Vol 14 No 10, October 2005
1009-1963/2005/14(10)/2083-07

Chinese Physics

© 2005 Chin. Phys. Soc.
and IOP Publishing Ltd

Adsorption and diffusion of Si adatom near single-layer steps on Si surface*

Zhu Xiao-Yan(朱晓焱)[a)b)†] and Huang Yan(黄 燕)[b)‡]

[a)] *Department of Physics, Suzhou University, Suzhou 215006, China*

[b)] *National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, China*

(Received 3 December 2004; revised manuscript received 27 June 2005)

By use of the empirical tight-binding (ETB) method, the adsorption and diffusion behaviours of single silicon adatom on the reconstructed Si(100) surface with single-layer steps are simulated. The adsorption energies around the S_A step, nonrebonded S_B step, rebonded S_B step, and rough S_B step with a kink structure are specially mapped out in this paper, from which the favourable binding sites and several possible diffusion paths are achieved. Because of the rebonded and kink structures, the S_B step is more suitable for the attachment of Si adatom than the S_A step or defective surface.

Keywords: step, adsorption, diffusion, empirical tight-binding
PACC: 6820, 6610C, 7115F, 6810C

1. Introduction

In recent years, with considerable interest in fabricating nanostructures such as quantum wires and dots, many studies have concentrated on the atomic-scale adatom surface behaviour.[1,2] The Si(100) surface has received special attention because it is widely used for not only device fabrications but also because it is a relatively simple surface with complex reconstructions under various sample preparation conditions. The prominent feature of Si(100) surface is that it forms parallel rows of dimerized atoms to reduce the surface energy. These dimer rows are usually separated by single(S)- or double(D)-layer steps. Step edges aligned parallel to the dimer rows of the upper terrace are denoted by A, and step edges perpendicular to the dimer rows on the upper terrace are denoted by B. So there are basically four step types: S_A, S_B, D_A, D_B. Furthermore, the S_B steps can be sorted into two types: nonrebonded S_B step and rebonded S_B step, because the step edges terminate in one of two locations with respect to the substrate dimer rows, ending either at the trough between the dimer rows or on the top of the dimer rows, so that the edge atoms of the upper terrace rebond with the nearest atoms on the lower terrace.[3−5] Generally speaking, the A-type step is smooth and straight.[6] But along the B-type step, there are many ledges or recessions that can be regarded respectively as dimer defects or small segments of A-type step in the direction perpendicular to the B-type step.[6] The popularity of the existence and complexity of step makes this an important subject about the microstructure in research of the Si surface.

Our early studies[7] show that defects on the surface can make the adsorption behaviours of adatoms different from those on a perfect surface. The large anisotropy of the diffusion on the perfect surface will be decreased due to the introduced dimer vacancies (DV). The single adatom can move into the DV easily, but it cannot fill it efficiently because it can also easily move out of the DV. Furthermore, the adatom can move into or out of the single-DV more easily than the double-DV because of the smaller energy barrier.

Like defects, steps can also play a crucial role on the surface. Jaloviar *et al* found that rebonded

*Project supported by the National Natural Science Foundation of China (Grant No 10374069) and the National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences (Grant No 200412).

†E-mail: zhuxy@suda.edu.cn

‡E-mail: hysherry@163.com; yhuang@mail.sitp.ac.cn

steps dramatically changed the optical anisotropy of the Si(100) surface.[8] Steps also had a suppressive influence on a phase transition of the Si(100) surface, which was found by Yokoyama *et al.*[9] Komura *et al* studied electronic structures of the steps and found the negative differential conductance at the B-type steps.[10] During the homoepitaxy on the vicinal Si(100) surface, step bunching instability was observed by Schelling.[11] Besides these experiments, much theoretical work is also devoted to the investigations on the characteristics of steps.[12−15]

In this paper, the adsorption of a single Si adatom on the reconstructed Si(100) surface with single-layer steps is simulated by use of the empirical tight-binding (ETB) method, and the detailed results about the adsorption and diffusion behaviours of the adatom are analysed and reported. Steps, particularly the rough S_B steps with kink structures, have a significant influence on the adsorption and diffusion behaviours of the adatom. The results can present some guidance to the crystal growth in nanostructure.

