

ENERGETICS OF BORON IN THE Si(111)-($\sqrt{3} \times \sqrt{3}$)-B SURFACE PHASE AND IN SUBSURFACE SILICON LAYERS

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The energetics of the boron substitution in the B/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface phase and in subsurface silicon layers has been studied using the semiempirical cluster method AM1. It has been found that the boron energy in the second layer (the B-S₅ site) is about 1 eV lower than in the adatom position (the B-T₄ site) and about 2 eV lower than in the fourth bulklike layer. The latter value may be interpreted as the surface segregation energy (enthalpy). The barrier height for the B-T₄-B-S₅ transfer has been found to be about 0.7 eV.

1. Introduction

It is well known that boron exhibits a segregation at Si surfaces.^{1–4} According to the classical McLean model,⁵ the segregation process is controlled by the value of the segregation free energy ΔG , which is the difference of free energies for the dopant at the surface and in the bulk. In this model the surface (C_s) and bulk (C_b) dopant equilibrium concentrations are connected by the expression

$$\frac{C_s}{1 - C_s} = \frac{C_b}{1 - C_b} \cdot \exp\left(-\frac{\Delta G}{kT}\right).$$

Segregating boron induces $\sqrt{3} \times \sqrt{3}$ reconstruction of the Si(111) surface.^{7,8} The majority of investigations are consistent with the model in which the boron atom is below the surface in the fivefold-coordinated substitutional site (S₅) under a silicon threefold-coordinated (T₄) adatom.^{9–12} The *ab initio* calculations^{9,13} revealed that among other candidates the B-S₅ model corresponds to the lowest energy. However, there are experimental data showing that in the real systems the boron atoms can be in different positions, depending on the annealing temperature. For instance, Cao, Yang and Pianetta¹⁴

have studied B/Si(111)-($\sqrt{3} \times \sqrt{3}$) structures prepared by the B₂O₃ deposition and have found that, as a function of annealing temperature (T_{anneal}), the system goes from B-terminated structure (B occupies T₄ adatom sites, $T_{\text{anneal}} \approx 700^\circ\text{C}$) to the sublayer B-stabilized structure (B occupies S₅ sites while Si occupies T₄ adatom sites, $T_{\text{anneal}} \approx 800^\circ\text{C}$), and finally to a pure Si stabilized structure (B diffuses to the bulk; $T_{\text{anneal}} \approx 900^\circ\text{C}$). Besides, some kinds of defects may be present in the B/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface phase, the main ones being the Si-S₅ sites instead of the B-S₅ sites.¹⁵

The segregation theory usually operates with the free energy.^{5,6} The boron segregation free energy for the B/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface (ΔG) was found to be ≈ -0.5 eV^{16,4} (Monte Carlo simulation; $T = 1245$ 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. (See, for instance, Refs. 17 and 18.) Therefore, by studying the dependence of the segregation process on the temperature, one can find the segregation enthalpy.

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The boron segregation enthalpy of -2 eV for the B/Si(111)- $(\sqrt{3} \times \sqrt{3})$ surface has been found by Thibaudau *et al.*⁴ using the STM technique and counting the B-S₅ atoms. It is curious that the authors of Ref. 4 have 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 by its rather high value, have performed Monte Carlo calculations to find the value of -0.52 eV. This value was really the free segregation energy, but the origin of the value of -2 eV was not discussed in Ref. 4 at all.

The present work is devoted to the computer investigation of the boron energetics at the surface and in subsurface layers of the B/Si(111)- $(\sqrt{3} \times \sqrt{3})$ surface phase, and to studying the B-T₄-to-B-S₅ transfer.

2. Method of Calculations and Its Verification

To study atomic geometry evolutions we used the advanced semiempirical quantum-chemical method AM1 (Austin model 1),¹⁹ a version of the modified intermediate neglect of differential overlap (MINDO),^{20–22} realized in the frame of the CLUSTER-Z1 package.²³ Optimizations of atomic configurations were achieved by minimization of the total energy gradients over atomic coordinates like it was described by Khavryutchenko *et al.*²⁴ Because the temperature is not presented in this approach, calculated energies may be interpreted as corresponding enthalpies.

Having a semiempirical 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 debatable. Although the method was used successfully to study some Si, Si–Al, Si–O and Si–B systems,^{24–27} we will present below its additional verification for the B/Si(111)- $(\sqrt{3} \times \sqrt{3})$ system.

