

H₂O on Si(001): surface optical anisotropy from first-principles calculations

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Abstract

Reflectance anisotropy spectra (RAS) for water covered Si(001) surfaces have been calculated within the independent-particle approximation. For low coverages we find essentially an attenuation of the features typical for clean Si surfaces. For the saturation coverage of one molecule per dimer, however, dissociative adsorption and oxygen insertion into the Si dimer give rise to clearly different optical anisotropies.

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Water has a sticking coefficient near unity on Si(001) surfaces at room temperature [1,2] and is a major component in the residual gas in most ultra-high vacuum apparatus. Water coadsorption therefore occurs on many Si(001) surfaces to a noticeable degree. On the other hand, the interaction of water with silicon surfaces plays an important role in semiconductor technology (wet oxidation, cleaning) and is relevant for interfaces formed between the inorganic semiconductor and organic, in particular biologically relevant mole-

cules. The interaction of water molecules with Si surfaces has therefore been extensively studied both experimentally (see, e.g., Refs. [1–4]) and computationally (see, e.g., Refs. [4–10]).

Reflectance anisotropy spectroscopy (RAS) has developed into a highly successful tool for the determination of surface structures of clean and adsorbate covered semiconductors as well as for real-time growth monitoring (see, e.g. Refs. [11,12]). The application of RAS for surface structure determination requires the comparison of the measured spectrum with either data known from previous experiments or with spectra numerically simulated for candidate structures. The RAS features characteristic for clean, hydrogen-covered or oxidized Si(001) surfaces, for example, are

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well-known from experiments [13–17] and have been investigated computationally [18–21]. However, despite their ubiquity, to our knowledge the influence of water molecules on the optical properties of Si(001) has not been addressed yet by theory or experiment. Our paper aims at filling that gap by performing accurate first-principles calculations on the influence of water molecules on the optical anisotropy of Si(001).

The calculations are performed using the Vienna Ab-initio Simulation Package (VASP) implementation [22] of the gradient-corrected [23] density functional theory (DFT-GGA). The electron–ion interaction is described by non-normconserving ultra-soft pseudopotentials [24], allowing for the accurate quantum-mechanical treatment of first-row elements with a relatively small basis set of plane waves. We expand the valence wave functions into plane waves up to an energy cutoff of 25 Ry. The reliability of our approach has been probed by calculations of gas-phase water molecules. We determine a O–H bond length of 0.97 Å and a H–O–H bond angle of 105.2°, in close agreement with the experimental values of 0.96 Å and 104.5°. Even the length and the strength of the hydrogen bond between two water molecules is reproduced in relatively good agreement with experiment [25]: we find an underestimation of the O–O distance and the dimerization energy of 3.3% and 7.5%, respectively. The surface is modeled with a periodically repeated slab, consisting of 12 atomic Si layers plus adsorbed water molecules. Further numerical details and the methodology for calculating RAS spectra are identical to Ref. [26].

The adsorption of water molecules leads initially to a configuration, where the oxygen atom is datively bonded to the down atom of the Si dimer. However, there is only a very small [10] or even vanishing [8] energy barrier for the decay of the molecular adsorption state: therefore the H₂O molecule dissociates across the dimer to produce H–Si–Si–OH, as shown in Fig. 1(a). The dissociated H and OH moieties saturate the dangling bonds of the Si surface dimers. The dissociation process is facilitated if in the immediate neighborhood there are other dissociated H₂O molecules: Adsorbed water tends to form islands on the surface [1]. For the saturation coverage of 0.5 ML, defined to correspond

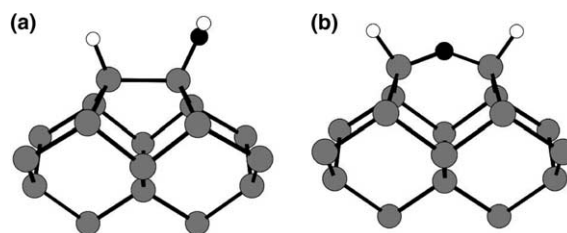


Fig. 1. Structurally optimized H₂O/Si(001) adsorption configurations: (a) dissociative adsorption and (b) oxygen insertion into the Si dimer. White, black and gray symbols indicate H, O and Si atoms, respectively.

