

Dissociation of water molecules on Si surfaces

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Molecularly adsorbed water is weakened due to the chemisorption bond between oxygen and surface silicon and has a Fermi level lying in the conduction band. This unstable binding structure dissociates to yield a lower-energy configuration. Binding structures that may result from the dissociation in the temperature range from 300 to 750 K are discussed. With state-density calculations it is demonstrated that a dissociative binding structure, in which OH and H are chemisorbed to closely lying surface silicon atoms, accounts for the room-temperature ultraviolet photoemission spectrum.

Interaction of a water molecule with silicon surfaces is a very important step towards the understanding of the kinetics involved in the formation of the wet oxide. Regarding the binding structure of the water molecule chemisorbed on silicon surfaces, one is able to find various models suggested so far in the current literature, yet there has been no theoretical investigation interpreting the related spectra. At the present time the major controversy is whether the room-temperature chemisorbed H₂O is in a molecular or a dissociated state. As early as 1971, on account of the ellipsometry measurements, Meyer¹ proposed that each H₂O dissociates into 2H and O to saturate four dangling bonds. As opposed to that, Fujiwara² interpreted his ultraviolet photoemission spectrum (UPS) to imply that the adsorption of H₂O is nondissociative. By using high-resolution electron-energy-loss spectroscopy (EELS) Ibach *et al.*³ studied the vibrational properties of H₂O on Si surfaces and concluded that H₂O dissociates upon adsorption and forms a silicon hydride and hydroxyl group. Recently, we investigated the electronic energy structure of H₂O, molecularly adsorbed on the Si(111) surface,⁴ and showed that the calculated state densities cannot be reconciled with the UPS spectrum. Then, a number of questions, such as how the dissociation takes place and what kind of binding structure results, lead us to further study.

Taking the uncertainties in the atomic configuration into account at this preliminary stage, we would rather use a semiempirical approach, yet one simple enough to allow investigation of various binding geometries, and to reveal the fundamental aspects of the spectra. This approach is derived from the extended Hückel theory,⁵ and has a secular equation in the following form:

$$\sum_{j,n} \{ [K_{ij}(\vec{R}_n)(I_i + I_j) - E(\vec{k})] S_{ij}(\vec{R}_n, \vec{k}) \} a_j(\vec{k}) = 0 .$$

In this equation I_i is the energy of the i th orbital,

and $S_{ij}(\vec{R}_n, \vec{k})$ denotes the overlap integral between i th and j th orbitals with an internuclear distance of \vec{R}_n . For a proper description of the polarization effects, here we have considered $K_{ij}(R_n \neq 0)$'s and orbital exponents as parameters to be obtained from more sophisticated calculations. For the substrate K_{ij} 's and the orbital exponents have been determined to reproduce the absolute energies of $\Gamma_1, \Gamma_{25}, \Gamma_{15}, \Gamma_2$ and the indirect energy gap of the bulk Si. The resulting band structure is found to be in good agreement with that obtained from the first principles.⁶ To determine the parameters related with an adsorbate (such as H₂O, OH, SiH₄, etc.), we have used the concept of the chemical transferability, and select them so as to reproduce the self-consistent field energy levels of the corresponding molecule.⁷ To describe the interactions between Si and O we have selected the corresponding parameters which are able to yield state densities agreeing with the features of the UPS spectra⁸ taken from O adsorbed on Si(111) and the recent interpretation⁹ related to it. Stability with respect to the chosen parameters has been tested, and overlaps up to 18th nearest neighbors have been taken into account. Calculations have been performed by using periodic slab geometry.

First we concentrate on the molecular adsorption of H₂O. Figure 1(a) displays the He1 UPS difference curves.² Calculated adsorbate features corresponding to an overlayer of H₂O with a molecular plane perpendicular to the (111) surface are shown by the bars at the bottom of the same panel. The adsorbate features reveal that the $3a_1$ state of H₂O disappears as a result of the Si-O bond formed between O_{p_z} and the Si dangling bond, and consequently the adsorbed H₂O is weakened. More importantly, the Fermi level of this particular adsorbate-substrate system rises up to the conduction band at the full coverage. Similar results have also been obtained from H₂O adsorbed in different geometries (e.g., with a molecular plane perpendicular and also parallel to the surface,