For test geometry calculations we used two clusters of different sizes, modeling the Si(111)- $(\sqrt{3} \times \sqrt{3})$ surface — the Si₁₀₉H₇₈ and Si₂₇H₂₄ clusters shown in Fig. 1. The first cluster had seven S₅ sites and the second cluster had one S₅ site. In this test all

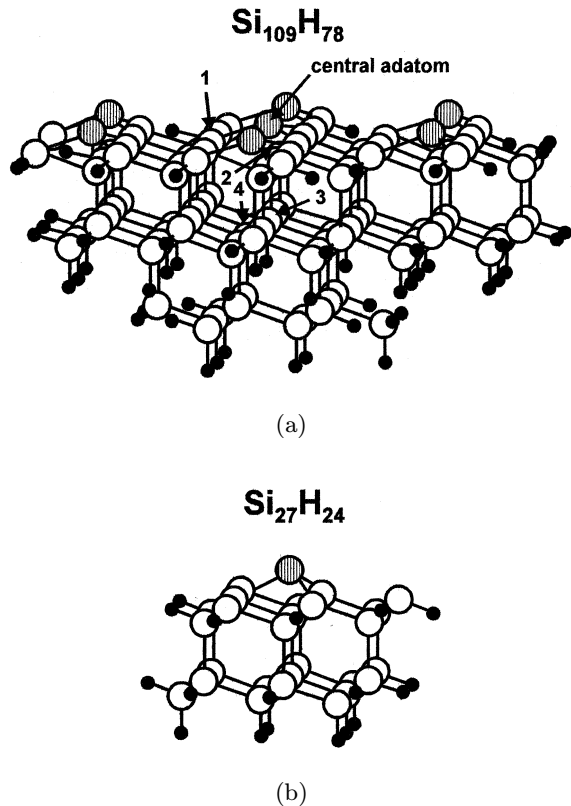


Fig. 1. Atomic schemes of clusters used for calculations: (a) Si₁₀₉H₇₈; (b) Si₂₇H₂₄. The small black circles are H atoms, the empty circles are Si atoms, and the vertical-lined circles are Si adatoms.

those S₅ sites were occupied by B atoms. Broken Si bonds were saturated with H atoms. Initially all Si atoms were placed in ideal bulk positions and all Si–H distances were equal to equilibrium 1.46 Å values. During the optimization procedure all H atoms were fixed.

The B-S₅ scheme of the atomic geometry is shown in Fig. 2(a) and the optimized values of interatomic distances are presented in Table 1 comparing with the experimental^{12,11} and theoretical *ab initio*¹³ results. Results presented for the Si₁₀₉H₇₈ cluster correspond to the central B-S₅ site. All cited values (in Å) were given as they were published except those labeled by a star (*). The last ones have been calculated by us using published displacement data. One can see that our geometry results are in satisfactory agreement with literature data. The cluster size effect is not large and demonstrates a convergence to experimental atomic geometry.

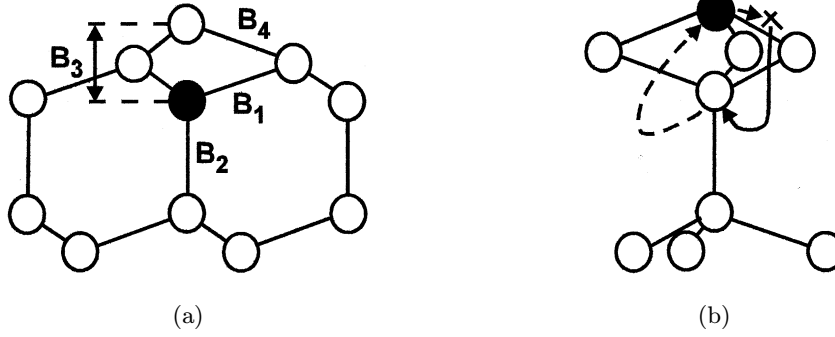


Fig. 2. (a) Scheme of atomic bonds near the optimized B_S site; (b) scheme of the studied reaction path for the $B\text{-T}_4\text{-B-S}_5$ transfer.

Table 1. Interatomic distances (\AA) near the optimized B_S site. The B_1 , B_2 , B_3 and B_4 notations are clear from Fig. 2(a).

