PHYSICAL REVIEW B **66**, 113306 (2002)

Theoretical study of water adsorption on the Ge(100) surface

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(Received 11 June 2002; published 12 September 2002)

We present first-principles density-functional calculations for the adsorption of water on the Ge(100) surface. The dissociation of water molecules into OH and H species is energetically favored over the molecular adsorption, where O forms a bond to the down atom of the Ge dimer, similar to the case of Si(100). However, on Ge(100) the energy barrier for water dissociation is calculated to be $\sim$0.49 eV, which is significantly larger than our previous value (0.15 eV) on Si(100). Since the molecular adsorption on Ge(100) has a relatively smaller adsorption energy of 0.33 eV compared to that (0.57 eV) on Si(100), adsorbed water molecules on Ge(100) prefer desorption rather than dissociation upon being thermally activated. This result provides an explanation for the experimental observations on Ge(100), where water does not stick easily at room temperature.

DOI: 10.1103/PhysRevB.66.113306 PACS number(s): 68.43.−h, 68.35.Bs, 71.15.Nc

The interaction of water and ammonia molecules with semiconductor surfaces is of considerable interest because of the importance of oxidation and nitridation in semiconductor device technology. During the last two decades, the single-crystal surfaces of silicon[1–3] and germanium[4] have been used in many adsorption studies. As a prototype system for chemisorption on semiconductor surfaces, the interaction of water molecules with the Si(100) surface[5–13] has received much attention, whereas only little work was spent on the investigation of the water-covered Ge(100) surface.[7,14,15] In spite of the superficial similarities of both surfaces in the crystal structure and the surface reconstruction, they show a chemically subtle difference in water adsorption, as we demonstrate in the present work.

It is well established both experimentally[7–9] and theoretically[10–13] that on Si(100) water dissociation easily occurs by saturating the dangling bonds of the Si dimers with the dissociated OH and H species. Using high-resolution infrared spectroscopy, Chabal and Christman[7] found that on Si(100) water chemisorbs dissociatively in the temperature range 80–500 K, whereas on Ge(100) water dissociation does not take place at 80 K but appears upon warming to room temperature. This contrasting behavior for water adsorption on Ge(100) has been subsequently confirmed by the different experimental tools such as photoelectron spectroscopy,[14] high-resolution electron energy-loss spectroscopy[15] (HREELS), and temperature-programmed desorption[16] (TPD). In addition, these experimental works[14–16] found that the sticking coefficient for water on Ge(100) is very low at room temperature compared to a unity value on Si(100). Despite all these experimental observations, it seems that there are no theoretical studies for understanding the somewhat surprising differences in the water adsorption on Si(100) and Ge(100).

In this paper, using first-principles density-functional theory calculations, we study not only the structural and bonding properties of adsorbed water on Ge(100) for coverages of $\theta = 0.25$ and 0.5 ML (half coverage is defined as one molecule per surface dimer[14–17]), but also the kinetics of water dissociation. Our results show that a water molecule weakly bonds to the down atom of the Ge dimer, with a relatively smaller adsorption energy compared to that on Si(100). Although the dissociative adsorption in which water molecules are dissociated into OH and H species is energetically favored over the molecular adsorption, the energy barrier for the dissociation is calculated to be larger than the adsorption energy of the molecular state. Thus, unlike Si(100) on which water dissociation readily occurs even at 80 K, we predict on Ge(100) that adsorbed water will not be dissociated at such a low temperature. Moreover, our results for the energy profile of water dissociation explain the very difference of water sticking on the Si(100) and Ge(100) surfaces.

