

Computer study of boron segregation at the Si(100)-2 × 1 and Si(111)-√3 × √3 surfaces

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Energetics of the boron substitution near the Si(100)-2 × 1 and Si(111)-√3 × √3 surfaces have been studied using the semi-empirical cluster AM1 method at substitutional positions at the Si(100)-2 × 1 surface. It has been found that in the both cases boron prefers to be in the second layer, that is it occupies substitutional positions that are bonded with dimers of the Si(100)-2 × 1 surface and S₅ sites under adatoms of the Si(111)-√3 × √3 surface. The energies, counting from the fourth bulk-like layer, for the Si(100)-2 × 1 and Si(111)-√3 × √3 surfaces are -1.3 and -2.1 eV, respectively. These values may be interpreted as corresponding segregation enthalpies. © 1999 American Vacuum Society. [S0734-2101(99)09405-1]

1. INTRODUCTION

Dopant segregation near surfaces and interfaces of semiconductors is frequently investigated because of its fundamental and technological interest. Accordingly to the classical McLean model¹ the segregation process is controlled by the value of the segregation free energy ΔG which is the difference in free energy between the dopant at the surface and that in the bulk. In this model the surface (C_s) and bulk (C_b) dopant equilibrium concentrations are connected by the following expression:

$$C_s/(1 - C_s) = C_b/(1 - C_b) \exp(-\Delta G/kT).$$

It is well known that boron exhibits segregation at Si surfaces,²⁻⁵ inducing several kinds of surface reconstructions. The 2 × 1, 2 × 2, and 4 × 4 reconstructions are known for the Si(100) surface⁶⁻⁸ and that for the √3 × √3 one has been found for the Si(111) surface.^{9,10}

In all these surface phases boron has a tendency to be in subsurface layers, substituting for Si atoms. For the B/Si(111)-√3 × √3 there are a lot of experimental and theoretical works showing that boron occupies fivefold-coordinated substitutional sites (S₅) under silicon threefold-coordinated (T₄) adatoms.¹¹⁻¹⁵ As for Si(100)-B surface reconstructions, there are several models of their atomic geometry,¹⁶⁻¹⁹ however all of them use Si-Si dimers as basic structure elements and place B atoms in the second atomic layer.

In spite of intensive investigations, there is a lack of quantitative information on the boron energetics near the silicon surface. Segregation theory usually operates with the free energy.^{1,20}

Boron segregation free energy of about -0.5 eV for the B/Si(111)-√3 × √3 surface (ΔG) has been found^{5,21} using the scanning tunneling microscopy (STM) technique and Monte-Carlo simulations at T=1245 K. However, the free energy depends on the temperature:

$$\Delta G = \Delta H - T\Delta S,$$

where H and S are the total enthalpy and entropy, respectively. Therefore, the free energy is hardly comparable with the results of total energy calculations in which temperature effects are not present. For this comparison the enthalpy is more suitable.

Boron segregation enthalpy of -2 eV for the B/Si(111)-√3 × √3 surface was found by Thibaudau *et al.*⁵ using the STM technique and counting the B-S₅ atoms. It is curious that the authors of the work⁵ obtained this value (-2 eV) from the linear dependence of the Arrhenius plot of $C_s/(1 - C_s)$, however, they supposed by mistake that it was the free energy (not the enthalpy) and, being surprised at its rather high value, performed Monte-Carlo calculations to find the value of -0.52 eV. The latter value was really the free segregation energy, but the origin of the -2 eV value was not discussed in their work⁵ at all.

Recently results of an *ab initio* study of B-Si(100) segregation were presented by Ushio *et al.*²² They used the local density approximation (LDA) cluster approach and found that the energy of the B atom in the second atomic layer is about 0.3 eV lower than in the first layer and about 0.5 eV lower than in the third layer. However, those authors used a rather small cluster (Si₁₂H₁₆) without surface dimers, therefore, their results may be regarded only as qualitative.

