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Adsorption and dissociation of PH₃ on Si(100) 2 × 1 and Si(111) 7 × 7: theoretical study

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Abstract. The adsorption structures and dissociation properties of PH₃ on Si(100) 2 × 1 and Si(111) 7 × 7 have been studied by the ASED MO method. Our calculation results show that, on the Si(100) 2 × 1 surface, PH₃ 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 PH₃ axis to the surface normal of 21°. The dissociation energy barrier of the first H atom for PH₃ is about 1.61 eV, in agreement with the experimental results of molecular adsorption of PH₃ on Si(100) at room temperature. On Si(111) 7 × 7, the most stable site for PH₃ adsorption of S₂DB, and then the S₁DB 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 PH₃ dissociation on S₁DB and S₂DB are 1.02 eV and 2.05 eV, respectively. If we replace the Si adatom in the DAS model by a Si₄ small cluster, the binding energies of PH₃ on S₂DB and S₁DB are 1.64 eV and negative, respectively. The dissociation energy barrier on S₂DB will reduce to 0.48 eV. It seems that the dissociation of PH₃ on Si(111) 7 × 7 is caused by some kind of defect on this surface.

1. Introduction

The interaction of PH₃ 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 PH₃ on the Si(100) 2 × 1 and Si(111) 7 × 7 surfaces.

On the Si(100) 2 × 1 surface, the results of x-ray photoelectron spectrometry and temperature-programmed desorption obtained by Yu *et al* [1] show that PH₃ mostly adsorbs non-dissociatively with an initial sticking coefficient of $S_0 = 1.0$ at room temperature; the PH₃ will begin to desorb molecularly at $\simeq 548$ K. The adsorbed phosphine was reported to decompose at temperatures near 475 K into three Si–H and Si–P. At $T \simeq 798$ 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 Si(111) 7 × 7, high-resolution electron-energy-loss spectroscopy study provides evidence for the dissociative adsorption of PH₃ on Si(111) 7 × 7 at 80 K. Depending upon the surface coverage, PH₂(ads) species are found on surface [4]. The thermal dissociation of the surface PH₂ species occurs between 450 and 500 K. However, Bozso and Avouris [5] have investigated the adsorption and reaction of PH₃ on Si(111) 7 × 7 between 100 K and 900 K

by UPS, LEED and ISS. Their results show that phosphine adsorption preferentially quenches the S₂DB sites; annealing the PH₃-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 × 7 surface.

Even with these experimental efforts applied to the system, the adsorption structure of PH₃ on Si(100) 2 × 1 and the adsorption structure and dissociation properties on Si(111) 7 × 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.