Our total-energy and force calculations were performed by using density-functional theory[18] within the generalized-gradient approximation[19] (GGA). The O (Ge and H) atom is described by ultrasoft[20] (norm-conserving[21]) pseudopotentials. The surface is modeled by a periodic slab geometry. Each slab contains eight Ge atomic layers plus adsorbed water molecules on both sides of the Ge surface. The thickness of the vacuum region between these slabs is about 9 Å. The electronic wave functions are expanded in a plane-wave basis set using a cutoff energy of 20 Ry, and the electron density is obtained from the wave functions calculated at eight and four **k** points in the surface Brillouin zone of the (2×1) and (2×2) unit cell, respectively. All the atoms except the innermost two Ge layers are allowed to relax along the calculated Hellmann-Feynman forces until all the residual

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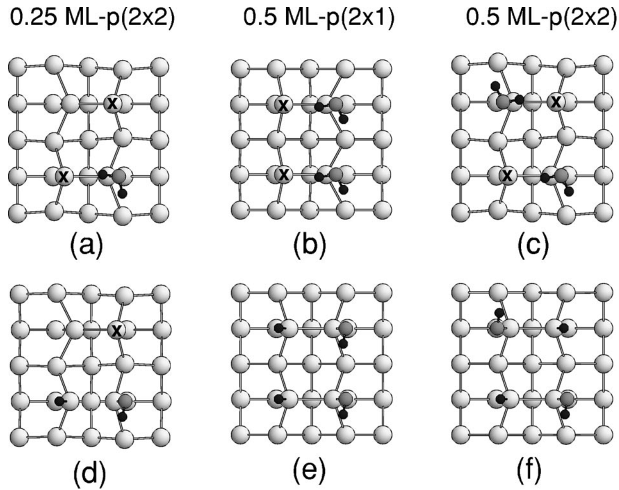

FIG. 1. Top views of several adsorption configurations of water on Ge(100) with $\theta=0.25$ and 0.5 ML: (a),(b),(c) the molecular adsorption and (d),(e),(f) the dissociative adsorption. The large, medium, and small circles represent Ge, O, and H atoms, respectively. For distinction the up atoms of the Ge dimers are marked (X).

force components are less than 1 mRy/bohr. These calculation parameters were successfully applied in our previous study of water adsorption on Si(100), yielding well-converged results for the adsorption geometries and energetics.[13,22]

We first determine the atomic structure of adsorbed water on Ge(100) for several configurations that were considered in our previous study[13] on the water-covered Si(100) surface. The top view of the optimized structure for each configuration is shown in Fig. 1, and the calculated adsorption energy and bond lengths are listed in Table I, together with our previous results[13] for water adsorbed on Si(100). We find that for $\theta=0.25$ ML the dissociative state [Fig. 1(d)] is largely stabilized over the molecular state [Fig. 1(a)] by 0.73 eV in adsorption energy (see Table I). In the molecular state the calculated adsorption energy ($E_{\mathrm{ads}}=0.33$ eV) for $\theta=0.25$ ML is found to be larger than that ($E_{\mathrm{ads}}=0.20$ eV) for 0.5 ML [Fig. 1(b)]. On the other hand, the dissociative state at $\theta=0.25$ ML [Fig. 1(d)] has a relatively smaller adsorption energy of 1.06 eV compared to that ($E_{\mathrm{ads}}=1.15$ eV) at 0.5 ML [Fig. 1(e)]. These results imply a repulsive interaction between adsorbed water molecules in molecular adsorption, but an attractive interaction between OH species in dissociative adsorption. We note that, when water molecules are adsorbed on all the down atom sites within the $p(2\times2)$ periodicity [shown in Fig. 1(c)], the adsorption energy increases by 0.08 eV compared to the $p(2\times1)$ configuration [Fig. 1(b)] with the same coverage of $\theta=0.5$ ML (see Table I). However, this trend is reversed in the dissociative adsorption: the adsorption energy of the $p(2\times2)$ configuration at $\theta=0.5$ ML [Fig. 1(f)] decreases by 0.05 eV compared to the $p(2\times1)$ configuration of Fig. 1(e) (see Table I). Thus, we can say that the $p(2\times1)$ dissociative state, where the dissociated OH species are aligned along the dimer row, becomes the most stable one.