The present work is a computational attempt to obtain some quantitative information on the energetics of boron at

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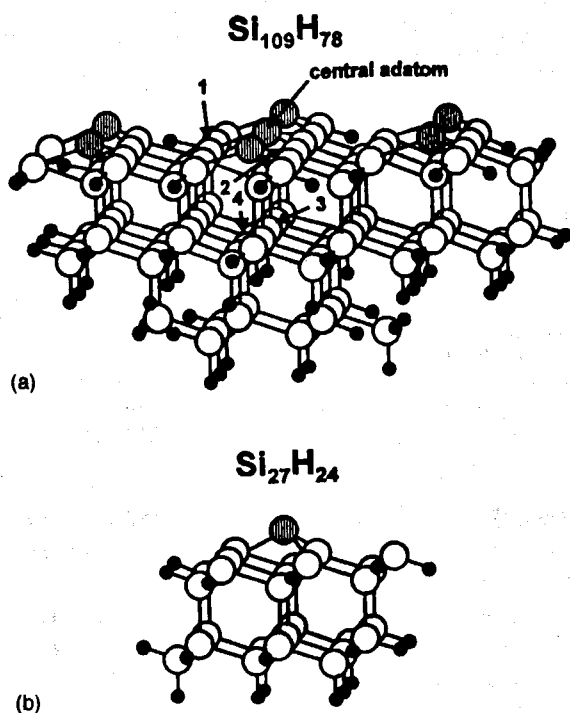


FIG. 1. Schemes of atomic clusters modeling the Si(111)- $\sqrt{3} \times \sqrt{3}$ surface: (a) $\text{Si}_{109}\text{H}_{78}$; (b) $\text{Si}_{27}\text{H}_{24}$. The small closed circles are H atoms, the open circles are Si atoms, and the vertical lined circles are Si adatoms. The Si atoms to be substituted by B ones are labeled by arrowed numbers and are described in the text.

the Si(100)- 2×1 and Si(111)- $\sqrt{3} \times \sqrt{3}$ surfaces and in sub-surface layers.

II. METHOD OF CALCULATION

To calculate the total energies of silicon-dopant systems we used the advanced semi-empirical quantum-chemical method AM1 (Austin model 1),²³ a version of the modified intermediate neglect of differential overlap (MINDO),²⁴⁻²⁶ realized within the framework of the CLUSTER-Z1 package.^{27,28} This package allows one to optimize atomic configurations by minimizing the total energy gradients over all atomic coordinates. Because temperature is not included in this approach, calculated energies may be interpreted as corresponding enthalpies.

Having a semi-empirical chemical nature the AM1 method is parametrized to reproduce heats of atomization and molecular geometries of many known systems. However, its accuracy for some nonstandard cases may be disputed. Although the method was used successfully to study some Si, Si-Al, Si-O, and Si-B systems,²⁹⁻³² we will present below additional verification for the B/Si(111)- $\sqrt{3} \times \sqrt{3}$ system.

For the test geometry calculations we used two clusters of different sizes, modeling the S(111)- $\sqrt{3} \times \sqrt{3}$ surface—the $\text{Si}_{109}\text{H}_{78}$ and $\text{Si}_{27}\text{H}_{24}$ clusters shown in Fig. 1. The first cluster had seven S_5 sites and the second cluster had one S_5 site. In this test all these S_5 sites were occupied by B atoms. Broken Si bonds were saturated with H atoms. Initially all the Si atoms were placed in ideal bulk positions and all Si-H

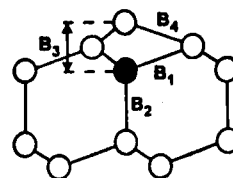


FIG. 2. Scheme of atomic bonds near the optimized B- S_5 site.

distances were equal to equilibrium 1.46 Å values. During the optimization procedure all H atoms were fixed. All clusters were neutral here as well as in all the following calculations.

The B- S_5 scheme of the atomic geometry is shown in Fig. 2 and the optimized values of interatomic distances are presented in Table I, which gives a comparison of the experimental^{13,14} and theoretical *ab initio*¹⁵ results. The results presented for the $\text{Si}_{109}\text{H}_{78}$ cluster correspond to the central B- S_5 site. All values (in Å) cited are given as published except those labeled by an asterisk which have been calculated by us using published displacement data. One can see that our geometry results are in satisfactory agreement with those in the literature. The cluster size effect is not large and demonstrates convergence to experimental atomic geometry.