to one adsorbed molecule per dimer, dissociative adsorption could possibly result in $p(2 \times 1)$ or $p(2 \times 2)$ symmetries, depending on whether the OH groups are adsorbed on the same side of two adjacent Si dimers along the dimer row or not. The $p(2 \times 1)$ configuration is energetically favored [10], due to the formation of weak hydrogen bonds. The dissociative adsorption of two H₂O molecules on neighboring Si dimers has recently been suggested to account for the observation of type-C defects on the Si(001) surface [27]. Annealing leads to surface oxidation. Thereby we find the oxygen insertion into the Si–Si dimer bond (i.e., the formation of H–Si–O–Si–H, Fig. 1(b)) to be clearly favored over oxygen insertion into the bonds between Si dimer atoms and its neighbors in the layer below. This is in contrast to total-energy results for the oxidation of Si(001) without co-adsorption of hydrogen [28], but corroborates earlier calculations [4,9] and experiments [3] on the interaction between water and the Si(001) surface.

Based on these findings we focus on the two structures shown in Fig. 1. Coverages of 0.125 and 0.5 ML are considered, corresponding to one or four molecules per Si(001) $p(4 \times 2)$ surface unit cell, respectively. For the low-coverage case we calculate adsorption energies of 2.34 and 3.10 eV for the dissociative adsorption and the oxygen insertion. These values increase to 2.46 and 3.18 eV for the saturation coverage, indicative for an attractive interaction between the fragmented molecules as found experimentally [1]. For the 0.5 ML case of the dissociative adsorption, we calculate bond lengths of 2.42, 1.68 and 1.49 Å for the Si dimer, the Si–O, and the Si–H bonds, respectively.

For the oxidized Si dimer we obtain a Si–O bond length of 1.66 Å and a Si–H bond length of 1.49 Å.

The calculated RAS spectra are shown in Fig. 2. The uppermost spectrum shows the result for the clean, $c(4 \times 2)$ reconstructed Si(001) surface. A strong, dimer-state related minimum occurs at 1.7 eV. An additional minimum/maximum structure slightly below/above the E_1/E_2 critical point energy of bulk Si at 3.5/4.3 eV results from surface-modified bulk states. The calculated results are in excellent agreement with the data measured on highly oriented, single-domain Si(001) surfaces prepared by electro-migration [16]. Experimental spectra obtained for vicinal Si(001) surfaces [13] show an additional feature around 3 eV that is due to surface steps [19,29].

The reflectance anisotropy of the Si surface changes upon adsorption of water. Irrespective of

the adsorption geometry, we find a H₂O coverage of 0.125 ML to mainly result in an attenuation of the optical anisotropies characteristic for the clean surface. In addition, the negative peak at the E_1 critical point energy is shifted to slightly higher energy in the case of the dissociated adsorption. Weak shoulders show up below the E_1 critical point and between the E_1 and E_2 energies for the dissociated and the dimer-inserted configuration, respectively. For energies higher than about 2 eV, the spectrum of the dimer-inserted configuration is somewhat down-shifted in comparison to the clean surface or the dissociative configuration. Altogether, however, the RAS spectra for Si(001) covered with few and isolated water molecules show no characteristic signatures that would allow for the detection of the water molecules or even the discrimination between different bonding configurations.

That changes with increasing coverage. For the saturation coverage of one molecule per dimer, both adsorption geometries lead to a complete cancellation of the dimer-related 1.7 eV feature. This is to be expected, because of the disappearance of the Si dimer-related states from the Si band gap region due to chemical saturation of the surface. The two adsorption geometries give rise to optical anisotropies that are clearly different for photon energies close to the Si bulk critical point energies. The RAS of the dissociative adsorption model nearly mirrors the one of the clean Si(001) surface: Positive/negative anisotropies occur at the E_1 and E_2 critical energies. The same phenomenon has been observed experimentally [15] and computationally [21] for the structurally similar monohydride-terminated Si(001) surface.

