

Supplementary Information

Three-dimensional ordering of water molecules reflecting hydroxyl groups on sapphire (001) and α -quartz (100) surfaces

Sho Nagai^a, Shingo Urata^b, Kent Suga^a, Takeshi Fukuma^{c, d}, Yasuo Hayashi^a
and Keisuke Miyazawa^{c, d*}

^aInnovative Technology Laboratories, AGC Inc., 1-1 Suehiro-cho, Tsurumi-ku, Yokohama, Kanagawa 230-0045, Japan

^bPlanning Division, AGC Inc., 1-1 Suehiro-cho, Tsurumi-ku, Yokohama, Kanagawa 230-0045, Japan

^cFaculty of Frontier Engineering, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

^dNano Life Science Institute (WPI-NanoLSI), Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

*Corresponding author e-mail: k.miyazawa@staff.kanazawa-u.ac.jp

Supplementary Figures

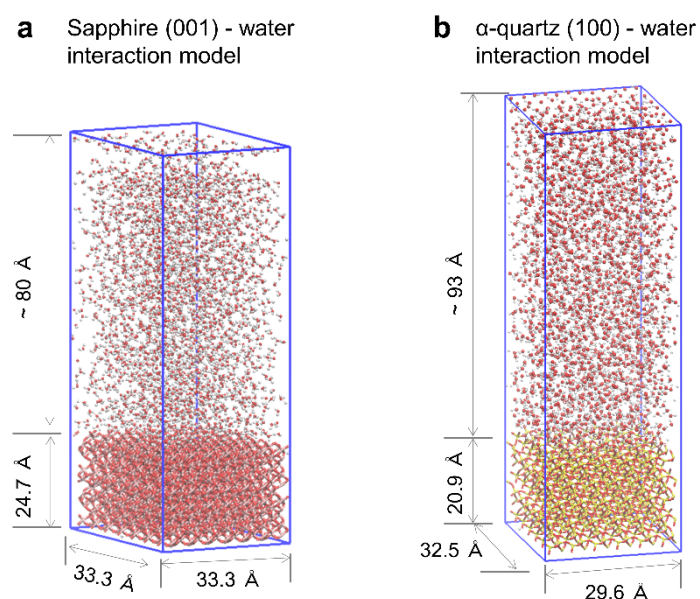


Fig. S1: MD simulation models showing the interaction between water molecules and (a) sapphire (001) or (b) α -quartz (100) surfaces. Only Z-direction (vertical direction) was controlled to be constant pressure at 0.1 MPa. Both models include 2,000 water molecules in the simulation boxes.

Table S1 □ The surface zeta potential of each substrate in aqueous solution at pH = 7

	Surface zeta potential (mV)
Si wafer	-1.69
Sapphire (001)	11.9
α -quartz (100)	-4.52

The surface zeta potential measurements were performed for each substrate in an aqueous solution at pH = 7. A commercially available apparatus (ELS-Z1, Otsuka Electronics Co., Ltd.) was used for measurements. The surface zeta potential of the samples used in AFM was evaluated using box-like quartz cell for flat surface measurement. The measurement was performed in a 10 mM NaCl solution with pH = 7 because it is difficult to measure the zeta potential in ultrapure water. The same evaluation was also performed for Si wafers (N-type Si (100), MITSUBISHI MATERIALS), which is the material used for the Si cantilever for AFM measurements. The Si wafer was cleaned by UV/ozone processing immediately before the surface zeta potential measurement. The surface zeta potentials of the substrates are presented in Table S1. The Si wafer was negatively charged at pH=7. This is probably due to the deprotonation of Si-OH to Si-O⁻. The α -quartz (100) was also negatively charged, suggesting the formation of Si-O⁻. For sapphire (001), the surface zeta potential was positively charged at pH = 7. This is probably due to the protonation of a part of Al-OH to Al-OH₂⁺.

