

The Effect of H₂O Chemisorption on the Reconstruction of the Si(100) Surface: a Theoretical Approach

Seongeun Yang and Hojing Kim*

Department of Chemistry, Seoul National University, Seoul 151-742, Korea

Received June 7, 1995

The structure and electronic properties of the Si(100) surface is studied using the atom superposition and electron delocalization method. The energy released when the symmetric dimer surface is reconstructed to form the buckled dimer surface with $p(2 \times 2)$ symmetry is calculated to be 0.99 eV per dimer in the case of ideal clean surfaces. This indicates that the surface dimer buckling is intrinsic from the viewpoint of thermodynamics. The relaxation energy, when water is adsorbed on the clean symmetric dimer surface to form the buckled dimer surface, is 2.25 eV per dimer for appropriate coverages. These results show that H₂O molecule could induce a reconstruction of the surface structure through adsorption. The buckling of the surface dimer is, therefore, more favorable under the existence of water vapour. This conclusion supports the recently obtained experimental observations by Chander *et al.*

Introduction

Due to the importance of wet oxidation in electronic device preparation, the water adsorption on Si surfaces has been of much interest. Among various Si surfaces, the Si(100) surfaces have been studied most rigorously due to its simple reconstructed phase and the common use as device substrates. The major concern in many experimental¹⁻⁶ and theoretical⁷⁻⁹ studies has been the chemisorption states – molecular or dissociative – of H₂O on the Si surface. These works have implied that the adsorption states of H₂O are determined by the local structure of the surface. In the present work, however, the main concern is the more active role of H₂O. H₂O induces a reconstruction of the Si surface to form the buckled dimer surface, or it stabilizes the buckled dimer surface through its adsorption on this surface. Experiments using scanning tunneling microscopy (STM) technique have reported common characteristics of Si surfaces that buckled dimers occur in the vicinity of defects.¹⁰⁻¹² Chander *et al.* argued that these buckle-inducing defects are produced by the adsorption of water.¹³ They suggested that the defect which is itself a buckled dimer adsorbed by H₂O stabilizes the buckled dimer along the dimer row. In other words, H₂O induces the buckling of dimers through its molecular adsorption on one dimer. In this work, these arguments are confirmed by the cluster model calculations and the analysis of the density of states (DOS) of the cluster. H₂O is molecularly adsorbed on the on-top site of a Si atom, and the defect is pictured as one buckled dimer on which H₂O is adsorbed rather than buckled dimers on which H₂O molecules form hydrogen bonds between them.²

The clean symmetric dimer surface is the starting geometry for discussions and this surface is reconstructed to form the buckled dimer surface. The optimized geometric variables such as the dimer bond length and the back bond length (the bond length between surface atom and second layer atom) are compared with other theoretical results. On these optimized surfaces, H₂O molecule is adsorbed and is set to relax. Through the comparison of the degree of stabilization of various surfaces from the clean symmetric dimer

Table 1. Parameters used in the calculations: *n* is the principal quantum number, IP is the ionization potential (eV) and ξ is the Slater orbital exponent (au)

atom	s			p		
	<i>n</i>	IP	ξ	<i>n</i>	IP	ξ
H	1	12.3	1.2			
O	2	27.18	2.146	2	12.32	2.127
Si	3	14.76	1.634	3	9.45	1.428

surface, the conclusion is drawn out that the configuration of the buckled dimer surface in the presence of H₂O is fixed with much longer duration than the clean buckled dimer surface.

Method

Throughout this study, we use the semi-empirical atom superposition and electron delocalization molecular orbital (ASED-MO) method developed by Anderson *et al.*¹⁴ This method evaluates the total energy as the sum of a repulsive atom superposition energy and the attractive energy caused by the electron delocalization, and approximates the delocalization energy to the difference between atomic and molecular orbital energies.

The atomic parameters (valence shell ionization potential and Slater orbital exponents) used in this study are taken from the studies of Anderson and coworkers on similar systems: those of silicon and hydrogen are taken from the study of acetylene adsorption on Si(111) surface¹⁵ yielding good estimates of bond lengths of surface dimers in the present studies, and those of oxygen are taken from the work of Yu and Anderson.¹⁶ The parameters are given in Table 1.