2. Methods

For diminishing computing complexity, the ETB scheme[16−18] with the steepest-descent (SD) method instead of the more accurate but complex *ab initio* method[19−22] is used in this work, which has been shown to be efficient and accurate enough for various Si systems[23−27] and brought about good results in our early work.[7] We adopt the scheme of Goodwin *et al.*[28] The Hellman–Feynman force on each atom in the system can be easily calculated by taking derivative of the total energy with respect to the positions of all atoms.

The perfect supercell contains five Si layers, and each Si atom at the bottom layer is terminated by two H atoms to saturate the dangling bonds of the Si atoms. To prevent any spurious forces by the H atoms, two bottom Si layers and an additional H layer are fixed. A vacuum region of 0.6nm is used to simulate the bulk structure. The dimerized bonds are along the x direction [$\bar{1}$10], while the dimer rows on the surface are parallel to the y direction [110]. The periodic boundary conditions are applied to the x and y directions. Then the directions and heights of part of the supercell are changed to form the S_A and S_B steps. The left (right) part is the upper (lower) terrace.

The total energy is calculated only at Γ point of the first Brillouin zone of the unit cell throughout the calculation. In order to consider the nearest atom–atom interaction of Si only, the potential cutoff is taken as 0.28nm.

3. Results and discussion

Our study focuses on the Si adatom deposited on single-layer step substrates because it can reveal the natures of barriers and interaction potentials about surfaces, which are essential parameters in controlling crystal growth. First, we use the energetically favourable $p(2\times2)$ reconstruction[5,29,30] to construct step surfaces. This kind of surface reconstruction is adopted in our early studies and has been demonstrated to be efficient.[7] All of the models are relaxed to equilibrium structures by our calculation method. Then, within the region marked by a dashed rectangle on the top view of the equilibrium structure, the Si adatom is adsorbed on the sample surface at a series of sites around the step edge, which forms an equidistant grid with the grid space being 0.096nm both in the x and y directions, in order to simulate crystal growth process. The adatom starts at 0.28nm above the surface. Both x and y coordinates of the adatom are fixed, while the z coordinate is relaxed.

After all grid points with the adatom are calculated, the adsorption energy around steps can be obtained. Although such an energy surface is a purely theoretical construct, we can extract a number of fundamental parameters from it. From the absolute minimum on the energy surface, we can identify the binding site of the adatom, and the saddle points of the energy surface give the activation energies or diffusion energy barriers for migration of the adatom. We use M to mark the absolute minimum points. We assume that the most probable path taken should be the one which can cross over the lowest possible energy barriers. By studying these contour plots carefully, the adsorption and diffusion behaviours of the adatom around steps can be drawn out.

3.1. S_A step

For the S_A step, we make the up dimer atoms at the edge of the higher terrace align with the center of the dimer in the lower terrace, while the down dimer atoms align with the gap between the dimer rows in the lower terrace according to the experimental results.[4,31] Although the other kind of S_A step structure, which has the opposite tilt of the dimers on

the upper terrace, has the same total energy within the accuracy of our calculation, its atomic structure adjacent to the step edge on both terraces has a slightly change compared with that on a flat surface. This is not accordant with STM observations. The *ab initio* calculation does not find any difference between their energies yet.[32] And this structure is not observed in experiments.[4,31] So the former structure (See Fig.1(a)) is used here in the present work.

Figure 1(b) shows the contour plot of adsorption energy of different Si adatom adsorption sites around the S_A step. The absolute minimal point (M) is on the upper terrace. Besides, the dimer atoms are at some local minimal points. On the upper terrace, the local minima are near the dimer atoms. On the lower terrace, situation is somewhat alike, except one of the local minimal being in the middle of the trough that has been reported by Zhang *et al.*[33] The energy barrier for the adatom to diffuse along the step edge is around 0.11–0.69eV. But whether can the adatom arrive at the step edge from upper or lower terrace? It will do if the adatom comes from the lower terrace, because the energy barriers are up to 1.13eV either along or across the dimer row. It is easy for the adatom to diffuse to other sites beside the dimer row on the upper terrace for the 0.40eV energy barrier. After it overcomes the 0.51eV energy barrier across the dimer row to reach the step edge, it will hop back preferably because of a lower energy barrier, 0.20eV. So if the adatom arrives at the step edge, it is also difficult to reach the lower terrace but just stays at the edge or goes back to the upper terrace. And the energy barrier for the adatom to escape from the binding site is about 0.89eV. Zhang *et al*'s *ab initio* calculation[33] shows the same trend, but their energy barrier difference is bigger than ours. The difficulty of the adatom growing around the S_A step has been experienced in experiments.[34] One may estimate the temperature from the Redhead's equation,[35]