Then, using the same clusters we have carried out the test calculations of the total cluster energy for the B- S_5 and B- T_4 cases. (In this test only the central B atom of the $\text{Si}_{109}\text{H}_{78}$ cluster was moved; the six B atoms were in B- S_5 positions every time during calculations.) The lowest energy was found for the B- S_5 case, and the B- T_4 value is higher by 1.1 eV for the $\text{Si}_{27}\text{H}_{24}$ small cluster and by 1.05 eV for the large $\text{Si}_{109}\text{H}_{78}$ cluster. These differences (ΔE) are in good agreement with the *ab initio* calculations of Kaxiras *et al.*¹⁵ ($\Delta E=1$ eV) and of Bedrossian *et al.*¹¹ ($\Delta E=0.93$ eV). Therefore, we can conclude that our semi-empirical simulation gives a good energetic representation of the B-Si(111) surface (with an accuracy of 0.1 eV) and the cluster size energy effect is not significant.

For the Si(100)- 2×1 surface we made special calculations to test the ability of the AM1 method to describe 2×1 Si dimers. We used the $\text{Si}_{83}\text{H}_{64}$ cluster shown in Fig. 3. This cluster consists of 83 Si atoms with 6 atomic layers.

Without dopants, the stable Si(100)- 2×1 geometry was determined. Like the known cluster investigations³³⁻³⁵ the

TABLE I. Interatomic distances (Å) near the optimized B- S_5 site. The B_1 , B_2 , B_3 , and B_4 notations are clear from Fig. 2.

	Present results		Literature data		
	$\text{Si}_{26}\text{H}_{24}\text{B}_1$	$\text{Si}_{102}\text{H}_{78}\text{B}_7$	Calculation ^a	Experiment ^b	Experiment ^c
B_1	2.00	2.02	2.14*	2.15	2.18*
B_2	1.94	1.96	2.04*	2.19	2.00
B_3	2.10	2.02	2.22*	2.32	1.98*
B_4	2.46	2.42	2.39*	2.34*	2.21*

^aReference 15.

^bReference 14.

^cReference 13.

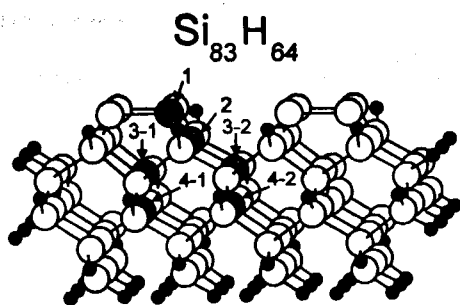


FIG. 3. Scheme of the atomic $\text{Si}_{83}\text{H}_{64}$ cluster modeling the $\text{Si}(100)-2\times 1$ surface. Open circles are Si atoms; closed circles are H atoms. Si atoms substituted by dopants are shown as lined circles. They are labeled by arrowed numbers and are described in the text.

symmetric dimer stable structure was obtained. It seems that the asymmetric dimer structure, reported by numerous authors³⁶⁻⁴¹ using zone methods, has a cooperative origin and cannot be obtained in a cluster approach. The dimer length was found to be 2.15 Å for the singlet spin state and 2.40 Å for the triplet one. (The experimental value is 2.3 Å.⁴²) The triplet state was found to be more stable energetically for the both surfaces, thus this state was used for the following calculations.

III. RESULTS AND DISCUSSIONS

A. $\text{B}/\text{Si}(111)-\sqrt{3}\times\sqrt{3}$ system

Calculations for the $\text{B}/\text{Si}(111)-\sqrt{3}\times\sqrt{3}$ system were made using the $\text{Si}_{109}\text{H}_{78}$ cluster. This cluster has six atomic layers, and its fourth layer atomic positions may be considered bulk-like ones. Since the $\text{B}/\text{Si}(111)-\sqrt{3}\times\sqrt{3}$ surface phase has different amounts of boron atoms at different segregation temperatures,⁵ we studied two extreme cases.

- (A) The $\text{Si}_{108}\text{H}_{78}\text{B}_1$ cluster. The only B atom is placed in the central adatom site or in the first-fourth atomic layers below the central adatom, as shown in Fig. 1(a). The other six S_5 sites are occupied by Si atoms.
- (B) The $\text{Si}_{102}\text{H}_{78}\text{B}_7$ cluster. One of the B atoms is placed in the same way as that described above, and the other six B atoms are in their $\text{B}-\text{S}_5$ sites.