It is likely that there are two contributions to the greater binding energy associated with Fig. 1(c) relative to Fig. 1(b). The first is that the water molecules are farther apart and the second is that the alternating tilt of the Ge dimers (found on the clean surface) is maintained, whereas in Fig. 1(b) all the dimers are tilted in the same direction with the O bonded Ge being lower. Because the dimers are flat in Figs. 1(e) and 1(f), their energy difference can only be due to attractive interactions between the species. Because the second neighbor H-OH distance is larger and the first neighbor OH-OH distance is smaller in Fig. 1(e), we conclude that its greater adsorption energy is a result of OH-OH attraction, in particular, an attraction between the hydroxyl O on one site and the hydroxyl H on a neighboring site. In addition to the OH-OH attraction some of the extra adhesion energy with 0.5-ML coverage may be due to a reduction in the strain energy per dimer when all the dimers are strained in the same way.

As shown in Table I, the adsorption energy of the molecular (dissociative) state on Ge(100) is smaller than that on Si(100), indicating that the bonding of water (hydroxyl) to Ge(100) is weaker than that on Si(100). For both coverages of 0.25 and 0.5 ML the adsorption energy difference of the molecular (dissociative) state between Si(100) and Ge(100) amounts to $\sim0.15(1.32)$ eV. Since the bond length $d_{\mathrm{O\text{-}Ge}}(d_{\mathrm{O\text{-}Si}})$ between the O atom and its bonded Ge (Si) atom reflects the strength of bonding, it is interesting to compare those bond lengths at the two surfaces. Considering that

TABLE I. Calculated adsorption energies and bond lengths of adsorbed water on Ge(100) for structures shown in Figs. 1(a)-1(f). M and D indicate molecular and dissociative. The asterisk indicates the data obtained from additional calculations with a plane-wave basis cutoff of 25 Ry (Ref. 22). For comparison our previous results (Ref. 13) on Si(100) are given in parentheses.

θ(ML)	Figure	E_{ads} (eV)	$d_{\mathrm{Ge\text{-}O}}$ (Å)	$d_{\mathrm{Ge\text{-}Ge}}$ (Å)	$d_{\mathrm{Ge\text{-}H}}$ (Å)
0.25M	1(a)	0.33(0.57)	2.28(2.03)	2.60(2.42)	
0.25M*		0.34	2.29	2.61	
0.5M	1(b)	0.20(0.36)	2.36(2.12)	2.56(2.38)	
0.5M	1(c)	0.28(0.53)	2.31(2.05)	2.59(2.41)	
0.25D	1(d)	1.06(2.37)	1.85(1.69)	2.58(2.43)	1.57(1.51)
0.25D*		1.04	1.86	2.58	1.57
0.5D	1(e)	1.15(2.47)	1.85(1.70)	2.58(2.44)	1.57(1.51)
0.5D	1(f)	1.10(2.42)	1.84(1.69)	2.57(2.44)	1.57(1.51)