$$E_A/k_B T_d = \ln(\alpha T_d) - \ln(E_A/k_B T_d), \qquad (1)$$

where α is a constant that is dependent on coverage, rate constant, and heating rate. Using the first order kinetics, one may obtain a reasonable diffusion temperature (T_d) for a given activation barrier (E_A). The temperature for the adatom to diffuse from the upper terrace to the S_A step is less than 270K, and the temperature is 430K for the adatom to escape from the binding site.

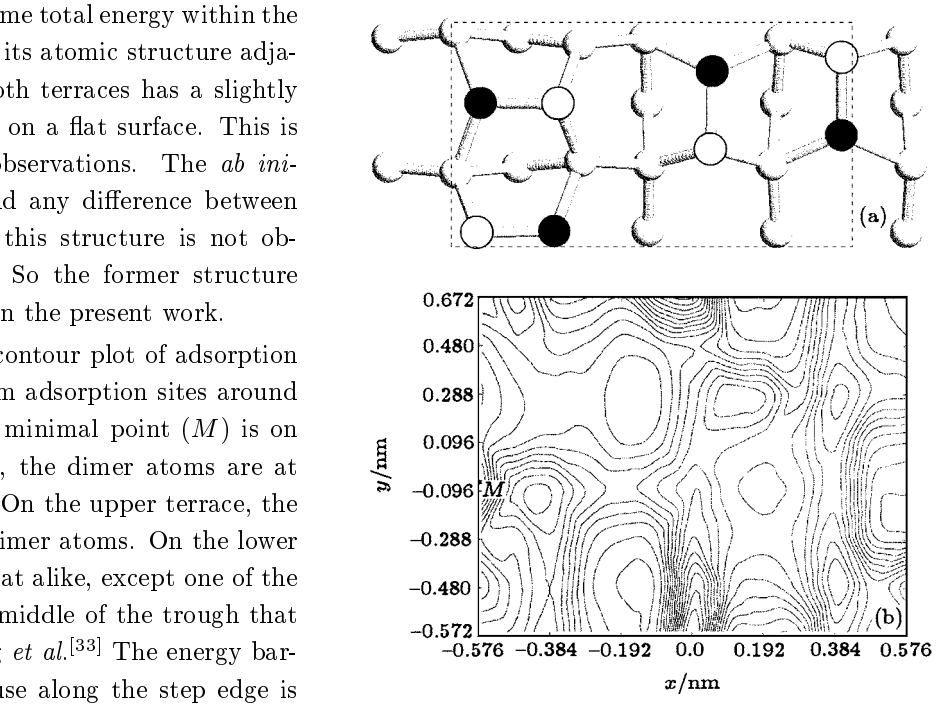


Fig.1. (a) Top view of the fully relaxed $p(2\times2)$ S_A step surface. (b) Contour plot of adsorption energy difference of different Si adatom adsorption sites within the dashed rectangle around the S_A step. In the step configuration, solid (open) circles represent down (up) atoms of the dimers and the grey circles denote the substrate layer atoms. The spacing between the contour plots is 0.14eV. The zero energy corresponds to the energetically lowest point.

3.2. Smooth S_B steps

There are two kinds of structures observed in experiments for the S_B step: nonrebonded and rebonded. Within the accuracy of our calculation, their energies are quite similar. Both of them are studied in the following.