	Present results		Literature data		
	$\text{Si}_{26}\text{H}_{24}\text{B}_1$	$\text{Si}_{102}\text{H}_{78}\text{B}_7$	Ref. 13 calculation	Ref. 12 experiment	Ref. 11 experiment
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*

Then, using the same clusters, we have carried out the test calculations of the total cluster energy for the $B\text{-S}_5$ and $B\text{-T}_4$ cases. (In this test, only the central B atom of the $\text{Si}_{109}\text{H}_{78}$ cluster was moved; the other six B atoms were in $B\text{-S}_5$ positions every time during calculations.) The lowest energy has been found for the $B\text{-S}_5$ case, and the $B\text{-T}_4$ 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. Those differences (ΔE) are in good agreement with the *ab initio* calculations of Kaxiras *et al.*¹³ ($\Delta E = 1$ eV) and Bedrossian *et al.*⁹ ($\Delta E = 0.93$ eV). Therefore, we can conclude that our semiempirical simulation gives us a good energetic representation of the $B\text{-Si}(111)$ surface (with an accuracy of 0.1 eV), and that the cluster size energy effect is not significant.

3. Results and Discussions

3.1. Layer-by-layer boron energetics

Layer-by-layer energy calculations were fulfilled using the $\text{Si}_{109}\text{H}_{78}$ cluster. This cluster has six atomic layers, and its fourth layer atomic positions may be

considered as bulklike ones. As far the $B/\text{Si}(111)-(\sqrt{3} \times \sqrt{3})$ surface phase has different amounts of boron atoms at different segregation temperatures,⁴ so 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-to-fourth atomic layers below the central adatom as it is labeled 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 was described above; the other six B atoms are in their $B\text{-S}_5$ sites.

Results are presented in Table 2. One can see that the lowest energy corresponds to the case in which boron substitutes a Si atom in the second atomic layer ($B\text{-S}_5$ site). Calculated values of the second-to-fourth-layer difference (-1.8 eV for the A case and -2.1 eV for the B case) are very close to the experimental segregation enthalpy (-2 eV⁴). Moreover, the detailed analysis of the data published in Ref. 4 allows us to conclude that the absolute value of the experimental segregation enthalpy also has a tendency to increase when the boron surface

Table 2. Energetics of a single B atom in the $\text{Si}_{108}\text{H}_{78}\text{B}_1$ cluster (A case) and in the $\text{Si}_{102}\text{H}_{78}\text{B}_7$ cluster (B case). Energies (in eV) are given with respect to the fourth bulklike layer.

Layer	A case	B case
adatom	-0.82	-1.05
1	-0.75	-0.84
2	-1.83	-2.10
3	-0.21	-0.32
4	0.00	0.00

concentration increases. In other words, we can here explain not only the value of the segregation enthalpy but also its dependence on the dopant concentration.

3.2. $B\text{-T}_4\text{-B-S}_5$ transfer

The $B\text{-T}_4\text{-B-S}_5$ transfer means that the boron adatom and the underlying Si atom of the second surface layer exchange their positions. Obviously, there must be an energy barrier for this process and the barrier height must depend on the transfer direction and path. In the general case one must study all possible reaction paths to find the minimum barrier. In the present case we limited the boron movements by the $\text{T}_4\text{-S}_5$ neighborhood and did not take into account any more extended paths.

Our simulation does not lead the system to the global energy minimum but to a local one only. In order to transfer the system from one local minimum ($B\text{-T}_4$) to another ($B\text{-S}_5$), we artificially moved the boron atom by some small steps. In each calculation step the boron position was kept but coordinates of all Si atoms were optimized. The space step for the boron movement was 0.1 \AA and about 500 atomic configurations were studied. Our computers were Pentiums-133, so we had no possibility of studying the $B\text{-T}_4\text{-B-S}_5$ transfer using the $\text{Si}_{109}\text{H}_{78}$ cluster. In order to fulfill the barrier calculations in a reasonable time, we used here the $\text{Si}_{27}\text{H}_{24}$ cluster. It seems to be acceptable, due to the small cluster size effect for the $B\text{-T}_4$ and $B\text{-S}_5$ states obtained above.

Our analysis had testified that there are three identical minimum energy paths (reaction paths) for the boron transfer from the $B\text{-T}_4$ to the $B\text{-S}_5$ position, and each of these paths passes between one

of three symmetrical pairs of surface silicon atoms. One of the reaction paths is shown in Fig. 2(b) by the solid curve arrow. The dashed curve arrow represents the self-moving path of a substituted silicon atom.