We do not consider the surface defects of surface OH groups in MD, but we do consider the protonation (and deprotonation) of the surface OH groups on both surfaces. A defect of the OH group can be repaired by immersing the surface in water¹. Thus, we consider that it is less possible to measure the part of the defect where the OH group is detached from the surface.

The surface OH groups of sapphire (001) and α -quartz (100) in pure water (pH = 7) may be mostly in the unprotonated state. However, some of the OH groups on both surfaces are protonated (or deprotonated), depending on the pH of the solution, which changes the surface potential. Generally, sapphire (Al_2O_3) is considered to be positively charged in pure water (pH = 7) because of the protonation of some OH groups on the surface. The protonation reaction on the sapphire (001) surface has a pK value of 3². Thus, unprotonated OH groups are dominant in pure water with a higher pH value. The acidic oxide α -quartz (SiO_2) was negatively charged by deprotonation in pure water (pH = 7). Although no report on a pK value for deprotonation of α -quartz (100), we can refer to reports on the same crystalline SiO_2 , α -quartz (001)^{3,4}. α -quartz (001) is predicted to have a pK value of 8.5 in pure water³. At pH = 7, which is more acidic, there should be a higher proportion of unprotonated Si-OH. In fact, when pH = 6, the SiO^- percentage decreased to approximately 9%⁴.

These results allow us to interpret the long-range forces observed in the AFM force curves. For the sapphire (001) surface, long-range attractive interactions were observed (Fig. 5a). This is likely due to the attractive electrostatic interaction between the negatively charged Si cantilever and the positively charged sapphire (001) surface. In contrast, a repulsive interaction was observed for α -quartz (100). This is possibly due to the electrostatic repulsive interactions between the cantilever tip and α -quartz (100); both surfaces are negatively charged.

1. J. Lutzenkirchen et al., *Adv. Colloid Interface Sci.* 251 (2018) 1-25
2. L. Zhang et al., *J. Am. Chem. Soc.* 130 (2008) 7686–7694.
3. M. Pfeiffer-Laplaud et al., *J. Phys. Chem. Lett.* 7 (2016) 3229–3234.
4. Z. Brkljača, et al., *J. Phys. Chem. C* 122 (2018) 24025–24036.

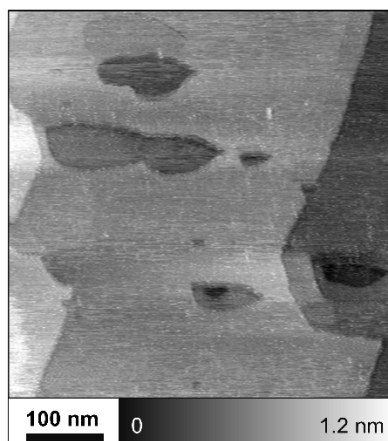


Fig S2: Frequency-modulation atomic force microscopy image of α -quartz (100) surfaces in ultrapure water.

The shadow effect at the step edges in Fig. 2c may have been caused by a slightly higher feedback gain during the AFM measurement. We used a slightly higher I-gain value than the optimal feedback gain for step edge measurements to prevent accidental collisions with contamination on the surface while measuring a large-scale scanning area. Thus, in Fig. 2c, when the tip climbs the edge from left to right, we can see a higher structure overshooting it. In the meanwhile, when the tip descends the step edge, we can see a structure that is overly recessed. We have also attached an additional large-scale AFM image of α -quartz obtained in Fig. S2 in the Supplementary Information. Fig. S2 shows a large-scale image obtained with a tip that is different from the experiment in Fig. 2c. We did not observe a shadow effect, as shown in Fig. S2 by optimizing the I-gain for the measurement of step edge structures.

