

## Adsorption and dissociation of $\text{PH}_3$ on $\text{Si}(100)2 \times 1$ and $\text{Si}(111)7 \times 7$ : Theoretical study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 6103

(<http://iopscience.iop.org/0953-8984/6/31/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 12/05/2010 at 19:04

Please note that [terms and conditions apply](#).

## Adsorption and dissociation of $\text{PH}_3$ on $\text{Si}(100) 2 \times 1$ and $\text{Si}(111) 7 \times 7$ : theoretical study

Pei-Lin Cao†‡, Lie-Quan Lee†‡, Jian-Jun Dai†‡ and Ru-Hong Zhou†‡

† China Center of Advanced Science and Technology (World Laboratory), PO Box 8730, Beijing 100080, People's Republic of China

‡ Department of Physics, Zhejiang University, HangZhou 310027, People's Republic of China

Received 30 September 1993, in final form 19 April 1994

**Abstract.** The adsorption structures and dissociation properties of  $\text{PH}_3$  on  $\text{Si}(100) 2 \times 1$  and  $\text{Si}(111) 7 \times 7$  have been studied by the ASEB MO method. Our calculation results show that, on the  $\text{Si}(100) 2 \times 1$  surface,  $\text{PH}_3$  is adsorbed undissociatively on the dangling bond, with a binding energy of 2.25 eV, Si–P bond length of 2.23 Å, an angle from the surface normal of 22°, a P–H bond length of 1.52 Å and an angle of the  $\text{PH}_3$  axis to the surface normal of 21°. The dissociation energy barrier of the first H atom for  $\text{PH}_3$  is about 1.61 eV, in agreement with the experimental results of molecular adsorption of  $\text{PH}_3$  on  $\text{Si}(100)$  at room temperature. On  $\text{Si}(111) 7 \times 7$ , the most stable site for  $\text{PH}_3$  adsorption of  $\text{S}_2\text{DB}$ , and then the  $\text{S}_1\text{DB}$  site; the binding energies are 2.11 eV and 1.00 eV, respectively. Using the DAS model in our calculation, our results show that the energy barrier for  $\text{PH}_3$  dissociation on  $\text{S}_1\text{DB}$  and  $\text{S}_2\text{DB}$  are 1.02 eV and 2.05 eV, respectively. If we replace the Si adatom in the DAS model by a  $\text{Si}_4$  small cluster, the binding energies of  $\text{PH}_3$  on  $\text{S}_2\text{DB}$  and  $\text{S}_1\text{DB}$  are 1.64 eV and negative, respectively. The dissociation energy barrier on  $\text{S}_2\text{DB}$  will reduce to 0.48 eV. It seems that the dissociation of  $\text{PH}_3$  on  $\text{Si}(111) 7 \times 7$  is caused by some kind of defect on this surface.

