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Interaction of condensed water molecules with hydroxyl and hydrogen groups on Si(0 0 1)

Hiroyuki S. Kato [a], Maki Kawai [a,*], Kazuto Akagi [b], Shinji Tsuneyuki [b]

[a] *RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan*
[b] *Department of Physics, Graduate School of Science, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan*

Abstract

Interaction of condensed water molecules with hydroxyl and hydrogen groups on Si(0 0 1) was investigated using high-resolution electron energy-loss spectroscopy (HREELS) in an ultrahigh vacuum system and also slab model calculations based on the density functional theory (DFT). Equal amounts of the hydroxyl and hydrogen groups were formed via dissociative adsorption of water molecules on a reconstructed Si(0 0 1)-(2 × 1) surface. The interaction between the hydroxyl group and condensed water molecules was clearly observed in vibrational peak shifts of the hydroxyl group, while the hydrogen group showed little interaction, reflecting its hydrophilic or hydrophobic property, respectively.

Keywords: Electron energy-loss spectroscopy (EELS); Vibrations of adsorbed molecules; Wetting; Silicon; Water; Low index single crystal; Solid–liquid interface

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1. Introduction

Interaction of condensed water molecules with the hydroxyl group and the hydrogen group is important for all chemistry under wet conditions: chemosynthesis in water solution, electrochemistry, biochemistry, atmospheric chemistry, surface chemistry such as wet processes for IC devices, surface corrosion, tribology, and so on. A great deal of effort has already been made to clarify the water-related phenomena at surfaces [1,2]. Here, we state the interaction of condensed water molecules with hydroxyl and hydrogen groups through vibrational analysis, which has not been described fully, so far.

The reactions of water molecules on Si(0 0 1), of course, have been investigated well using vibrational spectroscopic methods: high-resolution electron energy-loss spectroscopy (HREELS) [3–9] and infrared reflection absorption spectroscopy

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[*] Corresponding author. Tel.: +81 48 467 9405; fax: +81 48 462 4663.
E-mail address: maki@riken.jp (M. Kawai).

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(IRAS) [10–17]. The water molecules (H_2O/D_2O) have been known to dissociatively adsorb on a clean reconstructed Si(001)-(2 × 1) surface at room temperature and to form hydroxyl groups (–OH/–OD) and hydrogen groups (–H/–D) on the surface, where they terminate dangling bonds at the surface keeping Si dimer structures [18,19]. This water reaction is quickly saturated under the water exposure of a few Langmuirs ($1\ \mathrm{L} = 1.33 \times 10^{-4}$ Pa s) at around room temperature [3,20–22]. Note that this reaction provides equal amounts of hydroxyl and hydrogen groups on the surface. Therefore, utilization of this modified surface gives a good advantage for comparison between hydroxyl and hydrogen groups interacting with condensed water.

In this work, we investigated the interaction of condensed water molecules with the hydroxyl and hydrogen groups on Si(001) using HREELS and also DFT calculations. A clear difference of the interaction with hydroxyl and hydrogen groups was obtained. The difference is understood as a difference of hydrophilic and hydrophobic properties of the groups, i.e., interaction with and without hydrogen bonding, respectively.

2. Experimental and theoretical

Experiments were performed using a HREELS system (DELTA0.5, Specs GmbH) in an ultrahigh vacuum (UHV) chamber ($<3 \times 10^{-8}$ Pa) equipped with a quadrupole mass spectrometer, a low energy electron diffraction (LEED) optics, and a pulsed gas doser. In the HREELS measurements, all vibration spectra were taken at a sample temperature of 90 K in the specular configuration ($\theta_i = \theta_f = 60°$ from the surface normal) with a primary beam energy of 2.5 eV, where an intense elastic peak of 5–8 meV FWHM was obtained.

The Si(001) sample was mounted at the end of a refrigerator tube and cooled down to lower than 90 K by liquid N_2. The sample temperature was monitored by a C-type thermocouple attached to the sample with a tantalum clip. The Si(001) sample was cleaned by flash-cleaning method up to about 1500 K by direct current heating. Cleanliness was confirmed by LEED and HREELS.

Normal water (H_2O) and deuterated water (D_2O, purity 99.8%) were used for our experiments. Although we carefully exchanged two types of water at the gas delivery line with repeated purges, H/D conversion reaction of water in the UHV chamber was not negligible and vibrations originating from HDO adsorption were not avoided, unfortunately.

Theoretical calculations were performed to evaluate our observed vibrational modes based on the density functional theory (DFT) with generalized gradient correction (PW91) [23,24]. Only valence electrons were explicitly treated by the pseudo-potential method. A Troullier–Martins type pseudo-potential [25] was applied to silicon atoms, and Vanderbilt ultrasoft type ones [26] were applied to oxygen and hydrogen atoms. The energy cutoff for the plane wave basis set was 49.0 Ry and the number of sample *k*-points was four.

3. Results and discussion

The modified Si(001) surface with hydroxyl and hydrogen groups was accomplished by exposing to 3 L of H_2O at 90 K followed by annealing up to 300 K. After this procedure, the vibrational spectrum obtained, Fig. 1(a), is completely identical to that of the surface exposed at room temperature [3–9], and thus the final products are attributed to hydroxyl and hydrogen groups bound to the Si dimer. Characteristic peaks at 103, 260, and 454 meV have been assigned to an overlap of Si–O–H bending and Si–OH stretching modes, an Si–H stretching mode, and an SiO–H stretching mode, respectively. The small peak at 205 meV is due to a double loss of the intense peak at 103 meV [3].

When the modified surface was exposed to H_2O at 90 K, an increase of broad peaks attributed to condensed water molecules was obtained in the vibrational spectra, as shown in Fig. 1(b)–(g). At the maximum H_2O dosage of 160 pulses, typical vibrational modes for condensed H_2O were observed: broad peaks of a hindered translational mode at 30 meV, a librational mode at 104 meV, a H_2O scissoring mode at 206 meV, and an O–H