For the nonrebonded S_B step, the wide separation between the upper and lower terraces weakens the interaction between them. So the atomic structure does not change much compared with that on the flat surface (see Fig.2(a)). The contour plot of adsorption energy of different Si adatom adsorption sites around the nonrebonded S_B step is shown in Fig.2(b). The absolute minimal points are located beside the down dimer atoms on both of the upper and lower terraces. Besides, other dimer atoms are at local minimal points. On both terraces, the path in the trough just beside the dimer row is the most possible diffusion path for the energy barrier is around 0.42–0.77eV. The difference in energy barrier between the two directions (from up dimer atom to down dimer atom and in the

sequence opposite to the former) is 0.20eV. The wide separation between upper and lower terraces provides the adatom with a sufficient diffusion space to cross the step. The adatom will experience an energy barrier being around 0.40–0.64eV. After the adatom is adsorbed at M sites, it must overcome an energy barrier about 0.93eV to run away from the binding sites. It is possible to make the adatom move from the upper or lower terraces to the step edge and turn into the trench, which has been proved by Mo *et al.*[34]

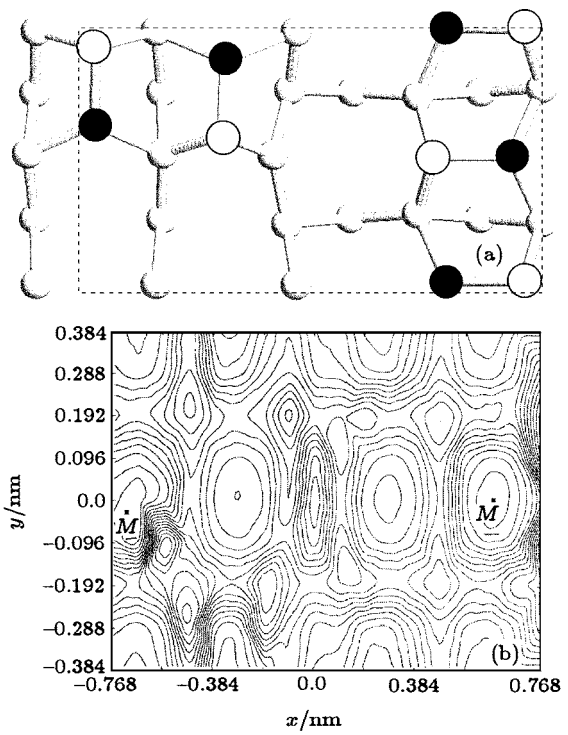


Fig.2. (a) Top view of the fully relaxed $p(2\times2)$ nonrebonded S_B step surface. (b) Contour plot of adsorption energy difference of different Si adatom adsorption sites within the dashed rectangle around the nonrebonded S_B step. The spacing between the contour plots is 0.11eV.

The step influence is stronger on the rebonded S_B step because the upper and lower terraces are very close to each other. It has been shown in Fig.3(a) that the dimer symmetries decrease dramatically to 0.033 or 0.045nm, only about half as large as those on the flat surface, especially on the lower terrace. And their bond lengths are stretched to 0.246 or 0.255nm. On the upper terrace, the situation is not so serious because the dimer symmetry only decreases by 0.005nm, about 7%. But the backbonds of the higher dimer atom are stretched by 0.006nm. This can help the step rebond and is similar to Boguslawski *et al*'s result.[32] In this structure, all hybridizations are weakened compared with their originals.

A great influence is also exercised on the adsorption behaviour of the adatom. Figure 3(b) shows the contour plot of adsorption energy of different Si adatom adsorption sites around the rebonded S_B step. The minimum is between the dimer atoms on the lower terrace. This is different from the former situations. Besides, the dimer atoms of the upper terrace are at local minima. The energy barriers crossing the step edge are 0.46–0.56eV either from the upper terrace or from the lower terrace. These are analogous with situations around the nonrebonded S_B step. But after the adatom is trapped at M sites, it must surmount an energy barrier being up to 1.29eV to escape from the binding sites. Thus rebonded S_B step is easier to trap adatoms. More and more atoms reach there and can form the step growth.

Around the S_B step, the adatom can diffuse easily at room temperature and must be at a temperature being up to 500K to escape from the binding sites.