### 1. Introduction

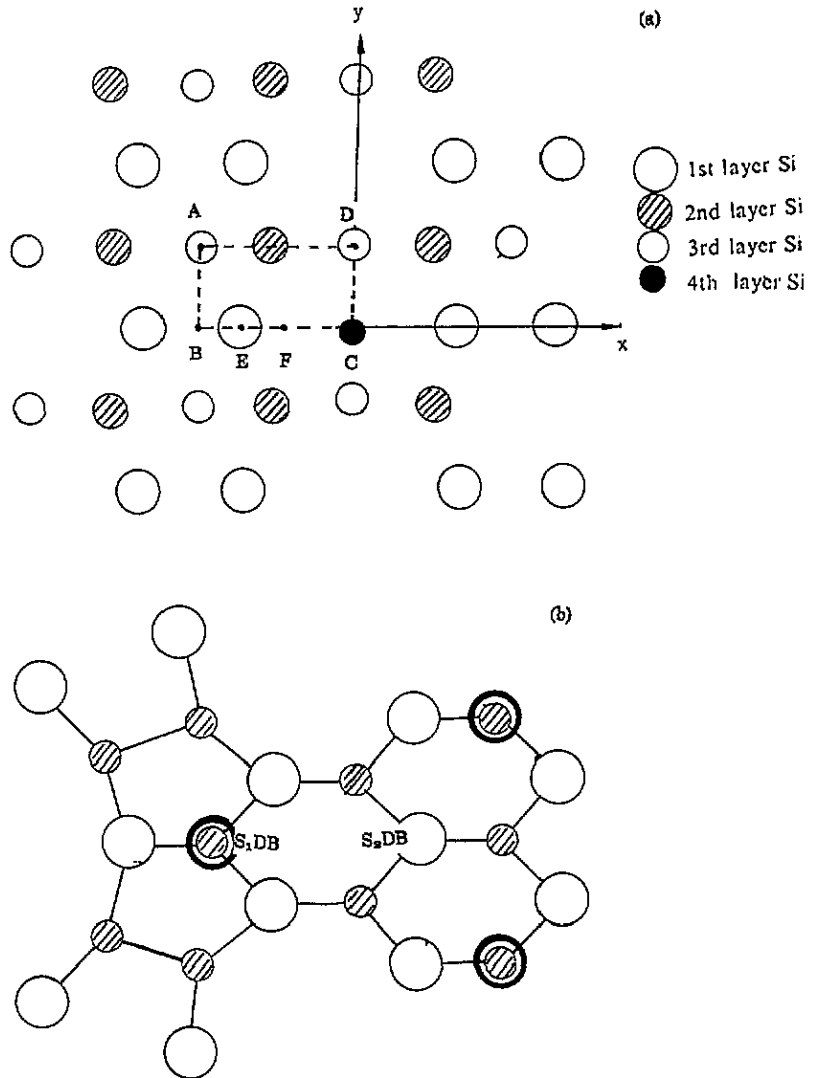
The interaction of  $\text{PH}_3$  with the silicon surface is of considerable interest, not only from the scientific viewpoint but also from the technological application viewpoint owing to the involvement in the chemical vapour deposition and doping of silicon. A number of experimental studies have been made on the adsorption and dissociation of  $\text{PH}_3$  on the  $\text{Si}(100) 2 \times 1$  and  $\text{Si}(111) 7 \times 7$  surfaces.

On the  $\text{Si}(100) 2 \times 1$  surface, the results of x-ray photoelectron spectrometry and temperature-programmed desorption obtained by Yu *et al* [1] show that  $\text{PH}_3$  mostly adsorbs non-dissociatively with an initial sticking coefficient of  $S_0 = 1.0$  at room temperature; the  $\text{PH}_3$  will begin to desorb molecularly at  $\approx 548$  K. The adsorbed phosphine was reported to decompose at temperatures near 475 K into three Si–H and Si–P. At  $T \approx 798$  K, the surface hydrogen was desorbed and, at temperatures above 823 K, phosphorus was depleted. The SIM, AES, LEED and UPS measurements made by Meyerson and Yu [2] and Yu and Meyerson [3] indicated similar conclusions to the above.

On  $\text{Si}(111) 7 \times 7$ , high-resolution electron-energy-loss spectroscopy study provides evidence for the dissociative adsorption of  $\text{PH}_3$  on  $\text{Si}(111) 7 \times 7$  at 80 K. Depending upon the surface coverage,  $\text{PH}_2(\text{ads})$  species are found on surface [4]. The thermal dissociation of the surface  $\text{PH}_2$  species occurs between 450 and 500 K. However, Bozso and Avouris [5] have investigated the adsorption and reaction of  $\text{PH}_3$  on  $\text{Si}(111) 7 \times 7$  between 100 K and 900 K

by UPS, LEED and ISS. Their results show that phosphine adsorption preferentially quenches the  $S_2DB$  sites; annealing the  $PH_3$ -exposed surface to 900 K or performing the reaction at 900 K results in phosphine dissociation and the formation of a somewhat disordered p-terminated P:Si(111)  $7 \times 7$  surface.