The Si(100) surface is modeled by a four-layer-thick Si₁₇H₆₀ cluster. The dangling bonds of the cluster are saturated with hydrogen atoms. But the surface which will be adsorbed by H₂O molecules is left as it is unsaturated. Before optimization, all Si atoms in the clusters are in their bulk positions.

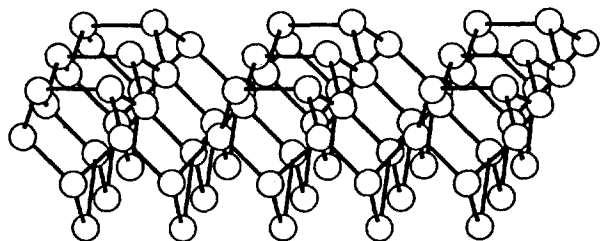


Figure 1. Si(100) surface with symmetric dimers on the surface. The surface dimer bond length is 2.54 Å after optimization and the bulk bond length is 2.35 Å.

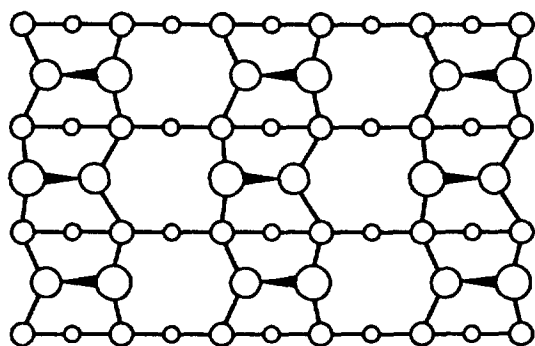


Figure 2. Top view of the p(2×2) surface. The largest circles are the atoms displaced upward through relaxation and this picture is drawn to the third layer denoted by the smallest circles.

Energy minimization is performed as the surface atoms are displaced from their ideal (1×) positions by 0.01 Å to obtain the optimized geometry of the reconstructed symmetric dimer surface shown in Figure 1. Furthermore, minimization of the total energy is carried out as each dimer of the symmetric dimer surface is relaxed to form the buckled dimer surface with p(2×2) symmetry shown in Figure 2. This optimization of the cluster is performed up to the second layer and the deeper layers are fixed at their bulk positions. The bond length between bulk Si atoms is fixed at 2.35 Å and Si-H distances is also fixed at 1.48 Å. The adsorption model of H₂O on these clusters is shown in Figure 3. The on-top site is chosen for the adsorption based on the observations in many STM experiments.^{10–13} The internal geometry of H₂O is unchanged from that of the free gas state because the change gives no significant lowering in the total energy. The results of energy minimization by the optimization of geometric variables are given in the next section. In all structure determinations, the intervals between each step of calculation are 0.01 Å for bond lengths and 1° for bond angles.

To explain the calculational results qualitatively, the DOS's of the Si cluster are analyzed. But it is difficult to compare the DOS curves of the Si cluster simply by overlapping them since the contribution from the Si bulk dominates over the H₂O's. To obtain useful informations or to compare with other experimental results, we use the concept of crystal orbital displacement (hereafter referred to as COD) which gives easy understanding about the changes in electronic structures of interacting sublattices in solid.¹⁷ The COD is defined as the difference between the projected density of states

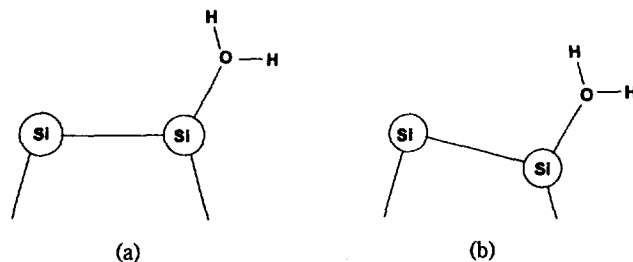


Figure 3. Adsorption geometries of H₂O bonded towards the direction of the dangling bond of a Si atom on Si(100) surface (a) adsorption on a symmetric dimer (b) adsorption on a buckled dimer with p(2×2) symmetry.