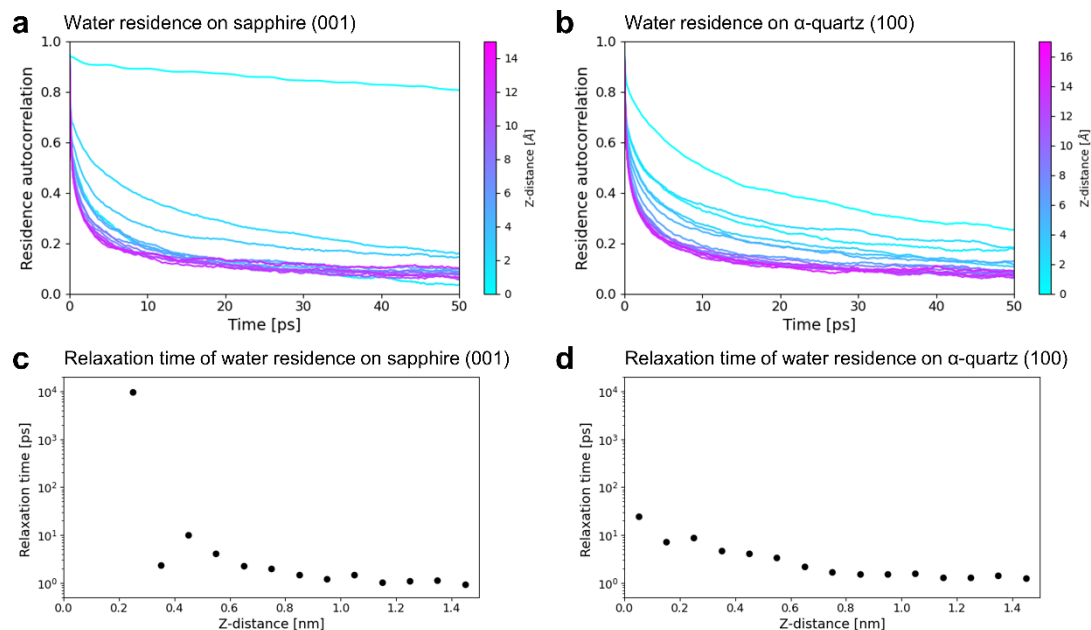


Fig. S3: (a, b) Water residence and (c, d) relaxation time of water residence on (a, c) sapphire (001) and (b, d) α -quartz (100) surfaces analyzed from the results obtained by MD simulation.

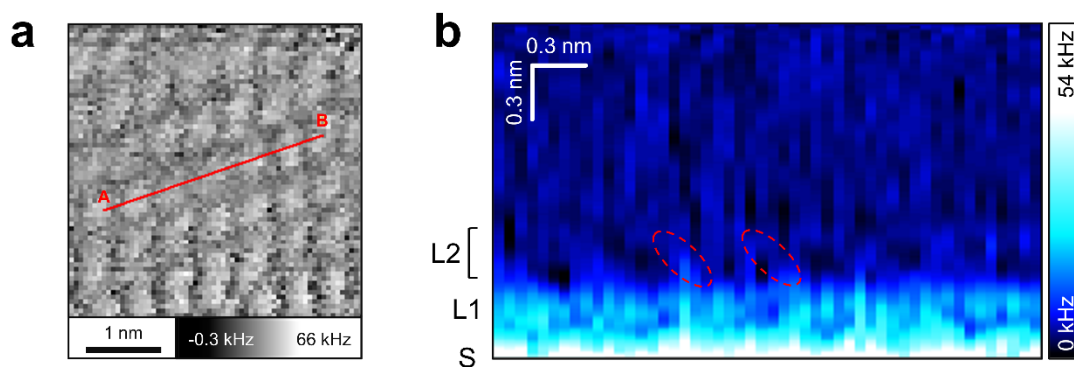


Fig. S4: Raw data of (a) XY and (b) Z cross-sections taken from 3D- Δf image on α -quartz surface measured by 3D-AFM. The Z cross-sections in (b) is taken along line AB in (a).

Figure S4 shows the raw data of the XY and Z cross-sections obtained from the 3D- Δf image on the α -quartz (100) surface. From this figure, vertically tilted hydration structures exist in the L2 position, even in the raw data. Thus, we imply that the tilted local contrasts in Fig. 4f represent the real hydration structures rather than artifacts caused by the filtering process.