Even with these experimental efforts applied to the system, the adsorption structure of  $PH_3$  on Si(100)  $2 \times 1$  and the adsorption structure and dissociation properties on Si(111)  $7 \times 7$  have not yet been definitely determined. On the other hand, no theoretical study of this system has been reported to our knowledge. The present work is just to develop a deeper insight into the adsorption and dissociation using the atom superposition and electron delocalization (ASED) molecular orbital (MO) and cluster models.



**Figure 1.** Cluster models of (a)  $Si_{31}H_{36}PH_3$  and (b)  $Si_{25}H_{24}PH_3$  for  $PH_3$  adsorption on Si(100)  $2 \times 1$  and Si(111)  $7 \times 7$ , and the possible adsorption sites:  $\circ$ , Si atom in the DAS model. The hydrogen atoms used to saturate the dangling bonds are not shown for convenience.

**Table 1.** Atomic parameters used in the calculation:  $n$ , principal quantum number;  $I_p$ , ionization potential;  $\zeta$ , the Slater orbital exponents

Atom	s orbital			p orbital		
	$n$	$I_p$ (eV)	$\zeta$ (au)	$n$	$I_p$ (eV)	$\zeta$ (au)
H	1	13.60	1.300			
P	3	16.15	1.881	3	10.49	1.629
Si	3	14.69	1.634	3	8.08	1.428

## 2. Models and methods

In this paper, cluster models of Si<sub>31</sub>H<sub>36</sub>PH<sub>3</sub> and Si<sub>25</sub>H<sub>24</sub>PH<sub>3</sub> (see figure 1) are used to simulate the PH<sub>3</sub> adsorption and dissociation on the Si(100) 2 × 1 and Si(111) 7 × 7 surface, respectively. For the Si(100) surface, we use the 2 × 1 symmetric-dimer model suggested by Roberts and Needs [6]. According to this model, the displacements of the first-layer Si atoms making up each dimer are 0.331 Å in [100] direction (closer to the second layer) and ±0.803 Å in the [011] direction (to form dimers). The second-, third- and fourth-layer Si atoms also have some small displacements with respect to their unreconstructed bulk sites. For Si(111), a model which embodies dimers, adatoms and stacking faults (DAS) proposed by Takayanagi *et al* [7] has been used in our calculations; the atomic structure is determined by the dynamical theory of LEED [8]. In our model, there are three adatoms (one of these is assigned as S<sub>1</sub>DB in figure 1(b)), one rest Si atom (S<sub>2</sub>DB in figure 1(b)) and two dimers. The H atoms are only used to saturate the bulk Si dangling bonds as in most of the studies. In our calculations, the substrate sites have been frozen unless specially needed. When the molecular adsorption of PH<sub>3</sub> on Si(100) and Si(111) is considered, a P–H bond length of 1.42 Å and a bond angle of 93.8° in the molecule PH<sub>3</sub> are employed. From the total energy minima, stable adsorption sites can be determined. In order to understand the dissociation process, we let one atom in the adsorbate move freely in three dimensions and calculate the total energy.

The ASEMO theory is used in the present calculations, which has been applied to studies of adsorption on both metal and semiconductor surfaces, and had proved to be quite successful in determining the potential surfaces, bonding geometries and force constants [9, 10]. In this theory the molecular charge density is partitioned into atomic components and the rest, which is an electron delocalization bonding charge. Thus, the total energy may be expressed by

$$E_{\text{total}} = E_R + E_D$$

where  $E_R$  is a repulsive component obtained from integrating the force on a nucleus due to atom superposition. It is determined without approximation with the use of atom densities from a valence atomic basis set.  $E_D$  is an attractive component approximated by the electron delocalization energy from a one-electron calculation using a modified extended Hückel Hamiltonian which is

$$H_{ii} = -I_i$$

$$H_{ij} = -(K/2)(I_i + I_j) \exp(-\alpha R_{ij}) \quad i \neq j$$

where  $I_i$  is the ionization potential of the  $i$ th atom state,  $R_{ij}$  is the distance of the atoms, and  $K$  and  $\alpha$  are adjustable parameters. In our calculations,  $\alpha$ -values of 0.043, 0.014 and 0.014 are used for the substrate, for the adsorbate and between substrate and adsorbate, respectively.  $K = 2.25$  is employed in all cases. The other parameters needed in the calculations are listed in table 1 [10, 11].