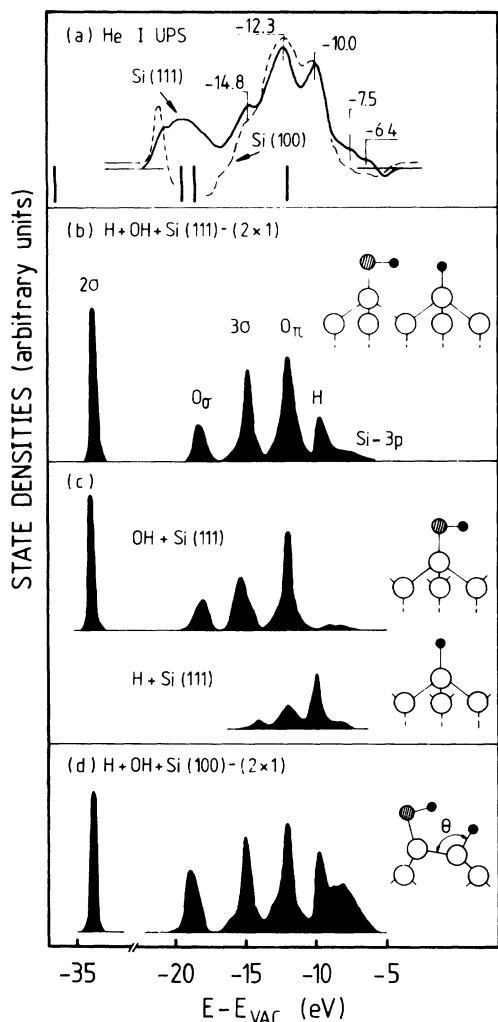


FIG. 1. (a) He I UPS difference curves of the Si(111) and Si(100) surfaces exposed to H_2O at room temperature are reproduced from Ref. 2. Bars at the bottom of the panel indicate the calculated states of molecularly adsorbed H_2O . (b) LDOS at OH and H calculated for a model structure where OH and H are attached to closely lying silicons to form a (2×1) structure on the ideal (111) surface of the 12-layer Si slab. (c) LDOS at OH, and H overlayers, each adsorbed on different surfaces of the 12-layer Si(111) slab. (d) LDOS at OH, H, and closely lying surface silicons of the 36-layer (100) slab reconstructed to form an asymmetric dimer. Insets describe the atomic configurations for each geometry. Internuclear distances of Si-O ($=2.93$ a.u.) and Si-H ($=2.79$ a.u.) are taken from SiO_2 and SiH_4 , respectively. $\theta = 109^\circ$. Empty, shaded, and small black circles denote Si, O, and H atoms, respectively.

but rotated in different angles), and lead to a conclusion that the binding structure resulting from the molecular chemisorption is unstable, and H_2O should dissociate to yield a lower-energy configuration. This conclusion is, in fact, substantiated by two important experimental results. One is the removal of the gap

states in the UPS spectrum² at a coverage of as low as 0.3–0.5 monolayer.¹ The other, which is a more conclusive one, is that the vibrational features (at 2090 and at 630 cm^{-1})³ of Si surfaces exposed to H_2O at 300 K coincide with features obtained from the H-adsorbed Si surface alone.^{10,11}

Let us now consider the dissociative adsorption of H_2O , and discuss a model³ that, among other theoretical models, gives the best account of the experimental data. The binding structure is simulated by a periodic overlayer consisting of alternating rows of OH and O, which are adsorbed to saturate closely lying dangling bonds. In Fig. 1(b), the local density of states (LDOS) at OH and H adsorbed together on the Si(111) surface¹² displays five distinct features (at -33.8 , -18.5 , -12.1 , and -9.9 eV). The sharp peak at -33.8 eV originates from the 2σ state of OH, and lies beyond the range of He I UPS. The combination of the Si s and O p_z orbitals establishes the chemisorption of OH, and also produces the O σ peak. In the previous interpretation the broad UPS structure at about -19 eV was not taken into account though its shape and energy location bear some resemblance to the theoretical peak. The most interesting feature in the calculated state density is the peak labeled by 3σ which lies very close to the -14.8 -eV UPS structure. The corresponding states are formed from the combination of O p_x and H s orbitals with a small contribution of the substrate, and thus resemble the 3σ state of OH. States resulting from the lone O $2p$ orbital (or 1π state of OH) and also from Si–H produce the O π peak, which coincides with the predominant peak of the UPS spectrum. At -9.9 eV the peak labeled by H is associated with the Si–H bond and is ascribed to the -10 -eV UPS feature. As one may note from Fig. 1(a), such an adsorbate state is not found in the molecular adsorption of H_2O . Based on this fact together with the small dispersions of the adsorbate bands we believe that the UPS data can safely be used to distinguish between dissociative and molecular adsorption models. The broad structure at the upper portion is derived primarily from the surface Si p orbitals. More importantly, our results indicate that the occupied conduction-band states of Si with a molecular H_2O adsorbed are emptied after the dissociation.

In Fig. 1(c) LDOS's of two overlayers, each formed from OH and H alone and adsorbed at different surfaces of the Si slab, give more insight into the electronic structure. The features in the UPS spectrum, as well as in Fig. 1(b), can clearly be understood in terms of the combination of the state densities obtained from OH and H overlayers. However, the interaction between closely lying Si–OH and Si–H groups tends to shift the peaks O σ and 3σ so as to yield a better agreement with the UPS spectrum. This may be interpreted to imply that H prefers to attach to surface Si in the close neighbor-

hood of OH. Also it should be noted that the state density associated with H overlayer is in good agreement with the work of Pandey *et al.*¹³

The UPS spectra obtained from the Si(111) and Si(100)-(2 × 1) both exposed to water show similar features, which can be explained by the same bond order in these surfaces. Calculations of the above dissociative adsorption on the Si(100) surface have been carried out for different (2 × 1) reconstruction geometries, leading to similar broad features. In Fig. 1(d) we present the LDOS where OH and H adsorbed on the raised and lowered Si atoms of the asymmetric dimer,¹⁴ respectively. This binding structure is favored because the raised Si provides more charge for OH, and thus yields to a higher total electronic energy. Adsorbate-induced states have the same character discussed for the (111) surface, and are in good accord with the experimental spectrum.