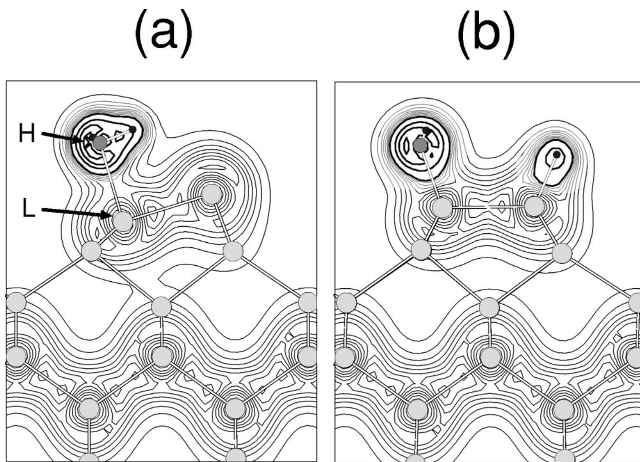

FIG. 2. Calculated charge densities for adsorbed water on Ge(100): (a) the molecular state [Fig. 1(a)] and (b) the dissociative state [Fig. 1(d)]. Two kinds of contour spacings are used. The first thin line is at 7.5 millielectron/$bohr^3$ with spacings of 7.5 millielectron/$bohr^3$ and the first thick line is at 75 millielectron/$bohr^3$ with a spacing of 75 millielectron/$bohr^3$ between thick lines. The high (H) and low (L) charge density regions are indicated. The plots are drawn in a vertical plane containing the buckled dimer atoms, the fourth-layer, and the fifth-layer atoms and do not include the O 2s bands.

the lattice constant of bulk Ge is larger than that of bulk Si by about 4%, the difference between $d_{\text{O-Ge}}$ and $d_{\text{O-Si}}$ in the molecular (dissociative) adsorption is significant as a ratio of $r \equiv (d_{\text{O-Ge}} - d_{\text{O-Si}})/d_{\text{O-Si}} \sim 12(9)\%$ (see Table I). Thus, this relatively larger ratio r indicates that the bondings of water and hydroxyl to Ge(100) are much weaker than to Si(100). Note that the magnitude of r in the molecular and dissociative adsorptions is similar to the corresponding value ($r \sim 10\%$) in germanium and silicon oxides which have ionic bonds. Thus, the bonding nature of water and hydroxyl on Ge(100) and Si(100) is expected to be ionic. This expectation is well demonstrated by the charge-density plots of the O−Ge bond in the molecular and dissociative adsorptions (see Fig. 2). Here, the high valence electron density (excluding the split off O 2s bands) locates around the O atom, whereas the low valence electron density locates around the bonded Ge atom, without any sign of covalent charges between O and Ge atoms. It is notable that the bond lengths of $d_{\text{O-Ge}}$ and $d_{\text{O-Si}}$ in the dissociative adsorption are significantly shorter than those in the molecular adsorption (see Table I). This is attributed to an enhanced ionic nature of the O−Ge bond in the dissociative adsorption because of the transfer of a H atom to the up atom. Note that the largest contour encircling the Ge is 37.5 millielectrons/$bohr^3$, while the smallest contour encircling the water or hydroxyl is 45 millielectrons/$bohr^3$. The shorter hydroxyl-Ge bond length is a consequence of the separation between those two contours being an order of magnitude smaller than for water-Ge. This we attribute to OH being able to attract charge better from Ge than is H_2O. The diminution of Ge charge due to the OH ion is also seen along the Ge dimer bond where the 67.5 millielectrons/$bohr^3$ contour, present for H_2O bonding, is missing.

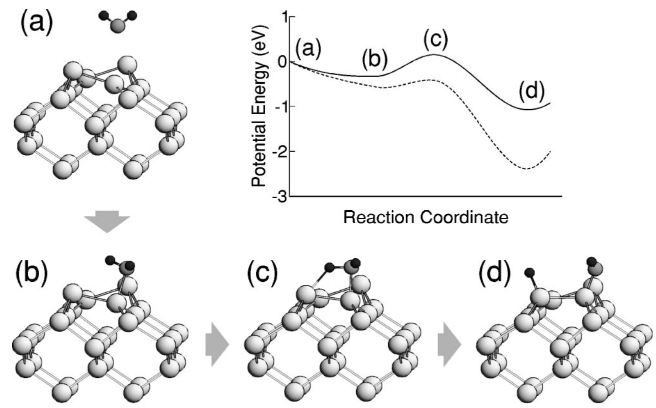

FIG. 3. Calculated energy profile (solid line) of adsorbed water molecule on Ge(100). The atomic geometries of four representative points are given: (a) the gas state, (b) the molecular state, (c) the transition state, and (d) the dissociative state. The dashed line represents the energy profile obtained in our previous study (Ref. 13) on Si(100).

