Cluster Modeling of the Trimethylphosphine Adsorption and Dissociation on the Si(111)–7 × 7 Surface

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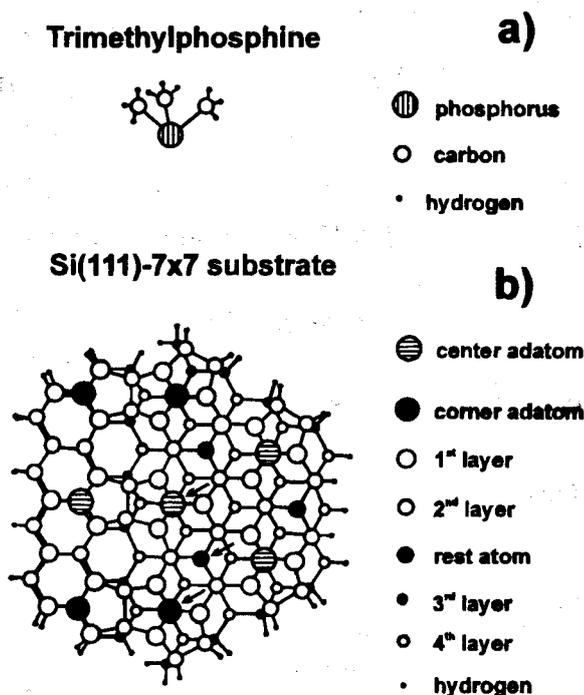[†] *Far Eastern State University, 8 Sukhanova, 690022 Vladivostok, Russia*

Using semiempirical and *ab initio* numerical methods we simulated the trimethylphosphine (TMP) molecule behavior on the Si(111)-7×7 surface. It was shown that the center adatom of the 7×7 cell is the best site for the TMP adsorption and the rest atom is the worse site. The TMP molecule can dissociate on rest atom sites in the following way: CH_3 groups leave the P atom and move to the nearest silicon adatoms. The reaction energy gain of 1 eV and the energy barrier of 5.3 eV have been obtained. The calculated atomic and electronic structure of the dissociated TMP state agrees with the reported STM images.

1. Introduction

Trimethylphosphine (TMP) is one of new chemical complexes interesting for doping of silicon with phosphorus. A schematic view of the TMP molecule is shown in Fig.1(a). It consists of one P atom and three CH_3 groups. Because of two unsaturated phosphorus bonds the chemical reactivity of this molecule is rather large, thus TMP is suitable for surface doping of silicon and for other technological applications.

As it was shown by the direct scanning tunneling microscopy observation [1], most of TMP molecules are adsorbed preferably on center adatom sites of the Si(111)-7 × 7 surface. Then it was observed [2] that after thermal annealing a TMP molecule moved from a center adatom site to a rest site in some strange way: its STM image changed from single to triple for negative sample voltage bias of −1.5 eV but remained single (decreasing the intensity) for positive sample voltage bias of +1.5 eV.

This work is devoted to the computer modeling of the TMP molecule behavior on the Si(111)-7 × 7 surface.

Trimethylphosphine **a)**

⦿ phosphorus

○ carbon

• hydrogen

Si(111)-7x7 substrate **b)**

⊜ center adatom

● corner adatom

○ 1ˢᵗ layer

○ 2ⁿᵈ layer

● rest atom

• 3ʳᵈ layer

○ 4ᵗʰ layer

• hydrogen

Figure 1. Atomic schemes of the TMP molecule (**a**) and the $Si_{145}H_{75}$ cluster (**b**) modeling the Si(111)-7 × 7 surface. The circles indicated by arrows are the atoms (the rest atom, the center and corner adatoms) used as adsorption sites in calculations.

2. Method of calculations and its verification

To study the energetics and geometry of the TMP molecule on the Si(111)-7× 7 surface we used the advanced semiempirical quantum-chemical AM1 method (Austin Model 1) [3], a version of the modified intermediate neglect of differential overlap (MINDO) [4, 5, 6] realized in the frame of the CLUSTER-Z1 package [7, 8]. This package allows one to optimize the atomic configurations by minimizing the total energy gradients over all atomic coordinates.

Semiempirical methods are significantly faster than *ab initio* methods, but their accuracy is limited by the need to choose the correct set of parameters. In particular, the AM1 method is usually parametrized to reproduce heats of atomization and molecular geometries. Therefore, the ability of a semiempirical method to describe an arbitrary configuration of atoms must be verified.

The AM1 method was recently verified for silicon-phosphorus systems in our recent work [9] where P-Si and P-P dimers on the Si(100) surface were studied. In accordance with the STM investigations [10, 11] and the *ab initio* molecular

	d(P-C) (Å)	d(C-H) (Å)	C-P-C angle (deg)
Our results	1.76	1.11	100.90
H-F calc. [12]	1.845	1.096	98.95

Table 1. Geometry parameters of the free TMP molecule.

orbital calculations [10] it was found that P-Si dimers are energetically favorable. All quantitative values (energy differences, bond lengths and angles) close to the known data [10, 11] have been obtained.