### 3. Results and discussion

#### 3.1. $\text{PH}_3$ adsorption on $\text{Si}(100) 2 \times 1$

**3.1.1. Molecular adsorption:  $\text{PH}_3$ .** As a first step, we considered the molecular adsorption of  $\text{PH}_3$  on  $\text{Si}(100) 2 \times 1$  using a P–H bond length of 1.42 Å and a bond angle of 93.8° in the  $\text{PH}_3$  molecule. For each adsorption site, including the pedestal A, bridge B, cave C, valley bridge D, atop E and dangling-bond position F (see figure 1), we have calculated the total energies of the  $\text{Si}_{31}\text{H}_{36}\text{PH}_3$  cluster at various adsorption heights (defined as the vertical distance of the P atom from the substrate), or at various Si–P bond lengths and the angles from the surface normal. The results show that, for the pedestal, bridge, cave and valley bridge sites, the binding energies are negative, i.e. the  $\text{PH}_3$  molecule cannot be adsorbed on these sites. However, for the atop site the dangling-bond site, the binding energies are 1.62 eV and 1.72 eV, respectively, the optimized bond lengths of Si–P are 2.27 Å and 2.23 Å, and the angle from the surface normal for the dangling-bond site is 22°. When the bond length  $l$  of P–H and angle  $\beta$  of the  $\text{PH}_3$  molecular axis to the surface normal are carefully varied, further calculations show that the most favourable site is on the dangling-bond site with  $l = 1.52$  Å,  $\beta = 21^\circ$  and a binding energy of 2.25 eV. It is clear that the most stable site for  $\text{PH}_3$  adsorption on  $\text{Si}(100) 2 \times 1$  is on the dangling-bond position.

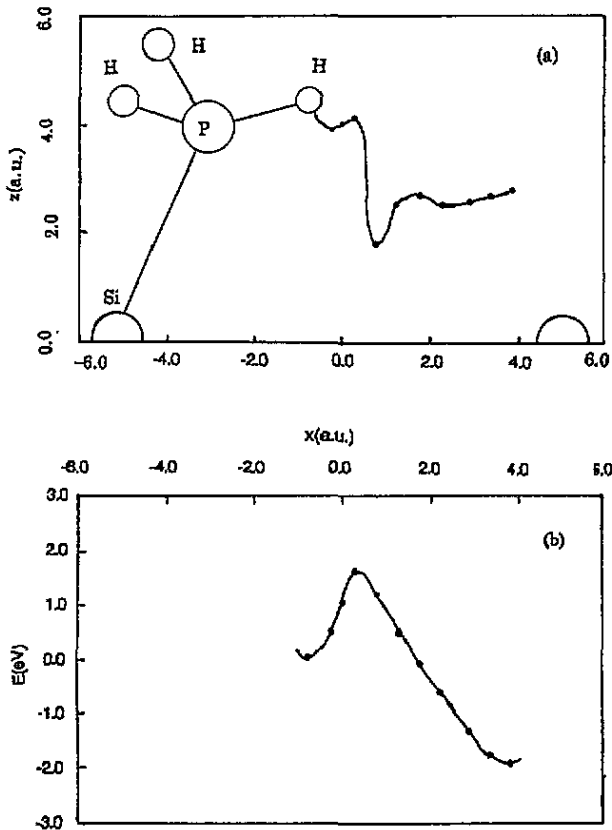


Figure 2. (a) The dissociation path of the H(1) atom on a dangling bond of  $\text{Si}(100)$ ; ---,  $\text{PH}_3$  molecular axis. (b) The corresponding variation in total energy.

