionized water to remove surface impurities. TappingMode™ AFM images were collected in air with a silicon tip by using a Digital Instruments MultiMode™ scanning probe microscope (SPM). Reflectivity measurements were recorded on the wet surfaces at the 12-ID-D station of the Basic Energy Sciences Synchrotron Radiation Center Collaborative Access Team (BESSRC-CAT) at the APS.

Results and Discussion

AFM images revealed the presence of ~0.1- to 1- μm -wide flat terraces delimited by steps of one to several unit cells in height. These steps essentially follow directions given by the intersection of growth faces. Modeling of XRR data indicates that the atomic structure near the quartz surface is obtained from the quartz bulk structure, by assuming a slight relaxation of atomic positions (<0.4 Å for terminal oxygens and <0.2 Å for silicon and oxygen atoms fully coordinated to structural tetrahedra). Vertical relaxation of atomic positions is limited to a depth of 14 Å. Surface silica groups on flat terraces have only one free Si-O bond each (presumably hydroxylated), except for some that have two free Si-O bonds observed on a single (1010) surface. Electron density profiles for the probed interfaces are consistent with a single layer of water being adsorbed in an amount equivalent to the number of surface silanol groups, but no additional organization of water was detected in the bulk solution (Fig. 1). We found no evidence for the presence of a layer

of disordered or amorphous silica, even for a (1011) quartz slab kept in deionized water for 10 months prior to reflectivity measurements. Similar interfacial structures

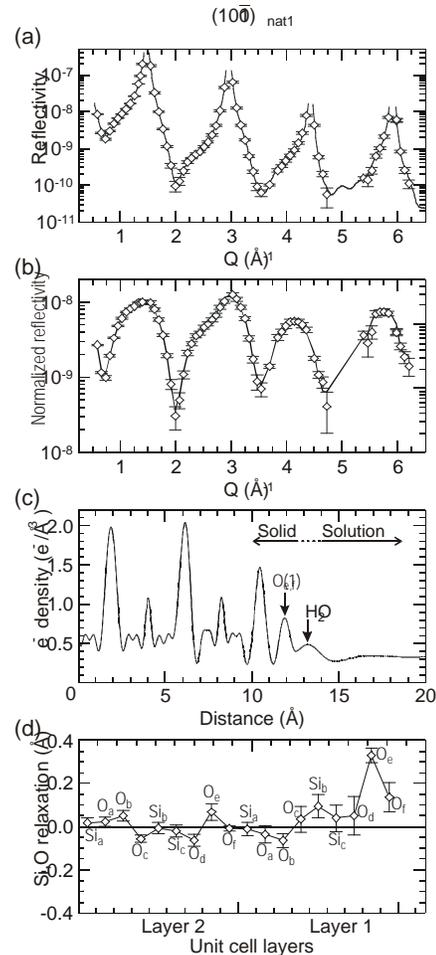


FIG. 1. (a) Reflectivity for (1010) natural surface and best model fit. (b) Normalized reflectivity and best fit. (c) Laterally averaged electron density profile. (d) Atom relaxations. Positive values are atom shifts toward the solution; negative values are shifts toward the solid. Surface-most oxygen is labeled O_f .

were determined for natural and annealed surfaces (to temperatures of 400°C). These results provide strong constraints on the nature of surface functional groups exposed at the (1010) and (1011) faces of quartz.

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References

[1] M. L. Schlegel, K. L. Nagy, P. Fenter, and N. C. Sturchio, *Geochim. Cosmochim. Acta* (in press, 2002).