The same conclusion can be obtained by calculating the jumping rate,[36]

$$k = A\exp\left[-\frac{V}{k_B T}\right]. \qquad (2)$$

Here $A = 10^{13}\mathrm{s}^{-1}$ and V is the energy barrier. The jumping rate for the adatom to diffuse into the binding site is much higher than that to escape from it. For example, k is 2.3×10^{-9} for the adatom to escape from the binding site (1.29eV energy barrier), while it is 4.0×10^{3} for the adatom to diffuse into the binding site (0.56eV), about 10^{12} times higher than the former at 300K. At 500K, the ratio is around 10^{7}. Even at 700K, the ratio is still as high as about 10^{4}.

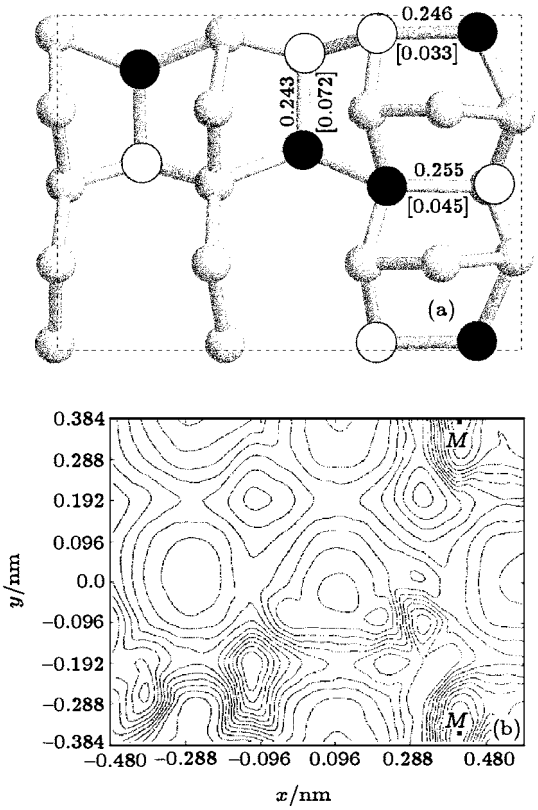


Fig.3. (a) Top view of the fully relaxed $p(2\times2)$ rebonded S_B step surface. (b) Contour plot of adsorption energy difference of different Si adatom adsorption sites within the dashed rectangle around the rebonded S_B step. The spacing between the contour plots is 0.16eV. In the step configuration, the numbers mark the lengths of the dimers. And the numbers in the square brackets indicate the asymmetries of the dimers. (Length is in units of nm).

3.3. Rough S_B step with a kink structure

From experimental results, the diffusion around the S_B step is easier than around the S_A step.[34] That means that the S_B step has a lower diffusion energy barrier. This can be seen from the results above but not so distinctly. Further investigations must be conducted in S_B steps. Contrast to the smooth S_A step, the S_B step is much rougher and contains many defects which are referred to as kinks. These kinks can be regarded as components of the S_A and S_B steps, which are dimer defects adjacent to the step edges. Experimental observation shows that the rearrangement, i.e. the missing or adding atoms at the step edge, is always comprised of four-atom units (two dimers).[37] So we construct a simplest kink structure for studying: just remove the two dimers in the same row from the upper terrace adjacent to the S_B step. The total energy for the kink structure found along the rebonded S_B step is 0.17eV lower than that along the nonrebonded S_B step. As an example, we discuss in detail the results obtained for the kink structure along the rebonded S_B step. The following study focuses on the former case.

From the equilibrium kink structure relaxed by our method, some atomic structure changes can be seen in Fig.4(a). On the lower terrace, the dimer symmetries are smaller while their bond lengths are enlarged just like the situation near the rebonded S_B step. On the higher terrace, the dimer bond symmetries near the joint of the kink and the lower terrace are lowered by 14%. At the recession of the kink, they are lowered by 7%. But their bond lengths do not change much.

Figure 4(b) shows the contour plot of adsorption energy of different Si adatom adsorption sites around the kink. The absolute minimum is at the recession of the kink where the adatom prefers to adhere there. From either the lower terrace or upper terrace, the energy barriers for the adatom diffusing to the point M are around 0.38–0.52eV from various directions. But the reversal path will set an energy barrier to be up to 1.71eV. In this case, the adatom is much easier to adsorb because the temperature is less than 200K, and the higher temperature (660K) will make the adatom difficult to escape from the recession.