Table 2. Comparison of the symmetric dimer bond lengths and the back bond lengths (d_{12})

	Present work	Tromp <i>et al.</i> ^a	Verwoerd ^b	Redondo <i>et al.</i> ^c
d	2.54 ^d (2.27) [†]	2.54	2.75 (2.24)	2.66 (2.47)
d_{12}	2.41	2.41		

^asee reference 18. ^bsee reference 19. ^csee reference 20. ^dspin-paired. [†]spin-unpaired.

of a sublattice in solid ($d^S(\epsilon)$) and the density of states of the sublattice alone ($d^A(\epsilon)$).

$$\Delta^A(\epsilon) = d^S(\epsilon) - d^A(\epsilon) \quad (1)$$

The equation (1) is applied to each energy state. From the analysis of COD curves, the perturbation by the other interacting sublattice is easily known. The necessary condition for the COD functions to be significant is that the DOS curves analyzed must be normalized in the whole region of energy so that the normalization gives the total number of orbitals per unit cell (N).

$$\int_{-\infty}^{+\infty} d^S(\epsilon) d\epsilon = \int_{-\infty}^{+\infty} d^A(\epsilon) d\epsilon = N \quad (2)$$

Results

Optimization of the symmetric and buckled dimer surfaces. The optimized geometry of the symmetric dimer surface reconstructed from the ideal (1×1) Si(100) surface is shown in Figure 1 and its geometrical variables are listed in Table 2. Since each surface atom possesses two dangling orbitals (or dangling bonds), the formation of the symmetric dimer is proceeded in two different ways: two dangling orbitals contribute to a dimer bond in spin-paired configuration, while only one of them participates in a dimer bond formation in spin-unpaired one. In spin-unpaired case, the optimized dimer bond length is 2.54 Å and the optimized back bond length (bond length of Si₁-Si₂) is 2.41 Å. These values are in good agreement with those from the ab initio calculations using a cluster with monohydride phase on the surface,¹⁸ but show large differences with the results of Verwoerd¹⁹ and Redondo *et al.*²⁰ In spin-paired case, the dimer bond length is determined to be 2.27 Å and it is much shorter than that of spin-unpaired case and is comparable with

Table 3. Optimized variables of the adsorbed surfaces

	Symmetric	Buckled
d^a	2.54	2.29
d_{12}^b	2.41	2.41
δ^c		3-4
r^d	1.55	1.55
θ^e	111	109

^a d : dimer bond length (Å). ^b d_{12} : back bond length (Å). ^c δ : tilting angle (°). ^d r : Si-O bond length (Å). ^e θ : the angle between atoms Si-Si-O (°)

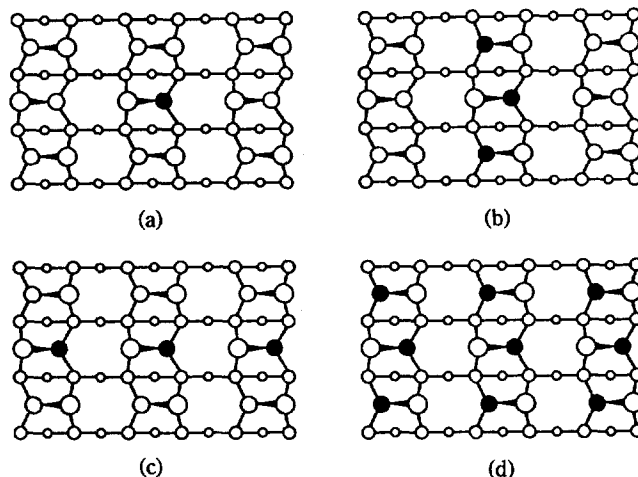
Table 4. Binding energy (eV) per H₂O molecule on surfaces of different coverages. The adsorption geometries are the same as in Figure 3 and the sites are represented in Figure 4 as dark circles. The coverage is defined as the number of H₂O molecules divided by the number of surface atoms. ΔE_B is the buckling energy per dimer (in eV) for each case. The second column is related with ΔE_3 , and the third with ΔE_2 in the schematic diagram of the Born-Haber cycle

Coverage	Symmetric surface	Buckled surface	ΔE_B
1/18	+3.06	-0.423	-1.38
1/6	+3.33	-0.443	-2.25
1/6	+3.34	-0.193	-2.27
1/2	+4.46	+1.087	-4.36

the bond length of the optimized buckled dimer. Although the cluster geometry is optimized up to the second layer, rather small changes in the second layer structure are observed. From now on, calculations are performed consistently in spin-unpaired way for the symmetric dimer.

