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Letter to the Editor

Energetics of P–Si and P–P dimers on the Si(100)-2 × 1 surface

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Abstract

The Austin Model 1 (AM1) semi-empirical numerical method combined with the geometry optimization procedure was used to study the energetics of P–Si and P–P dimers on the Si(100)-2 × 1 surface in a cluster approach. It has been found that the P–Si dimers are more preferable energetically. The energy profit depends on the cluster size and is about 0.8–0.9 eV for large clusters. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Dopant segregation on surfaces of semiconductors is frequently investigated because of its fundamental and technological interest. Phosphorus is a common dopant used in the fabrication of n-type silicon, and the Si(100) surface is the most technologically important silicon surface. It is well-known that the clean Si(100) surface prefers to be reconstructed to the dimerized Si(100)-2 × 1 surface and phosphorus does not induce any new reconstruction on the Si(100)-2 × 1 surface [1]. Wang et al. [2], using scanning tunneling microscopy, observed P–P and Si–P dimers on this surface. Counting statistics were used to study the equilibrium between Si–Si, P–Si, and P–P dimers, showing that the formation of P–Si heterodimers is more preferable. Ab initio molecular orbital calculations [3] have shown that the overall energy change for 2(Si–P) → Si–Si + P–P is +0.27 eV, or about +0.13 eV per P–Si dimer. However, in Ref. [3], a small cluster having only nine Si atoms was used as a model of the Si(100)-(2 × 1) surface; therefore, the results are rather discussable. The present work is an attempt to obtain more realistic information on the energetics of P–Si and P–P dimers on the Si(100)-2 × 1 surface.

2. Method

To calculate the total energy of silicon–dopant systems, we used the advanced semi-empirical quantum-chemical method Austin Model 1 (AM1) [4], realized in the frame of the CLUSTER-Z1 package [5,6]. This package allows one to optimize atomic configurations by the minimization of the total energy gradients over all atomic coordinates.

First of all, we carried out the calibration calculations using the same cluster and the same method-

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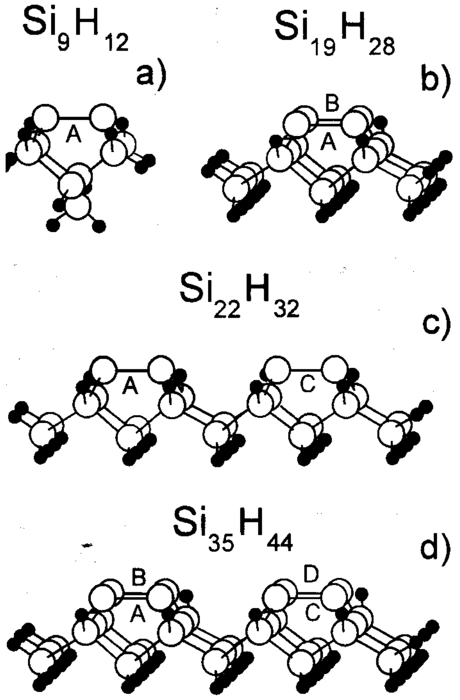

Fig. 1. Clusters used to compare the energetics of P–Si and **P–P** dimers. White circles are Si atoms; black circles are H atoms. Letters A, B, C, and D are used for marking the different dimers as it is clarified in the text.

ology as were used in Ref. [3]. Each dimer (Si–Si, P–P or P–Si) was studied using a separated Si_9H_{12} cluster (Fig. 1a) modeling the Si(100) surface (only one surface dimer, all H atoms are fixed); then energies of two clusters ([P–Si + P–Si] or [P–P + Si–Si] were summarized and the difference ([P–Si + P–Si] − [P–P + Si–Si]) was calculated. In other words, the correlation between dimers was ignored and a small cluster approach was used.

The energy profit for (P–Si) + (P–Si) → (Si–Si) + (P–P) was found to be 0.35 eV, or about 0.18 eV per P–Si dimer. Thus, the agreement with ab initio results of Hamers et al. [3] is rather good.

Then, in a frame of the non-correlated dimers approach, we studied the cluster size effect. To do this, we have repeated the above calculations using larger clusters ($Si_{19}H_{28}$, $Si_{22}H_{32}$ with two dimers and $Si_{35}H_{44}$ with four dimers) shown in Fig. 1b,c,d. These clusters have three atomic layers (one dimerized and two bulk). Like in the small cluster case, only one of the dimers may be a P–P or P–Si dimer. The [P–P + Si–Si] or [P–Si + P–Si] energies were obtained as sums of energies of corresponding clusters. All results for non-correlated dimers are collected in Table 1.

3. Results and discussion

The correlation between P–Si dimers was studied placing two P–Si dimers in the same cluster (one of the $Si_{19}H_{28}$, $Si_{22}H_{32}$, $Si_{35}H_{44}$ clusters). Because P–Si dimers may be oriented by different ways. we studied the following different cases.

1. AB/PSi–PSi. Two P–Si dimers with identical orientations in the same row.
2. AB/PSi–SiP. Two P–Si dimers with opposite orientations in the same row.
3. AC/PSi–PSi. Two P–Si adjacent dimers with identical orientations in different rows.
4. AC/PSi–SiP. Two P–Si adjacent dimers with opposite orientations in different rows. Si atoms look out at the same valley.
5. AC/SiP–PSi. Two P–Si adjacent dimers with opposite orientations in different rows. Si atoms look out on different valleys.
6. AD/PSi–PSi. Two P–Si non-adjacent dimers with identical orientations in different rows.
7. AD/PSi–SiP. Two P–Si non-adjacent dimers with opposite orientations in different rows. Si atoms look out on the same valey.