3.1.2. *Dissociation process:  $\text{PH}_2(\text{ads}) + \text{H}(\text{ads})$ .* In order to have a clear picture of the dissociation process, we let one of three hydrogen atoms (named H(1)) be drawn from the molecule  $\text{PH}_3(\text{ads})$  and move freely in the  $X$ - $Z$  plane or in the  $y$  direction. Firstly, in the  $x$ - $z$  plane, the detailed calculations have been performed for the dissociation path with a proper step in the  $x$  and  $z$  directions. For each  $x$  position, we can find the  $z$  position from the minimum total energy. Then the optimized dissociation path is obtained (figure 2(a)). The corresponding variation in the total energy is shown in figure 2(b)). For the final stable position of the H(1) atom, the bond length of Si-H is 1.64 Å and the angle between the Si-H bond and the surface normal is 25°. The results in figure 2(b) show that there is an activation barrier of about 1.61 eV in the process. Then, in the  $y$  direction, considering the complexity of the dissociation path in three dimensions, the total energies have been calculated in the  $y = 3.6$  atom unit (au) plane for various  $x$  positions and  $z$  positions. The minimum total energy is obtained at the  $x = 3.95$  au and  $z = 4.79$  au position with a binding energy of 0.42 eV, that is to say, there is an activation barrier of 1.83 eV at least in the process in the  $y$  direction, 0.22 eV larger than that in the  $x$  direction. It is clear that  $\text{PH}_3$  is adsorbed on Si(100)  $2 \times 1$  molecularly at room temperature, in agreement with the results in [1]. The adsorption position is on the dangling-bond site, with the Si-P bond length of 2.23 Å.

As we reported in [12], the  $\text{NH}_3$  is dissociatively adsorbed on the Si(100)  $2 \times 1$  surface as  $\text{NH}_2(\text{ads}) + \text{H}(\text{ads})$ . The analysis of occupation numbers of  $\text{NH}_3(\text{ads})$  shows that, although charge transfer between  $\text{NH}_3$  and the substrate is almost zero, but 0.44e is transferred from the  $3a_1$  bonding level to the  $4a_1$  antibonding level, this weakens the N-H bond strength and results in the activation of  $\text{NH}_3$ . However, for  $\text{PH}_3(\text{ads})$  on Si(100)  $2 \times 1$ ,  $\text{PH}_3$  will lose about 0.75e in our result, and almost no electrons exist in the antibonding level; this is why  $\text{PH}_3$  will be adsorbed on Si(100)  $2 \times 1$  non-dissociatively.

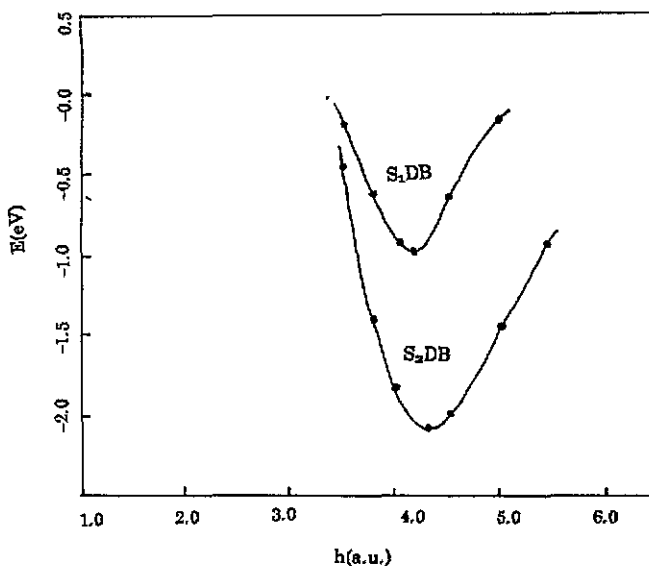


Figure 3. Total-energy  $E$  curves versus the adsorption heights  $h$  for  $\text{PH}_3$  adsorption on the  $\text{S}_1\text{DB}$  and  $\text{S}_2\text{DB}$  sites of the Si(111)  $7 \times 7$  surface.