The optimized geometry of the buckled dimer surface is shown in Figure 2 and its geometrical variables are given in Table 3. The optimized bond length is 2.29 Å and the tilt angle (the angle between Si₁-Si₂ and the ideal Si(100) surface) is 3 to 4 degrees within the uncertainty of the calculations. The bond length is in a good agreement with others (2.25 Å to 2.44 Å): the tilt angle is rather small compared with others (7.4° to 20.5°)²¹⁻²⁶ but they are in a qualitative agreement. The buckled dimer surface is stabilized by the amount of 0.99 eV per dimer compared with the symmetric dimer surface. The overestimation of this stabilization energy (or buckling energy) compared with the results of Roberts *et al.*²⁷ (0.35 eV for the Si(001) surface), those of Artacho *et al.*²⁸ (0.40 eV in the closed-shell approximation) and those of Chadi²¹ (0.46 eV) stems from the systematic errors of the ASED method.²⁹ But these results indicate qualitatively that the buckling of symmetric dimers on the Si(100) surface could occur intrinsically. The sign of atomic charges implies a charge transfer from the down atom to the up atom. The amount of this charge transfer is 0.28 e and agrees reasonably well with other results of 0.36 e.²¹

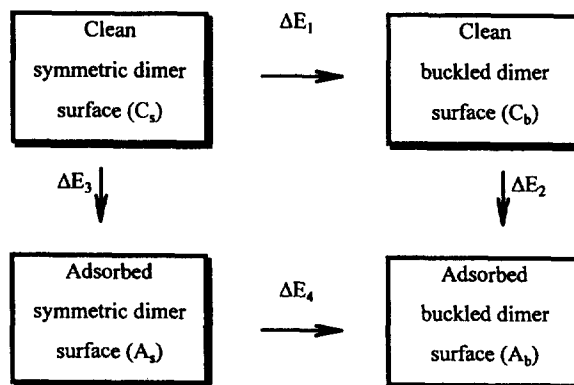
Adsorption of H₂O on the optimized clean surfaces. To examine that H₂O adsorbed on the Si(100) surface could induce surface buckling, the buckling energies of the clean and the adsorbed surfaces are compared. The

**Figure 4.** The H₂O adsorption sites for the various coverages: (a) 1/18, (b) 1/6, (c) 1/6, and (d) 1/2. The coverage is defined as the number of Si atoms adsorbed by H₂O over the surface Si atoms.

buckling energy here (denoted as ΔE_B in Table 4) is defined as the difference in total energy between the final buckled configuration and the initial symmetric configuration of the surface covered with H₂O.

The optimized geometrical variables of the adsorbed configuration on the symmetric and the buckled dimer surface are listed in Table 3. The dimer bond length and the back bond length show no change from the values of the corresponding clean surfaces. The Si-O bond length⁸⁻⁹ turns out to be the same on both symmetric and buckled dimer surfaces. The optimized angle between the dimer bond and the Si-O bond shows that H₂O is most stable when the Si-O bond is nearly along the dangling bond direction of the Si atom. This may be due to the repulsion by the neighboring dangling orbital.

Based on these optimized adsorption geometry, H₂O molecules are adsorbed at a coverage of 1/18, 1/6, and 1/2 as shown in Figure 4. The chemisorption energies are listed in Table 4 and the Born-Haber cycle connecting the various states of Si surface is drawn schematically below.



The negative sign implies that chemisorption is preferred. Table 4 shows that it is energetically favorable for the symmetric dimer surface adsorbed by H₂O to relax to form the buckled dimer surface. The large chemisorption energy on