The boron moving along the reaction path has two stages. In the first stage the B atom transfers from the $B\text{-T}_4$ position to one of the intermediate surface positions situated between a pair of the surface silicon atoms (some kind of bridge sites). This bridge position (T'_4) is marked in Fig. 2(b) by a cross. The T'_4 site is 0.2 eV higher than the T_4 one, and the barrier height between them is 0.6 eV . In this transfer stage silicon atoms almost do not move from their start positions. The T'_4 site is situated 0.9 \AA from the T_4 site and 0.2 \AA under the line connecting the nearest Si atoms of the first silicon layer.

The second stage of the boron transfer consists of the boron penetrating into the silicon bulk and, simultaneously, of the silicon being forced out of the Si-S_5 position to the Si-T_4 adatom position. The barrier height of this transfer is about 0.5 eV and the energy of the final $B\text{-S}_5$ state is lower than that of the initial $B\text{-T}_4$ state by 1.1 eV . A view of the total barrier is shown in Fig. 3, and the total height of this two-humped barrier is 0.7 eV .

One should note that all silicon movements were results of the optimization procedure. The boron atom was moved “by hand” from the T'_4 site into the “bulk” of the cluster until it reached the barrier top (the arrowed point in Fig. 3). As soon as the boron atom had penetrated through the barrier top, the Si-S_5 atom jumped impetuously up to the

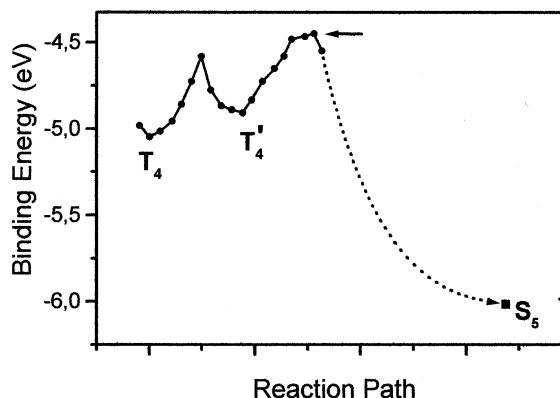


Fig. 3. Barrier shape for the $B\text{-T}_4\text{-B-S}_5$ transfer along the reaction path that is shown in Fig. 2(b).

T₄ position and the boron atom substituted it. The barrier top point was found at 0.7 Å just under the T'₄ site (approximately 0.15 Å under the second silicon layer).

Thus, we have found that the activation energy of the B-T₄-B-S₅ transfer is about 0.7 eV. Correctly speaking, the value of 0.7 eV is to be considered as the highest limit for the activation energy, because we did not study all possible paths of the reaction. (For example, any long paths were not studied.) However, the nearest environments of the T₄ adatom and S₅ sites were studied rather carefully, and it is doubtful that some long paths have lower barriers than short ones.

There are no published data on the activation energy of the B-T₄-B-S₅ transfer in the B/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface phase. There is only the information on the bulk diffusion activation energy for boron in silicon (3.7 eV⁷) and on the energy of the B/Si(111)-($\sqrt{3} \times \sqrt{3}$) phase formation from the HBO₂ source (1.2 eV²⁸). However, results of Kumagai *et al.*²⁸ have been obtained at rather low substrate temperatures (600–744°C), so they most probably correspond to the B-T₄ kind of the B/Si(111)-($\sqrt{3} \times \sqrt{3}$) phase and are not to be compared with our results.

4. Conclusion

Our calculations show that boron prefers to be in the second atomic layer of the Si(111)-($\sqrt{3} \times \sqrt{3}$) surface phase. The energy difference between the second layer and the bulklike fourth layer depends on the surface boron concentration. It is -1.8 eV for the initial stage of the Si(111)-($\sqrt{3} \times \sqrt{3}$) surface phase formation (a B-S₅ site has no nearest B-S₅ neighbors), and it goes down to -2.1 eV when the Si(111)-($\sqrt{3} \times \sqrt{3}$) surface phase is saturated (a B-S₅ site has six B-S₅ nearest neighbors). Those values are close to the experimental segregation enthalpy (-2 eV⁴).

The simulation of the B-T₄-B-S₅ transfer in the B/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface phase has shown that the transfer has two stages. In the first stage the B atom transfers from the T₄ adatom position to one of the bridge surface positions (T'₄) situated between a pair of the surface silicon atoms. This bridge state is 0.2 eV higher energetically than the T₄ adatom state, and the barrier height between them is 0.6 eV.