In order to understand why water dissociation on Ge(100) is less likely than on Si(100),[7,14,15] we calculate the energy profile for the dissociation by optimizing the structure as a function of increasing distance $d_{\text{O-H}_\text{d}}$ between the O atom and the dissociated H atom. Here we optimize the structure for each fixed value of $d_{\text{O-H}_\text{d}}$ using the gradient-projection method.[23] In Fig. 3, the calculated energy profile and the atomic geometries of several representative states are displayed. The energy barrier from the molecular state [Fig. 3(b)] to the dissociative state [Fig. 3(d)] is $E_\text{b} = 0.49$ eV, larger than $E_{\text{ads}} = 0.33$ eV of the molecular state. Assuming an Arrhenius-type activation process with a typical value ($\sim 10^{13}$) for the preexponential factor, we estimate that at a temperature of 80 K the thermal reaction rate for water desorption is $\sim 2 \times 10^{-8} \text{s}^{-1}$, indicating the trapping of adsorbed water molecules in the molecular state. On the other hand, at room temperature the reaction rate for dissociation is $\sim 6 \times 10^4 \text{s}^{-1}$ which would make it probable were it not for the fact that this is only 0.2% of the desorption rate of $\sim 2.9 \times 10^7 \text{s}^{-1}$. Thus, we can say that at room temperature water desorption is easily activated, accompanied by a very small portion of water dissociation. Obviously, this aspect for adsorbed water on Ge(100) results in low sticking at room temperature, as observed in the photoelectron spectroscopy,[14] the HREELS,[15] and the TPD[16] experiments. Especially, the HREELS study[15] observed no detectable molecular adsorption nor dissociation at room temperature up to a water exposure of 100 L. In contrast, on Si(100) water dissociation easily takes place because of a shallow energy barrier of $E_\text{b} = 0.15$ eV (see the dashed line in Fig. 3),[13] leading to an observed unity sticking coefficient.[7]

Since the sticking coefficient of water on Ge(100) is very low at room temperature, a water layer was formed at low termperature and then warmed up to the desired temperature.[7,14,15] Kuhr and Ranke[14] found by photoelectron spectroscopy that at 110 K water adsorbs molecularly without dissociation, but annealing the surface at temperatures between 140 and 300 K causes the dissociation of water

molecules with the formation of hydroxyl radicals. The HREELS experiment carried out by Papagno *et al.*[15] reported that even at 100 K both molecular and dissociated water are present. Our calculated energy barrier for water dissociation on Ge(100) is too high to explain this experimental evidence for the dissociation. However, a condensed water layer formed at low temperature may lower the dissociation barrier as a consequence of the interaction between adsorbed water molecules. As a matter of fact, we find that the dissociation barrier (E_b=0.37 eV) calculated by using $p(2\times1)$ unit-cell is reduced by 0.12 eV compared to that (E_b=0.49 eV) obtained from the $p(2\times2)$ unit-cell calculation. Thus, we believe that water dissociation may be facilitated in the condensed water layer by the reduced dissociation barrier due to the interaction between adsorbed water molecules.

In summary, we have performed first-principles density-functional calculations for the adsorption of water on the Ge(001) surface. We found that the bonding of water molecules and dissociated hydroxyls to Ge(100) is much weaker than to Si(100). The calculated energy profile for water dissociation on Ge(100) qualitatively differs from that on Si(100). Unlike Si(100), which has a shallow energy barrier for water dissociation, we found that Ge(100) has a high-energy barrier relative to the adsorption energy of the molecular state, thereby contributing to the low sticking coefficient.

This work was supported by the National Science Foundation under Grant No. DMR-0073546, the Welch Foundation (Houston, TX), National Partnership for Advanced Computational Infrastructure at UC San Diego, and the Advanced Computing Center for Engineering and Science (The University of Texas at Austin). K.S.K. acknowledges the support from Creative Research Initiatives of the Korean Ministry of Science and Technology. K.J.J. acknowledges the research support from a grant for State Key Program of China.

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