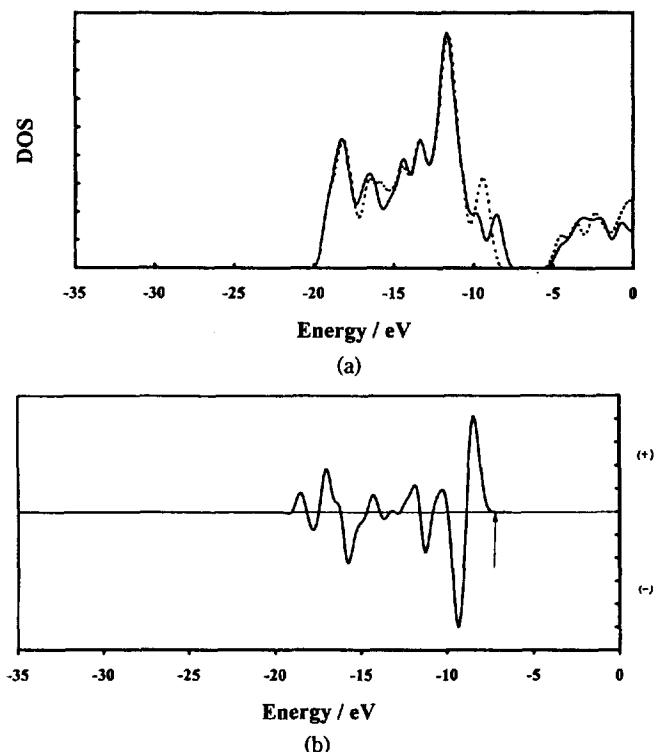


Figure 5. Electronic structure of the clean surfaces: (a) DOS's of the symmetric (solid line) and the buckled dimer surfaces (dotted line), (b) difference curve of the DOS's between the two surfaces in (a) obtained by subtracting the DOS of the symmetric dimer surface from that of the buckled dimer surface. The tip of arrow points to the Fermi level E_F .

the buckled dimer surface is related with the atomic charges of the buckled dimer (-0.471 for the up atom, $+0.136$ for the down atom). The chemisorption energy for the configuration (b) in Figure 4 is largest and it can be said that this type of adsorption is favorable for the $p(2 \times 2)$ surface. The buckling energies ΔE_B 's are all calculated to be negative, implying that the buckling of dimers is also favorable when H₂O is adsorbed on the surface as well as when the surface is clean. The ΔE_B (the ΔE_4 divided by the number of surface dimers, namely the buckling energy per dimer) for the configuration (b) in Figure 4 is -2.25 eV and much larger compared with -0.99 eV for the clean surface buckling.

Discussions

In the schematic diagram described in the previous section, ΔE_1 is the energy change for the buckling of the clean surface and the value is -8.91 eV (-0.99 eV per dimer as mentioned in the previous section). If the absolute value of ΔE_4 is greater or much greater than the absolute value of ΔE_1 , then it can be said that the buckled Si surface is stabilized by the H₂O adsorption when it has the buckled configuration as a result of surface reconstruction. The path $C_s \rightarrow A_s \rightarrow A_b$ is replaced by the alternative path $C_s \rightarrow C_b \rightarrow A_b$ because the former path is more elaborate to optimize the geometric variables. For the process $C_s \rightarrow C_b \rightarrow A_b$, ΔE_1 (-8.91 eV) and ΔE_2 (-1.33 eV) are all negative, and each step