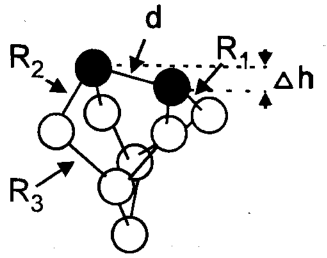

Fig. 2. Generalized atom scheme of Si–Si, **P–Si**, and **P–P dimers**. Black circles represent Si atoms which may be substituted by P; ***d*** is the dimer length; Δh is the height difference between dimer atoms; R_1 and R_2 are the bond lengths between dimerized atoms and the underlying Si layer; R_3 is the bond length between Si atoms of first and second bulk layers. In the **P–Si** case, the lowest dimer atom is the P atom.

Table 1
Energy differences of the (P–Si)+(P–Si) and (P–P)+(Si–Si) non-correlated dimer systems at the Si(100)-2×1 surface

Si_9H_{12}		$Si_{22}H_{25}$	$Si_{22}H_{32}$	$Si_{35}H_{44}$
Hamers et al. [3]	Present			
0.27	0.35	1.09	1.11	0.82

Each dimer is on a separate cluster. The Si_9H_{12} cluster has one surface dimer; the $Si_{19}H_{28}$ cluster has one row with two dimers; the $Si_{22}H_{32}$ cluster has two dimers in neighbouring rows; the $Si_{35}H_{44}$ cluster has two rows with two dimers in each.

Table 3
Geometric parameters of Si–Si, P–Si and P–P dimers on Si(100)

	Wang et al. [2]					Present				
	d	Δh	R_1	R_2	R_3	d	Δh	R_1	R_2	R_3
Si–Si	2.30	–	2.41	2.41	2.35	2.42	0	2.38	2.38	2.37
P–Si	2.25	0.30	2.25	2.35	2.35	2.16	0.31	2.13	2.41	2.37
P–P	2.25	–	2.20	2.20	2.35	2.04	0	2.27	2.27	2.35

All details are described in the caption to Fig. 2.

8. AD/SiP–PSi. Two P–Si non-adjacent dimers with opposite orientations in different rows. Si atoms look out on different valleys.

Letters A, B, C, and D are used for marking the different dimers (see Fig. 1). For example, AC/SiP–PSi means that this case includes a A/SiP dimer in the one row and a C/PSi dimer in the second row. Orientations of the dimers are opposite. Results for correlated dimers are summarised in Table 2. Analysing data of Tables 1 and 2, one can see that the size effect for the non-correlation approach is rather large. The energy difference for the (P–Si) + (P–Si) → (Si–Si) + (P–P) transition changes from 0.35 to 0.82 eV when moving from Si_9H_{12} to $Si_{35}H_{44}$. The 0.82 eV value, obtained for the largest $Si_{35}H_{44}$ cluster without taking into account the P–Si—P–Si correlations, is very close to the values (0.82–0.86 eV) obtained for the P–Si—P–Si correlated pairs situated in different dimer rows in the same cluster. Or, in other words, the correlation between P–Si dimers, which are situated in different rows, is very small. On the other hand, the energy of a P–Si—P–Si pair, which is situated in the same row, depends on the mutual orientation of P–Si dimers: energy is lower for P–Si dimers with the same orientation. For cases in which dimers are in different rows, the mutual dimer orientation is practically negligible. Small increase of energy up to 1.09–1.11 eV for the middle clusters ($Si_{19}H_{28}$ and $Si_{22}H_{32}$) may be the result of the known size oscillation effect.

It is interesting to compare our Si–Si, P–Si and P–P dimer geometries with the data obtained by Wang et al. [2]. The generalized atom scheme of the dimers is shown in Fig. 2. Calculated geometry parameters (for the $Si_{35}H_{44}$ cluster) are collected in Table 3. One can see that the discrepancy between our results and the results of Wang et al. is rather small except the P–P dimer bond. We have found this bond shorter by 0.21 Å than Wang et al. have reported. This difference may be accounted for by the size effect (using the Si_9H_{12} cluster, we have obtained the P–P dimer bond of 2.15 Å, which is closer to 2.25 Å of Wang et al. than 2.04 Å obtained at the $Si_{35}H_{44}$ cluster). However, the short P–P bond may also be an artefact of our semi-empirical calculation.

Table 2
Energy differences of (P–Si + P–Si) and (P–P + Si–Si) correlated dimer systems at the Si(100)-2 × 1 surface

	Dimers in the same row		Dimers in different rows					
			Adjacent dimers			Non-adjacent dimers		
	1	2	3	4	5	6	7	8
$Si_{22}H_{25}$	0.89	0.73						
$Si_{22}H_{32}$			0.94	0.92	0.96			
$Si_{35}H_{44}$	0.91	0.47	0.83	0.82	0.85	0.83	0.83	0.86

Dimers of the studied dimer pair are situated at the same cluster. The numbers 1, 2,..., 8 correspond to the cases described in the text.

4. Conclusion

We have provided a semi-empirical cluster study of the energetics of P–Si and P–P dimers on the Si(100)-2 × 1 surface. We have found that P–Si dimers are more preferable energetically than P–P dimers. The energy profit depends on the cluster size and is about 0.8–0.9 eV for large clusters.

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