### 3.2. $\text{PH}_3$ adsorption on the $\text{Si}(111) 7 \times 7$ surface

**3.2.1. Adsorption on the ideal  $\text{Si}(111) 7 \times 7$  surface.** As the result of  $\text{PH}_3$  on  $\text{Si}(100) 2 \times 1$ ,  $\text{PH}_3$  is adsorbed on the dangling-bond site; so we shall consider the dangling-bond sites on  $\text{Si}(111) 7 \times 7$  only. There are two different kinds of dangling-bond site in the DAS model; the dangling bond site of the adatom  $\text{S}_1\text{DB}$  and the dangling-bond site of the first-layer Si atoms  $\text{S}_2\text{DB}$  as shown in figure 1(b). With similar calculations to obtain the optimized Si-P bond lengths, the total energy curve versus the adsorption height on  $\text{S}_1\text{DB}$  and  $\text{S}_2\text{DB}$  are shown in figure 3. The results show that, for  $\text{PH}_3$  on  $\text{Si}(111) 7 \times 7$ , the binding energies are 1.00 eV and 2.11 eV on  $\text{S}_1\text{DB}$  and  $\text{S}_2\text{DB}$  sites, respectively, and the Si-P bond lengths are 2.18 Å and 2.30 Å. It is clear that the binding energy on the  $\text{S}_2\text{DB}$  site is much larger than that on the  $\text{S}_1\text{DB}$  site; so  $\text{PH}_3$  will adsorb preferentially on the  $\text{S}_2\text{DB}$  site, in agreement with the UPS results of Bozso and Avouris [5].

For the dissociation of  $\text{PH}_3(\text{ads})$  on the  $\text{S}_1\text{DB}$  and  $\text{S}_2\text{DB}$  sites, our studies show that the energy barriers of the first P-H bond break are 1.02 eV and 2.05 eV. These results imply that  $\text{PH}_3$  is adsorbed molecularly on the  $\text{Si}(111) 7 \times 7$  surface if the temperature is not very high. As pointed out by Bozso and Avouris, annealing a  $\text{PH}_3$ -exposed  $\text{Si}(111) 7 \times 7$  sample to  $T > 700$  K resulted in a drastic change in ultraviolet photoelectron spectrum, that is to say, below 700 K,  $\text{PH}_3$  will remain in molecular form. Our calculations confirm this result.

**3.2.2.  $\text{PH}_3$  on  $\text{Si}(111) 7 \times 7$  with some defects.** In order to investigate the influence of surface defects on the dissociation of  $\text{PH}_3(\text{ads})$  on  $\text{Si}(111) 7 \times 7$ , we replace the adatom in the DAS model by a  $\text{Si}_4$  cluster, as suggested by Yang and Zhao [13]. After repeating all the calculations as above, the results show that the binding energies are negative and 1.64 eV for  $\text{PH}_3$  adsorption on  $\text{S}_1\text{DB}$  and  $\text{S}_2\text{DB}$  sites, respectively. Now  $\text{PH}_3$  will not be adsorbed on the  $\text{S}_1\text{DB}$  site and the binding energy on the  $\text{S}_2\text{DB}$  site is reduced to about 0.47 eV. However, it is very interesting to note that, the energy barrier of  $\text{PH}_3(\text{ads})$  dissociation to  $\text{PH}_2(\text{ads}) + \text{H}(\text{ads})$  is greatly reduced to 0.48 eV. It seems that some kind of surface defect will promote the  $\text{PH}_3(\text{ads})$  dissociation on  $\text{Si}(111) 7 \times 7$ . We shall study this problem in more detail in the near future.