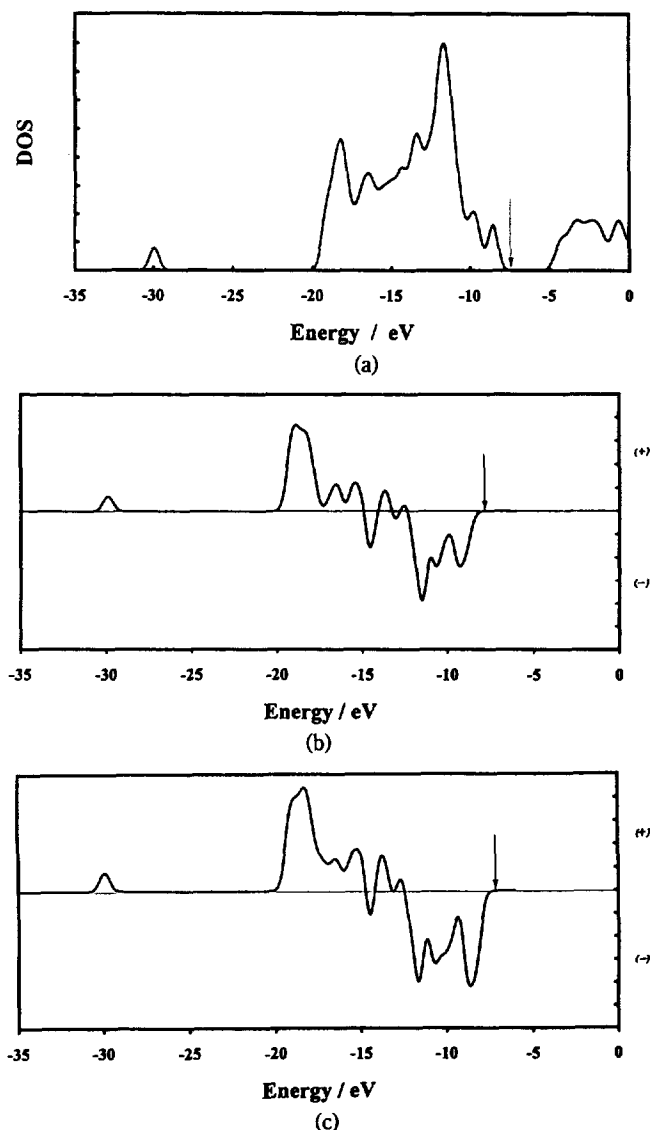


Figure 6. Comparisons of the COD curves: (a) DOS of the adsorbed buckled dimer surface, (b) COD of the adsorbed symmetric dimer surface and (c) COD of the adsorbed buckled dimer surface. The tip of arrow points to the Fermi level E_F . The peaks in positive and negative region of COD indicate the gain and the loss of electron density.

of buckling ($C_s \rightarrow C_b$) and chemisorption ($C_b \rightarrow A_b$) is favored thermodynamically. The amount of energy-release for the process $C_s \rightarrow C_b \rightarrow A_b$ is much greater than for the process $C_s \rightarrow C_b$. Therefore, the buckled dimer surface adsorbed by H₂O is more stable thermodynamically than the clean surface buckled intrinsically.

Figure 5 shows the electronic structures of the clean surfaces. The difference curve is calculated by subtracting DOS of the symmetric dimer surface from that of the buckled dimer surface.

Figure 6 shows DOS and COD curves of the adsorbed surfaces discussed in the previous section. The goal of the analysis of DOS or COD is to assign the peaks or features in COD curve using the information obtained from the com-

parison of features appeared in the electronic structures of the H₂O-adsorbed Si surface with experimental results, and to argue the importance of H₂O adsorption for the buckling of the Si surface qualitatively.

The curves in Figure 6(b) and 6(c) exist in the positive region of the difference function in $-15 \sim -20$ eV range. The positive peaks represent the increase in DOS due to the adsorption of H₂O on the surface, and the total energy of the Si cluster is lowered. Therefore, from the comparison of this curve and the difference curve in Figure 5(b), it is shown that the negative peak at around -15.75 eV (-8.90 eV below Fermi energy E_F) in Figure 5(b) is most influenced by the H₂O adsorption. In addition, it is also shown that the electron density near the Fermi level for the buckled dimer surface is decreased by the adsorption of water. In other words, by the adsorption the electronic states of the Si surface shift downward in energy and the surface is stabilized.

The sharp and intense positive peaks in Figure 6(a) are at -18.3 , -17.3 and -13.75 eV (-11.45 , -9.75 , -6.90 eV below E_F , respectively) and other peaks at the region of $-16.0 \sim -15.2$ eV ($-8.45 \sim -8.35$ eV below E_F). From the comparison of the position of these peaks and those argued as induced by H₂O from related experiments,¹⁻³ it is found that the former group of peaks is due to the surface buckling, and the contribution by the water adsorption is dominated in the latter case. Consequently, it is argued that the latter band of peaks and the peak at -15.75 eV discussed above are due to the $1b_1$ and the $2a_1$ molecular orbital of H₂O.

Conclusions

The stabilization of the buckled dimer surface by the H₂O adsorption has been studied using the Si₇₇H₆₀ cluster model and the semi-empirical atom superposition and electron delocalization (ASED) method. The buckled dimer is thermodynamically stable by 0.99 eV per dimer compared with the symmetric dimer, but at room temperature it switches the buckling orientation rapidly so leading to the appearance of the symmetric dimer.¹¹ The buckled dimer configuration is much more stabilized by the water adsorption. The degree of lowering in total energy for the chemisorbed Si surface is 2.25 eV per dimer compared to the clean symmetric dimer surface. The tilting angle of the buckled dimer is rather small compared to the values from other studies, this is due to the restriction posed on the number of relaxable variables. But, as concluded by Jing and Whitten,³⁰ the small tilting angle seems to be stemmed from the systematic errors of the ASED method in addition to the above reason.