In this case, the jumping rate ratio between the adatom diffusing into the binding site and the adatom escaping from it is about 10^{20} at 300K. And even at 700K, the ratio is still as high as about 10^8.

By comparing with our early results, our present results show that most of the energy barriers for the adatom diffusing around single-layer steps are smaller than those around dimer vacancies.[7] This may help illuminate that during the adsorption and diffusion for the adatom on the surface the adatom prefers to adhere around the S_B step and cannot fill dimer vacancies efficiently.

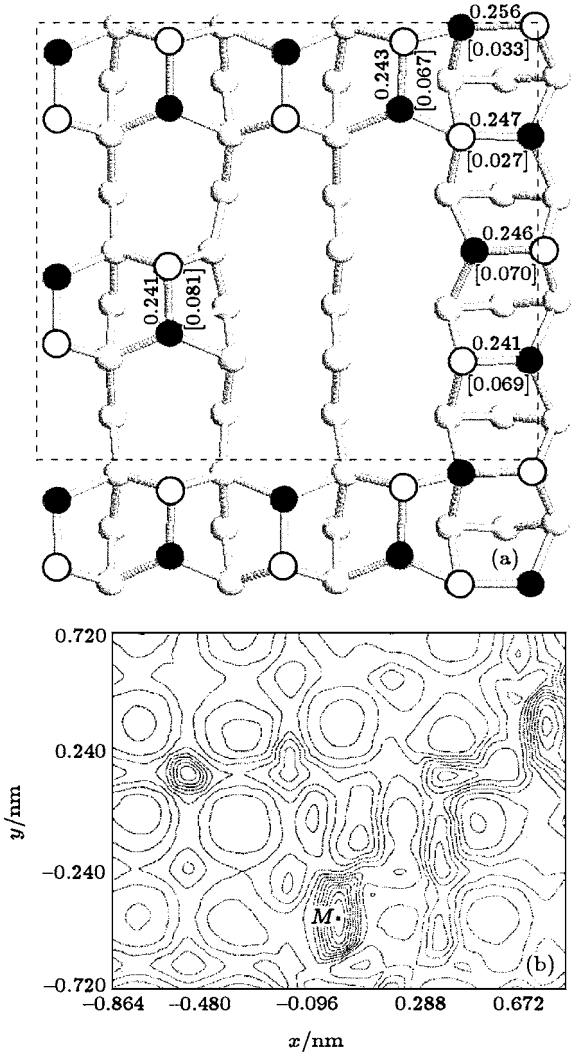


Fig.4. (a) Top view of the fully relaxed rough $p(2\times2)$ rebonded S_B step surface with a kink structure. (b) Contour plot of adsorption energy difference of different Si adatom adsorption sites within the dashed rectangle around the kink structure. The spacing between the contour plots is 0.2eV.

Here, only one single adatom adsorbed near single-layer steps has been investigated. There are double-layer steps and more complex kinks on the real surface. And some STM results show that the nonbonded step with a missing dimer is often observed.[29] Furthermore, the real crystal growth process must be more complex. The adatom is affected reciprocally, and other formations of surface defects such as vacancies, islands *etc.* can also make the adsorption of adatom more different. Discussion about them is prepared for our further work.

4. Conclusion

In this paper we calculate the adsorption energies of different Si adatom adsorption sites near the S_A step, smooth S_B step, and rough S_B step with a kink structure on the $p(2\times2)$ Si(100) surface by use of the ETB method. Several binding sites and some possible diffusion paths of a Si adatom around those steps have been achieved, which are very different from those on the perfect surface. Because of the rebonded and kink structures, the S_B step is more suitable for the attachment of the Si adatom than the S_A step or defective surface. By using denuded-zone analysis in STM images, Mo *et al* have obtained the same conclusion.[34] The corresponding temperatures are calculated during the adsorption and diffusion processes. These may provide some useful guidance to further theoretical and experimental studies on the atomic-scale adsorption in fabrication of semiconductor devices.