Before studying the TMP molecule on the Si(111)-7 × 7 surface, the test calculations of the TMP molecular geometry have been carried out. Calculated geometry parameters (bond lengths and angles) are compared with the *ab initio* Hartree-Fock results [12] in Table 1. The AM1 method gives us a good accuracy for the TMP calculations as shown in Table 1.

3. Results of calculations

3.1 TMP adsorption

As it follows from the experiment [1], the adsorption and migration behaviors of TMP molecules on the unfaulted and faulted regions of the 7 × 7 surface are similar. Therefore, the TMP molecule on the unfaulted region only was studied. To simulate the Si(111)-7 × 7 surface we used the $Si_{145}H_{75}$ cluster shown in Fig.1(b). This cluster models the unfaulted part of the 7 × 7 cell and consists of four atomic layers and eight adatoms. All broken Si bonds were terminated by H atoms with the equilibrium Si-H 1.46 Å distances. The initial Si coordinates were taken from the reported data [13] and then the cluster geometry was additionally optimized by the AM1–CLUSTER-Z1 procedure. The final atomic positions were in agreement with the previous data [13] to within 0.05 Å.

To study the energetics of the TMP adsorption on the Si(111)–7 × 7 surface, the TMP molecule was placed on three different sites: on a rest atom, on a center adatom, and on a corner adatom. These sites are marked by arrows in Fig.1(b). The binding energies together with the P-Si and P-C bond lengths for the three cases are listed in Table 2. It is clear that the center adatom is the best site for adsorption and the rest atom is the worst one in agreement with the experiment [1]. The energy difference between the center and corner adatom sites is 0.09 eV. From the experimental diagram of the distribution of adsorption sites [1] one can obtain the energy difference of 0.06 eV, which is in good agreement with the calculated result.

| Site	Binding energy (eV)	d(P-Si) (Å)	d(P-C) (Å)
Center adatom	-1.94	2.38	1.77
Corner adatom	-1.85	2.38	1.77
Rest atom	-1.68	2.42	1.78

Table 2. Binding energy and geometry parameters of the TMP molecule placed upon the Si(111)7 × 7 surface.

3.2 TMP surface dissociation

A rest atom has three symmetrical neighbors (adatoms) with dangling bonds. Each center and corner adatom is located close to two or one neighbor rest atoms, respectively. Therefore, we studied the dissociation case in which a P atom was on a rest atom and three CH_3 groups were on adatoms. The binding energy was found to be -2.67 eV, i.e. 1 eV lower than in the adsorption case. In other words, the full surface dissociation of a TMP molecule on a rest atom is energetically possible. In this case the P-Si distance is 2.42 Å (like in the adsorption case) and C-Si distances are 1.85 Å for center adatom sites and 2.08 Å for a corner adatom site.

As noted above, STM results show [2] that the TMP images on the rest atom are different for positive and negative sample voltage biases (V_S). Namely, three bright protrusions are seen on the adatom sites for $V_S = -1.5$ V and there is a darker protrusion on the rest atom for $V_S = +1.5$ V. To clarify these results the calculations of the electronic structure for the TMP molecule dissociated on the Si(111)-7 × 7 surface have been carried out assuming the above configuration. Since the AM1 method does not correctly describe silicon electronic states (it gives, for example, a forbidden gap of several eV), we used here the *ab initio* local-density approximation method in a cluster approach [14].

Calculated partial densities of states for P and C atoms are plotted in Fig.2 (H atoms are invisible in STM). One can see that carbon atoms have peaks of occupied states between the Fermi level and -1.5 eV. The phosphorus atom has also some states near -1.5 eV. However, C atoms are located higher above the silicon substrate than the P atom: the C atom on the corner and center adatoms are higher by 0.91 Å and 0.72 Å than the P atom. Thus, the C-tip distances are less than the P-tip distance, leading to the result that the P-tip tunnel currents at $V_S = -1.5$ V should be lower. Furthermore, the C (corner) image must be more intensive than the C (center), which is in good agreement with the STM results. On the other hand, the phosphorus atom has an intensive peak at $+0.2$ eV but C atoms have very small number of unoccupied states between the Fermi level and $+1.5$ eV. Thus, the P image at $V_S = +1.5$ V is brighter
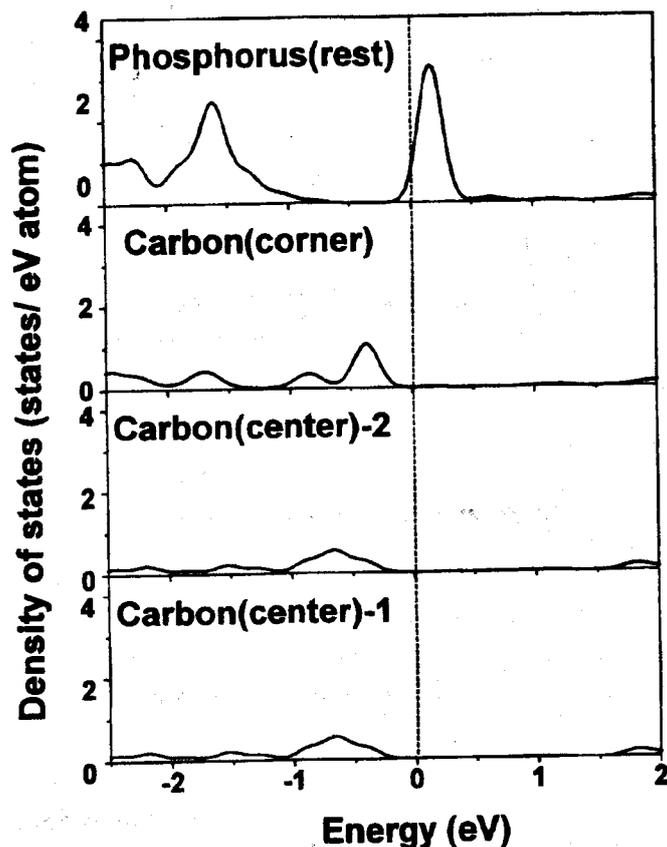
Figure 2. Partial densities of states of the TMP molecule dissociated on the rest atom of the Si(111)-7 × 7 surface. Vertical dotted line indicates the Fermi level position.