Oxygen insertion into Si dimers causes a broad negative feature for photon energies below E_1 and another negative peak near the E_2 transition energy. This is characteristic for Si(001) surfaces where the second Si layer has been oxidized [17]. This result appears at first sight puzzling, because in the dimer-inserted model studied here (Fig. 1(b)) only the first layer has been attacked by oxygen. However, the presence of hydrogen changes the surface energetics and thus the oxidation mechanism: for clean Si(001) surfaces the oxidation of the back bonds is energetically preferred over the oxidation of the Si dimers [28]. Therefore, oxidation of clean

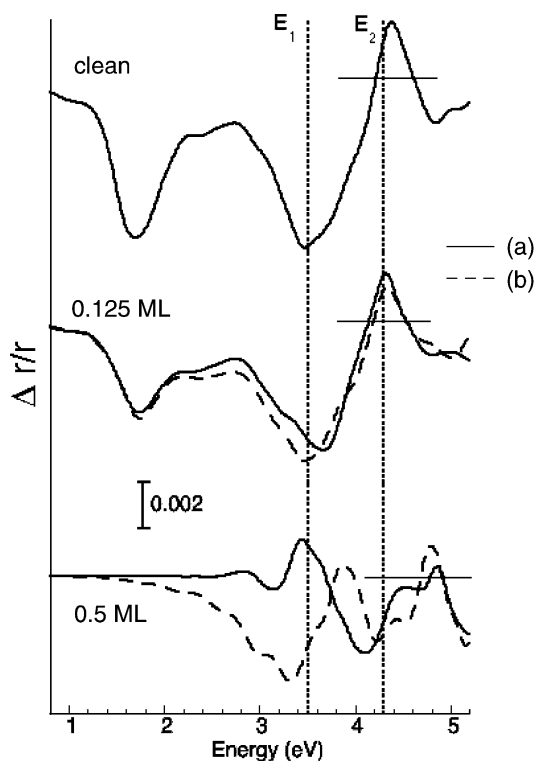


Fig. 2. RAS spectra $[Re\{(r_{[110]} - r_{[\bar{1}\bar{1}0]})/\langle r \rangle\}]$ calculated for the H₂O/Si(001) adsorption configurations shown in Fig. 1 are compared with results for the clean surface. The calculated positions of the E_1 and E_2 critical point energies as well as the positions of zero anisotropy are indicated.

Si(001) surfaces yields Si–O bonds parallel to the dimer direction only after the oxidation of the first layer. The H₂O-induced oxidation of the Si(001) surface, however, starts with the uppermost Si dimers [4]. Bearing the different oxidation mechanisms in mind, the spectrum calculated here for the dimer-inserted model is actually in excellent agreement with the experiment of Yasuda et al. [17].

We did not succeed in establishing a relation between the calculated RAS features and specific chemical bonds at the Si surface. Instead a large multitude of electronic states of predominantly bulk character was found to contribute to the optical anisotropies. This indicates that the H₂O-induced optical anisotropies arise predominantly in the Si bulk layers via an electronic coupling [30] or due to strain [31], at least in the energy range considered here.

In summary, we predict for low H₂O coverage the attenuation of the optical anisotropy of the Si(001) surface. For saturation coverage, i.e. if every Si dimer is involved in the interface bonding, the optical anisotropies are strongly structure dependent. Nevertheless, the detection of adsorbed H₂O molecules and the determination of their bonding configuration by means of RAS is difficult: the RAS spectrum of the dissociative adsorption is similar to that of the monohydride-terminated Si(001) surface, while the spectrum calculated for the oxygen-inserted model resembles measurements on oxidized Si(001).

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