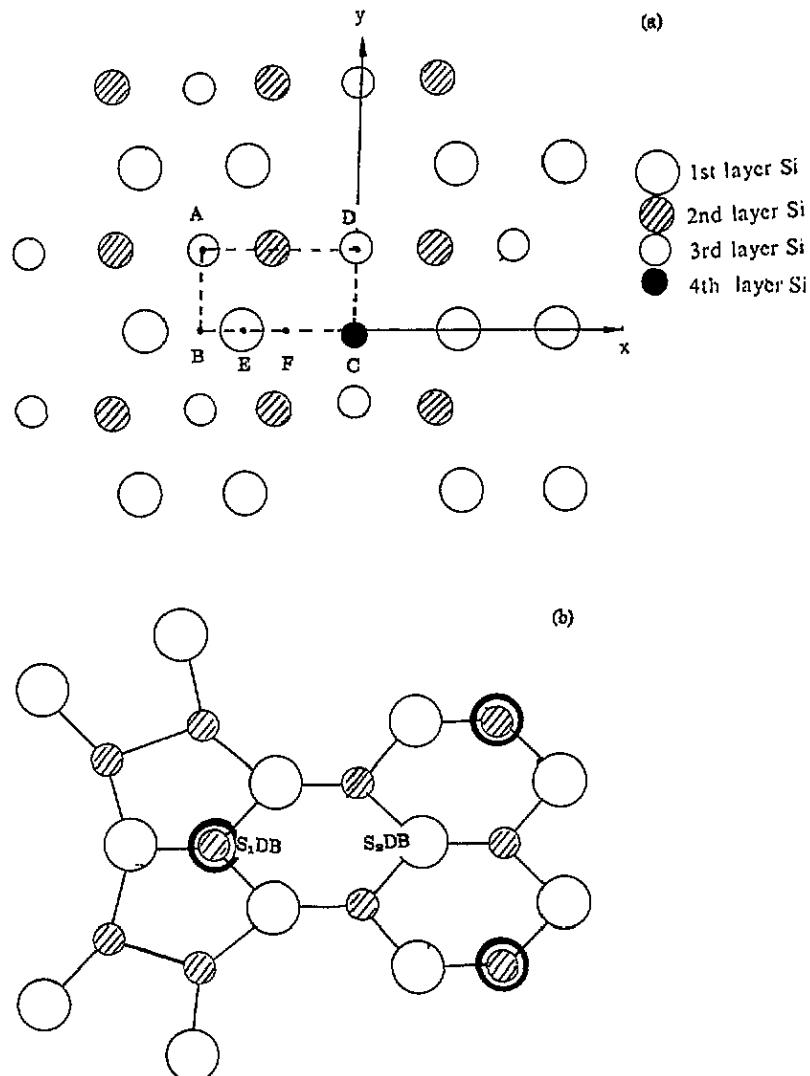


Figure 1. Cluster models of (a) Si₃₁H₃₆PH₃ and (b) Si₂₅H₂₄PH₃ for PH₃ adsorption on Si(100) 2 × 1 and Si(111) 7 × 7, and the possible adsorption sites: O, Si adatom in the DAS model. The hydrogen atoms used to saturate the dangling bonds are not shown for convenience.

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

Atom	s orbital			p orbital		
	n	I_p (eV)	ζ (au)	n	I_p (eV)	ζ (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 Si₃₁H₃₆PH₃ and Si₂₅H₂₄PH₃ (see figure 1) are used to simulate the PH₃ 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 S₁DB in figure 1(b)), one rest Si atom (S₂DB 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 PH₃ 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 PH₃ 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 ASED MO 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 α are adjustable parameters. In our calculations, α -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. PH_3 adsorption on $\text{Si}(100) 2 \times 1$

3.1.1. Molecular adsorption: PH_3 . As a first step, we considered the molecular adsorption of 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 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 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 β of the 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 PH_3 adsorption on $\text{Si}(100) 2 \times 1$ is on the dangling-bond position.

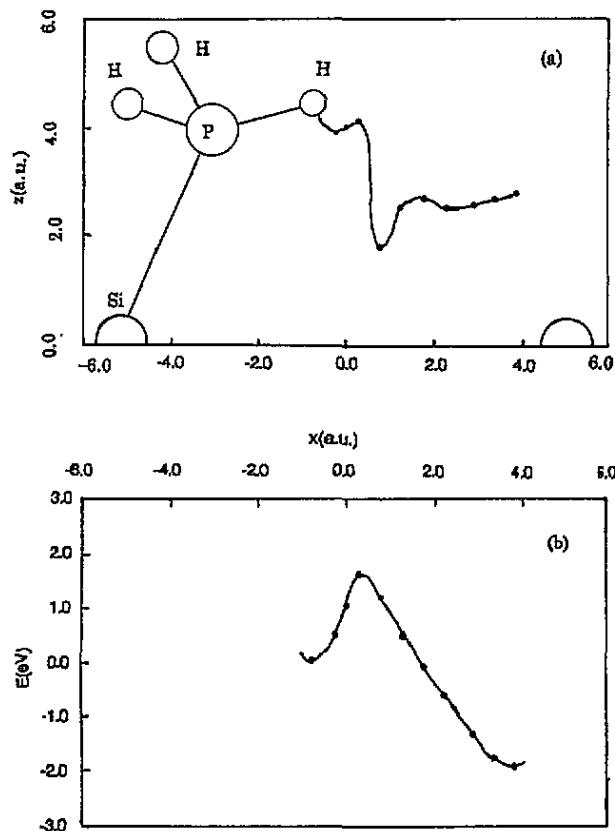


Figure 2. (a) The dissociation path of the H(1) atom on a dangling bond of $\text{Si}(100)$; —, PH_3 molecular axis. (b) The corresponding variation in total energy.