compared with C images. However, the P-tip distance is large resulting in the low image intensity. All these results are in good agreement with experimental data [2].

To understand why TMP does not dissociate on adatoms (where only two or one dangling bond neighbors are present) we studied the case where only one of CH_3 groups was removed from the P-$(CH_3)_3$: namely, the P-$(CH_3)_2$ complex was on the center adatom and one of CH_3 groups was placed on the rest atom. The binding energy was found to be positive (+5.46 eV). This suggests that only a simultaneous breaking of three P-(CH_3) bonds is favorable.

Moving the three CH_3 groups away from a P atom and optimizing all other coordinates, the energy difference was calculated to obtain the dissociation reaction barrier. The result of the calculation is plotted as a function of the P-C
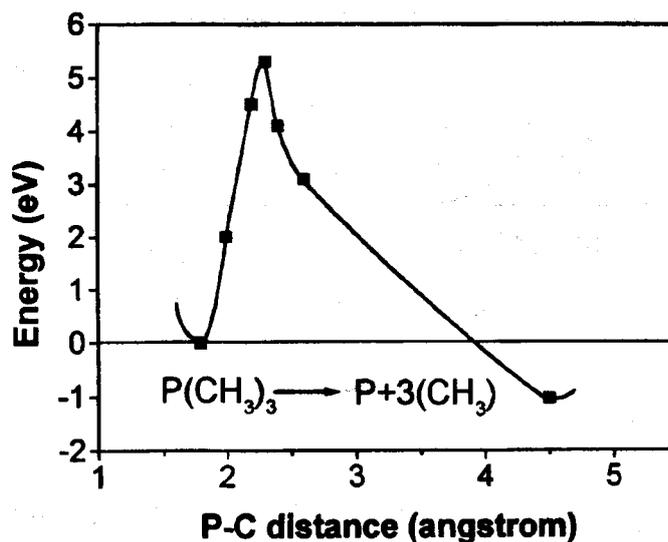
Figure 3. The dissociation reaction barrier for the TMP molecule placed on the rest atom of the Si(111)-7 × 7 surface. The left minimum corresponds to the adsorption state (C atoms are bonded with the P atom). The right minimum corresponds to the full surface dissociation (C atoms are bonded with Si adatoms).

distance in Fig.3. The sharp barrier with a 5.3 eV height is found at the P-C distance equal to 2.3Å. For comparison, the dissociation energy of the free TMP molecule ($P(CH_3)_3 \rightarrow P + 3\ CH_3$) was calculated. It is found to be 10.4 eV which is twice as large as the TMP dissociation energy on the Si surface.

The binding energy of the P atom on the rest atom site was calculated for the surface without the CH_3 groups. The energy was found to be -0.77 eV. Replacing the P atom and the Si rest atom, the binding energy of -6.08 eV is obtained. The binding energy of the CH_3 group on the Si adatom was also found to be -2.95 eV. This implies that a rest atom can be substituted by the phosphorus atom upon annealing, resulting in doping of the silicon substrate, while the CH_3 groups can stay alone on the silicon surface.

4. Conclusion

Our computer simulation describes the behavior of a TMP molecule on the Si(111)-7 × 7 surface in good agreement with STM experiments. It shows that the center adatom of the 7 × 7 cell is the best site for the TMP adsorption and the rest atom is the most unfavorable site. The TMP molecule can dissociate on the rest atom in the following way: CH_3 groups leave the P atom and move to

the nearest silicon adatoms. This reaction is characterized by a 5.3 eV energy barrier. The P atom can substitute the rest Si atom with the energy gain of 5.3 eV. The calculated electronic structure of the dissociated TMP state allows to explain the triple splitting of the TMP STM image under the negative sample voltage bias.

Acknowledgements

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