On the basis of the present calculations and the comparison with the experimental UPS data² as well as in view of the vibrational spectra,^{3,10,11} the dissociative adsorption via OH and H is clearly favored at room temperature. At this point we briefly comment on the model proposed by Meyer.¹ The ellipsometric results indicated the removal of the dangling bond surface states indigenous to the clean surface upon water adsorption. Therefore the model rationalizes the saturation of dangling bonds by bridge-bonded oxygen and hydrogen atoms. The water molecule is hence assumed to be fully dissociated. Interestingly, the polarizability derived for oxygen after water adsorption was found to be different from the polarizability after the pure oxygen adsorption. In the latter case the data could be explained by the optical constants of the SiO₂ layer. This may point to the fact that water adsorption does not lead to the bridge-bonded oxygen. Let us discuss the coverage values derived by Meyer,¹ which were shown to be compatible with the saturation of all dangling bonds existing on the Si(111) and Si(100) surface, respectively. Because coverage-dependent measurements in the course of the vibrational study are available for the Si(100) surface we will compare the results for this surface. In both studies a saturation coverage of 0.5 was obtained. In favor of the model presented here the LEED pattern observed after water adsorption on Si(100) shows a perfect (2 × 1) superstructure as in the case of the clean surface. As is also confirmed by our orbital population analysis this superstructure is fully accounted for by an asymmetric dimer formation on the clean surface leaving two different dangling bonds per (2 × 1) surface unit cell. The saturation of these dangling bonds by H and OH needs half a monolayer of water.

It is interesting to note that Meyer's model can (at least partially) be realized at elevated temperatures. Figure 2 shows vibrational spectra¹¹ obtained after H₂O exposure to the Si(100) surface and heating suc-

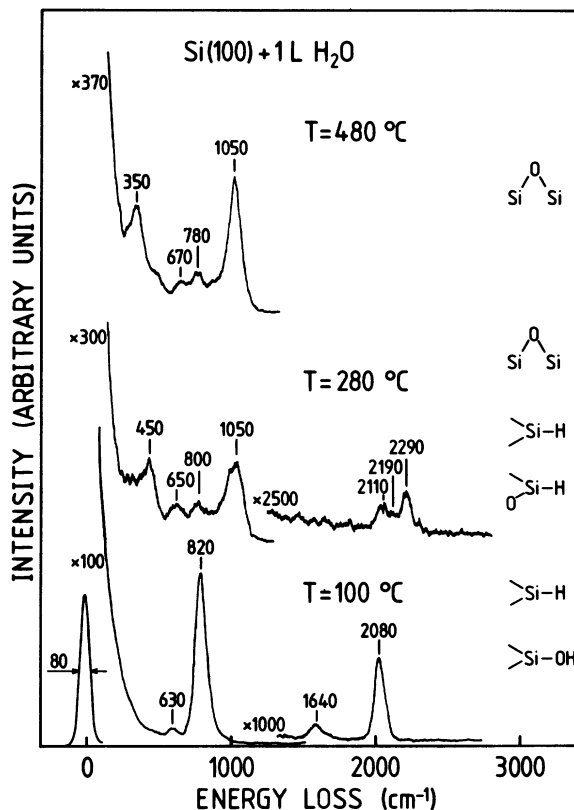


FIG. 2. EELS spectra after 1 L of H₂O on the Si(100) surface are taken from Ref. 11. The lower trace was observed at 100 °C. The middle and upper traces were obtained by heating successively to 280 and 480 °C, respectively. Insets describe possible atomic configurations associated with each temperature.

cessively to higher temperatures. The spectrum observed after adsorption is consistent with the formation of SiOH and SiH complexes.^{3,11} Heating to 280 °C causes the vibrational features to change drastically. The vibrational loss at 820 cm⁻¹ characteristic for the hydroxyl group disappears and a feature at 1050 cm⁻¹ develops which is easily interpreted as the asymmetric stretch mode of bridge-bonded oxygen. Note that the Si-H stretch mode around 2100 cm⁻¹ is still present, and additional modes at 2190 and 2290 cm⁻¹ appear which are associated with H bonded to Si being backbonded to either one or two oxygen atoms. In this adsorption state the water molecules are fully dissociated as proposed by the Meyer model. At even higher temperatures ($T = 480$ °C) H has desorbed and only oxygen is left in a bridge-bonded configuration.

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¹²Because there is no well-established geometry for Si(111)-(2 × 1) we assumed that silicon atoms of the (111) surface stay in their ideal positions.

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