References

[1] Wei S Y, Wang J G and Ma L 2004 *Chin. Phys.* **13** 85

[2] Tao X M, Tan M Q, Xu X J, Cai J Q, Chen W B and Zhao X X 2004 *Acta Phys. Sin.* **53** 3858 (in Chinese)

[3] Chadi D J 1987 *Phys. Rev. Lett.* **59** 1691

[4] Hamers R J, Tromp R M and Demuth J E 1986 *Phys. Rev.* B **34** 5343

[5] Chadi D J 1979 *Phys. Rev. Lett.* **43** 43

[6] Mo Y W, Kariotis R, Swartzentruber B S, Webb M B and Lagally M G 1990 *J. Vac. Sci. Technol.* A **8** 201

[7] Huang Y and Zhu X Y 2004 *Chin. Phys.* **13** 725

[8] Jaloviar S G, Lin J L, Liu F, Zielasek V, Mccughan L and Lagally M G 1999 *Phys. Rev. Lett.* **82** 791

[9] Yokoyama T and Takayanagi K 1998 *Phys. Rev.* B **57** R4226

[10] Komura T, Yao T and Yoshimura M 1997 *Phys. Rev.* B **56** 3579

[11] Schelling C, Springholz G and Schäffler F 1999 *Phys. Rev. Lett.* **83** 995

[12] Schmidt W G, Bechstedt F and Bernholc J 2001 *Phys. Rev.* B **63** 45322

[13] Sato M, Uwaha M, Saito Y and Hirose Y 2003 *Phys. Rev.* B **67** 125408

[14] Zandvliet H J W, Gurlu O, Gastel R and Poelsema B 2004 *Phys. Rev.* B **69** 125311

[15] Filimonov S N and Voigtlander B 2004 *Surf. Sci.* **549** 31

[16] Alerhand O L and Mele E J 1987 *Phys. Rev.* B **35** 5533

[17] Jeong M S, Lee Y H and Hwang Y G 1995 *Phys. Rev.* B **51** 17151

[18] Lee S M and Lee Y H 1996 *Surf. Sci.* **347** 329

[19] Wang J, Arias T A and Joannopoulos J D 1993 *Phys. Rev.* B **47** 10497

[20] Brocks G, Kelly P J and Car R 1991 *Phys. Rev. Lett.* **66** 1729

[21] Borovsky Krueger B M and Ganz E 1999 *Phys. Rev.* B **59** 1598

[22] Brocks G and Kelly P J 1996 *Phys. Rev. Lett.* **76** 2362
[23] Smith A P, Wiggs J K, Jónsson H, Yan H, Corrales L R, Nachtigall P and Jordan K D 1995 *J. Chem. Phys.* **102** 1044
[24] Lee G D, Wang C Z, Lu Z Y and Ho K M 1998 *Phys. Rev. Lett.* **81** 5872
[25] Lee G D, Wang C Z, Lu Z Y and Ho K M 1999 *Surf. Sci.* **426** L427
[26] Fa W and Luo C L 2000 *Acta Phys. Sin.* **49** 430 (in Chinese)
[27] Li Y L and Luo C L 2002 *Acta Phys. Sin.* **51** 2589 (in Chinese)
[28] Goodwin L, Skinner A J and Pettifor D G 1989 *Europhys. Lett.* **9** 701
[29] Ramstad A, Brocks G and Kelly P J 1995 *Phys. Rev.* B **51** 14504
[30] Northrup J E 1993 *Phys. Rev.* B **47** 10032
[31] Komura T, Yoshimura M and Yao T 1996 *J. Vac. Sci. Technol.* B **14** 906
[32] Boguslawski P, Zhang Q M, Zhang Z and Bernholc J 1994 *Phys. Rev. Lett.* **72** 3694
[33] Zhang Q M, Roland C, Boguslawski P and Bernholc J 1995 *Phys. Rev. Lett.* **75** 101
[34] Mo Y W and Lagally M G 1991 *Surf. Sci.* **248** 313
[35] Masel R I 1996 Principles of Adsorption and Reaction on Solid Surfaces (New York: Wiley) p513
[36] Lu Y T, Zhang Z and Metiu H 1991 *Surf. Sci.* **257** 199
[37] Kitamura N, Swartzentruber B S, Lagally M G and Webb M B 1993 *Phys. Rev.* B **48** 5704