The second stage of the boron transfer consists of the boron penetrating into the silicon bulk and, simultaneously, of the silicon being forced out of the S₅ position to the T₄ adatom position. The barrier height of this transfer is about 0.5 eV and the energy of the final B-S₅ state is lower than that of the initial B-T₄ state by 1.1 eV. The total barrier height of the B-T₄-B-S₅ transfer is predicted to be about 0.7 eV.

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References

1. E. de Frésart, K. L. Wang and S. S. Rhee, *Appl. Phys. Lett.* **53**, 48 (1988).
2. H. Jorke and H. Kibbel, *Appl. Phys. Lett.* **57**, 1763 (1990).
3. M. R. Sardela Jr., W.-X. Ni, J. O. Ekberg, J.-E. Sundgren and G. V. Hansson, *Mat. Res. Soc. Symp. Proc.*, Vol. 220 (Materials Research Society, 1991), p. 109.
4. F. Thibaudau, T. P. Roge, Ph. Mathiez, P. Dumas and F. Salvan, *Europhys. Lett.* **25**, 353 (1994).
5. D. McLean, *Grain Boundary in Metals* (Oxford University Press, London, 1957).
6. S. Hofmann and J. Erlewein, *Surf. Sci.* **77**, 591 (1978).
7. V. V. Korobtsov, V. G. Lifshits and A. V. Zotov, *Surf. Sci.* **195**, 466 (1988).
8. H. Hirayama, T. Tatsumi and N. Aizaki, *Surf. Sci.* **193**, L47 (1988).
9. P. Bedrossian, R. D. Meade, K. Mortensen, D. M. Chen, J. A. Golovchenko and D. Vanderbilt, *Phys. Rev. Lett.* **63**, 1257 (1989).
10. I.-W. Lyo, E. Kaxiras and Ph. Avouris, *Phys. Rev. Lett.* **63**, 1261 (1989).
11. R. L. Headrick, I. K. Robinson, E. Vlieg and L. C. Feldman, *Phys. Rev. Lett.* **63**, 1253 (1989).
12. H. Huang, S. Y. Tong, J. Quinn and F. Jona, *Phys. Rev.* **B41**, 3276 (1990).
13. E. Kaxiras, K. C. Pandey, F. J. Himpsel and R. M. Tromp, *Phys. Rev.* **B41**, 1262 (1990).
14. R. Cao, X. Yang and P. Pianetta, *J. Vac. Sci. Technol.* **A11**, 1817 (1993).
15. In-Wham Lyo and P. Avouris, *Science* **245**, 1369 (1989).
16. D. Gandolfo, J. Ruz, F. Thibaudau and V. A. Zagrebnoy, *Europhys. Lett.* **30**, 145 (1995).

17. M. Polak, J. Deng and L. Rubinovich, *Phys. Rev. Lett.* **78**, 1058 (1996).
18. J. L. Rousset, J. C. Bertolini and P. Miegge, *Phys. Rev.* **53**, 4947 (1995).
19. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
20. N. C. Baird and M. J. S. Dewar, *J. Chem. Soc.* **50**, 1262 (1969).
21. M. J. S. Dewar and Haselbach, *J. Am. Chem. Soc.* **92**, 590 (1970).
22. R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.* **97**, 1285 (1975).
23. V. A. Zayetz, CLUSTER-Z1 Quantum Chemical Software (Institute of Surface Chemistry, Natl. Acad. Sci. Ukraine, Kiev, 1990).
24. V. Khavryutchenko, E. Nikitina, A. Malkin and E. Sheka, *Phys. Low-Dim. Struct.* **6**, 65 (1995).
25. V. Khavryutchenko, E. Sheka, D. H. Huang and M. Aono, *Phys. Low-Dim. Struct.* **9/10**, 15 (1996).
26. V. G. Zavodinsky, E. N. Chukurov and I. A. Kuyanov, *Phys. Low-Dim. Struct.* **3/4**, 183 (1998).
27. V. G. Zavodinsky, *Comp. Mat. Sci.* **11**, 138 (1998).
28. Y. Kumagai, K. Ishimoto, R. Mori and F. Hasegawa, *Jpn. J. Appl. Phys.* **33**, L1 (1994).