The buckled dimer surface is more stable in the presence of H₂O and it may be more difficult to change the buckling direction than the clean one does so. In other words, the orientation of the buckled dimer on which H₂O is adsorbed is fixed and the neighboring dimers are also buckled to form

the alternatively buckled dimer rows as commonly observed in many experiments.^{11,13,31}

Acknowledgment. This work was supported by a grant from Korea Science and Engineering Foundation, S. N. U. Daewoo Research Fund, Ministry of Education, and Non-directed Research Fund of Korea Research Foundation.

References

1. (a) Fujiwara, K. *J. Chem. Phys.* **1981**, *75*, 5172. (b) *Surf. Sci.* **1981**, *108*, 124.
2. Schmeisser, D.; Himpsel, F. J.; Hollinger, G. *Phys. Rev. B* **1983**, *27*, 7813.
3. Schmeisser, D. *Surf. Sci.* **1984**, *137*, 197.
4. Chabal, Y. J.; Christman, S. B. *Phys. Rev. B* **1984**, *29*, 6974.
5. Schaefer, J. A.; Stucki, F.; Frankel, D. J.; Göpel, W.; Lapeyre, G. *J. Vac. Sci. Technol. B* **1984**, *2*(3), 359.
6. Bu, H.; Rabalais, J. W. *Surf. Sci.* **1994**, *301*, 285.
7. Ciraci, S.; Wagner, H. *Phys. Rev. B* **1983**, *27*, 5180.
8. Katircioglu, S. *Surf. Sci.* **1987**, *187*, 569.
9. Al-Hayek, I.; Katircioglu, S. *Surf. Sci.* **1993**, *286*, 92.
10. Hamers, R. J.; Tromp, R. M.; Demuth, J. E. *Phys. Rev. B* **1986**, *34*, 5343.
11. Wolkow, R. A. *Phys. Rev. Lett.* **1992**, *68*, 2636.
12. Andersohn, L.; Köler, U. *Surf. Sci.* **1993**, *284*, 77.
13. Chander, M.; Li, Y. Z.; Patrin, J. C.; Weaver, J. H. *Phys. Rev. B* **1993**, *48*, 2493.
14. Anderson, A. B.; Grimes, R. W.; Hong, S. Y. *J. Phys. Chem.* **1987**, *91*, 4245.
15. Chu, S. Y.; Anderson, A. B. *Surf. Sci.* **1988**, *194*, 55.
16. Yu, J.; Anderson, A. B. *J. Am. Chem. Soc.* **1990**, *112*, 7218.
17. Ruiz, E.; Alvarez, S.; Hoffmann, R.; Bernstein, J. *J. Am. Chem. Soc.* **1994**, *116*, 8207.
18. Chabal, Y. J.; Raghavachari, K. *Phys. Rev. Lett.* **1984**, *53*, 282.
19. Verwoerd, W. S. *Surf. Sci.* **1981**, *103*, 404.
20. Redondo, A.; Goddard III, W. A. *J. Vac. Sci. Technol.* **1982**, *21*, 344.
21. Chadi, D. J. *Phys. Rev. Lett.* **1979**, *43*, 43.
22. Appelbaum, J. A.; Hamann, D. R. *Surf. Sci.* **1978**, *74*, 21.
23. Yin, M. J.; Cohen, M. L. *Phys. Rev. B* **1981**, *24*, 2303.
24. Holland, B. W.; Duke, C. B.; Paton, A. *Surf. Sci.* **1984**, *140*, L269.
25. Zhu, Z.; Shima, N.; Tsukada, M. *Phys. Rev. B* **1989**, *40*, 11868.
26. Jedrecy, N.; Sauvage-Simkin, M.; Pinchaux, R.; Massies, J.; Grieser, N.; Etgens, V. H. *Surf. Sci.* **1990**, *230*, 197.
27. Roberts, N.; Needs, R. J. *Surf. Sci.* **1990**, *236*, 112.
28. Artacho, E.; Ynduráin, F. *Phys. Rev. Lett.* **1989**, *62*, 2491.
29. Shiller, P.; Anderson, A. B. *J. Phys. Chem.* **1993**, *97*, 189.
30. Jing, Z.; Whitten, J. L. *Phys. Rev. B* **1994**, *50*, 2598.
31. Tromp, R. M.; Hamers, R. J.; Demuth, J. E. *Phys. Rev. Lett.* **1985**, *55*, 1303.