The results are presented in Table II. One can see that the lowest energy corresponds to the case in which boron substitutes for a Si atom in the second atomic layer ($\text{B}-\text{S}_5$ site). The calculated values of the second-fourth layer difference (-1.8 eV for case A and -2.1 eV for case B) are very close to the experimental segregation enthalpy (-2 eV).⁵ Moreover, detailed analysis of the data in Ref. 5 lets us conclude

TABLE II. Layer-by-layer energies of a single B atom in the $\text{B}/\text{Si}(111)-\sqrt{3}\times\sqrt{3}$ system. Case A is the $\text{Si}_{108}\text{H}_{78}\text{B}_1$ cluster, and case B is the $\text{Si}_{102}\text{H}_{78}\text{B}_7$ cluster. Energies (in eV) are given with respect to the fourth bulk-like layer.

Case	Adatom	1	2	3	4
A	-0.82	-0.75	-1.83	-0.21	0.00
B	-1.05	-0.84	-2.10	-0.32	0.00

TABLE III. Energies of boron in the $\text{B}/\text{Si}(100)-2\times 1$ system. Energies (in eV) are given with respect to the fourth bulk-like layer (4-2 site). Notations of the boron positions are clear from Fig. 3.

Position	1	2	3-1	3-2	4-1	4-2
Energy	-1.01	-1.33	-0.25	+0.28	+0.10	0.00

that the absolute value of the experimental segregation enthalpy also has a tendency to increase when the boron surface concentration increases. In the other words here we can explain not only the value of the segregation enthalpy but also its dependence on the dopant concentration.

It is known that in bulk Si boron is a negatively charged acceptor. Our calculations give a boron charge of -0.9 in the fourth layer and of -1.1 in bulk silicon. As for the positive charge, in our approach it is distributed between the nearest Si atoms. That is, a Si adatom has a charge of about $+0.5$ when a B atom is in the fourth layer. The $\text{B}-\text{S}_5$ configuration is neutral: charges on the boron and the Si adatom are equal to zero. In other words charge transfer takes place.

B. $\text{B}/\text{Si}(100)-2\times 1$ system

To study the boron energetics near the $\text{Si}(100)-2\times 1$ surface we placed a B atom in substitutional positions in the first, second, third, and fourth layers of the $\text{Si}_{83}\text{H}_{64}$ cluster as shown in Fig. 3. As is clear from Fig. 3 there are nonequivalent sites in the third and fourth layers of the cluster studied. We have labeled them 3-1, 3-2, 4-1, and 4-2 and have studied them especially. The 3-1 and 4-1 sites are situated directly under a dimer row, while the 3-2 and 4-2 sites lie between the dimer rows.

The results of the calculations are summarized in Table III. One can see that boron is able to substitute for Si atoms in dimers; however the most favorable position is a substitution site in the second atomic layer. This agrees with the model of the formation of the boron-induced phases at the $\text{Si}(100)$ surface,^{15,43} in which boron atoms substitute for Si the first full atomic layer of the Si lattice. This layer is then capped with Si-Si dimers and/or dimer vacancies. The relative numbers of Si-Si dimers and dimer vacancies can vary, resulting in several related reconstructions. The energy difference between the second and fourth layers (4-2 site) is about -1.3 eV. Considering the fourth atomic layer to be a bulk layer we can say that the calculated segregation enthalpy of boron at the $\text{Si}(100)-2\times 1$ surface is -1.3 eV.

In comparing our results with the data of Ushio *et al.*²² we conclude that they are in good qualitative agreement. We have obtained an energy difference of -0.22 eV between the second and first layers and of -1.08 eV between the second and third layers. Their values are -0.3 and -0.5 eV, respectively. However, we consider our results to be more correct because we used larger clusters and took the surface Si dimerization into account.

IV. CONCLUSION

In summary, the segregation of boron at the Si(100)- 2×1 and Si(111)- $\sqrt{3} \times \sqrt{3}$ surfaces may be described to be a result of the moving of dopants from high-energy substituted bulk sites to low-energy subsurface sites. The preferred placement for boron is in the second atomic layer. The energy differences between the second layer and the bulk-like fourth layer are about -2 eV for the B/Si(111)- $\sqrt{3} \times \sqrt{3}$ system and about -1 eV for the B/Si(100)- 2×1 system.

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