## 4. Conclusions

The adsorption structures and dissociation properties of  $\text{PH}_3$  on  $\text{Si}(100) 2 \times 1$  and  $\text{Si}(111) 7 \times 7$  have been studied by the ASED MO method. Our calculation results show the following:

(1) On the  $\text{Si}(100) 7 \times 7$  surface,  $\text{PH}_3$  is adsorbed undissociatively on the dangling bond, with a binding energy of 2.25 eV, a Si-P bond length of 2.23 Å, an angle from the surface normal of  $22^\circ$ , a P-H bond length of 1.52 Å and an angle of  $\text{PH}_3$  axis to the surface normal of  $21^\circ$ .

(2) The dissociation energy barrier of the first H atom for  $\text{PH}_3$  on  $\text{Si}(100) 2 \times 1$  is about 1.61 eV; it is in agreement with the experimental results of molecular adsorption of  $\text{PH}_3$  on  $\text{Si}(100)$  at room temperature.

(3) On  $\text{Si}(111) 7 \times 7$ , the most stable site for  $\text{PH}_3$  adsorption is  $\text{S}_2\text{DB}$ , and then the  $\text{S}_1\text{DB}$  site; the binding energies are 2.11 eV and 1.00 eV, respectively.

(4) Using the DAS model, our results show that the energy barrier for  $\text{PH}_3$  dissociation on  $\text{S}_1\text{DB}$  and  $\text{S}_2\text{DB}$  are 1.02 eV and 2.05 eV, respectively.

(5) If we replace the Si adatom in the DAS model by a  $\text{Si}_4$  small cluster, the binding energies of  $\text{PH}_3$  on  $\text{S}_2\text{DB}$  and  $\text{S}_1\text{DB}$  are 1.64 eV and negative, respectively. The dissociation energy barrier on  $\text{S}_2\text{DB}$  will reduce to 0.48 eV. It seems that the dissociation of  $\text{PH}_3$  on  $\text{Si}(111) 7 \times 7$  is caused by some kind of defect on this surface.

## Acknowledgments

This work is supported by the National Science Foundation of China and the Science Foundation of the National High Pure Silicon and Silicane Laboratory of Zhejiang University.

## References

- [1] Yu M L, Vitkavage D J, Meyerson B S 1986 *J. Appl. Phys.* **59** 4032
- [2] Meyerson B S and Yu M L 1984 *J. Electrochem. Soc.* **131** 2366
- [3] Yu M L and Meyerson B S 1984 *J. Vac. Sci. Technol. A* **2** 446
- [4] Chen P J, Colaianni M L, Wallace R M and Yates J T Jr 1991 *Surf. Sci.* **244** 177
- [5] Bozso F and Avouris Ph 1991 *Phys. Rev. B* **43** 1847
- [6] Roberts N and Needs R J 1990 *Surf. Sci.* **236** 112
- [7] Takayanagi K, Tanishiro Y, Takahashi M and Takahashi S 1985 *J. Vac. Sci. Technol. A* **3** 1502
- [8] Tong S Y, Huang H, Wei C M, Packard W E, Men F K, Glandor G and Webb M B 1988 *J. Vac. Sci. Technol. A* **6** 615
- [9] Domanek D and Bennemann K H 1985 *Phys. Rev. B* **31** 2485
- [10] Ru-Hong Zhou, Pei-Lin Cao and Lie-Quan Lee 1993 *Phys. Rev. B* **47** 10601
- [11] Clementi E and Raimondi D L 1963 *J. Chem. Phys.* **38** 2686
- [12] Zhou Ru-Hong, Cao Pei-Lin and Fu Song-Bao 1991 *Surf. Sci.* **249** 129
- [13] Yang W S and Zhao R G 1987 *Proc. 18th Int. Conf. on the Physics of Semiconductors* ed O Engstroin (Singapore: World Scientific)