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 PH_3 is adsorbed on $\text{Si}(100) 2 \times 1$ 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 NH_3 is dissociatively adsorbed on the $\text{Si}(100) 2 \times 1$ 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 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 NH_3 . However, for $\text{PH}_3(\text{ads})$ on $\text{Si}(100) 2 \times 1$, PH_3 will lose about 0.75e in our result, and almost no electrons exist in the antibonding level; this is why PH_3 will be adsorbed on $\text{Si}(100) 2 \times 1$ non-dissociatively.

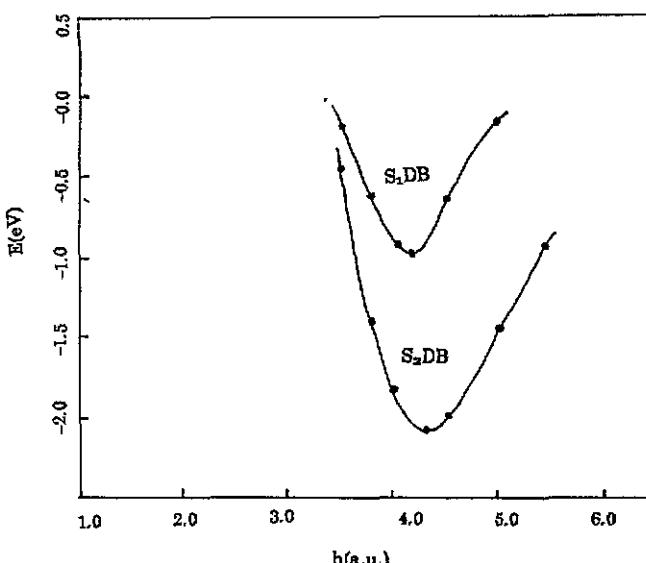


Figure 3. Total-energy E curves versus the adsorption heights h for PH_3 adsorption on the S_1DB and S_2DB sites of the $\text{Si}(111) 7 \times 7$ surface.

3.2. 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 PH_3 on $\text{Si}(100) 2 \times 1$, 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 S_1DB and the dangling-bond site of the first-layer Si atoms S_2DB 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 S_1DB and S_2DB are shown in figure 3. The results show that, for PH_3 on $\text{Si}(111) 7 \times 7$, the binding energies are 1.00 eV and 2.11 eV on S_1DB and S_2DB 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 S_2DB site is much larger than that on the S_1DB site; so PH_3 will adsorbed preferentially on the S_2DB site, in agreement with the UPS results of Bozso and Avouris [5].

For the dissociation of $\text{PH}_3(\text{ads})$ on the S_1DB and S_2DB 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 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 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, PH_3 will remain in molecular form. Our calculations confirm this result.

3.2.2. *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 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 PH_3 adsorption on S_1DB and S_2DB sites, respectively. Now PH_3 will not be adsorbed on the S_1DB site and the binding energy on the S_2DB 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 PH_3 on $\text{Si}(100) 2 \times 1$ and $\text{Si}(111) 7 \times 7$ have been studied by the ASE MO method. Our calculation results show the following:

(1) On the $\text{Si}(100) 7 \times 7$ surface, 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°, a P-H bond length of 1.52 Å and an angle of PH_3 axis to the surface normal of 21°.

(2) The dissociation energy barrier of the first H atom for 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 PH_3 on $\text{Si}(100)$ at room temperature.

(3) On $\text{Si}(111) 7 \times 7$, the most stable site for PH_3 adsorption is S_2DB , and then the S_1DB 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 PH_3 dissociation on S_1DB and S_2DB are 1.02 eV and 2.05 eV, respectively.

(5) If we replace the Si adatom in the DAS model by a Si_4 small cluster, the binding energies of PH_3 on S_2DB and S_1DB are 1.64 eV and negative, respectively. The dissociation energy barrier on S_2DB will reduce to 0.48 eV. It seems that the dissociation of PH_3 on $\text{Si}(111) 7 \times 7$ is caused by some kind of defect on this surface.

Acknowledgments

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