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FIRST PRINCIPLES STUDY OF BORON SEGREGATION ON THE Si(111)($\sqrt{3} \times \sqrt{3}$)R30° SURFACE

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Segregation of boron on Si(111)($\sqrt{3} \times \sqrt{3}$)R30° surface has been studied using the periodical calculations within the local density approximation. The obtained segregation energy (enthalpy) of about −1.9 eV is close to the published data of experimental studies and previous cluster semiempirical calculations. The influence of plane-wave basis set cutoff energy and the slab unit cell depth on the value of segregation energy has been investigated.

Keywords:

1. Introduction

Dopant segregation near the semiconductor surfaces and interfaces is frequently investigated because of its fundamental and technological importance. According to the classical McLean model,[1] the segregation process is controlled by the value of the segregation free energy ΔG, which is the difference of free energies for the dopant being 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 following expression:

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

It is well known that boron exhibits a segregation at (111) silicon surface[2–4,9] leading to the Si(111)$\sqrt{3}\times\sqrt{3}$-B reconstruction. In the Si(111)$\sqrt{3}\times\sqrt{3}$-B structure, boron atoms occupy S_5 sites substituting of the second-layer silicon atoms. This site was independently proposed by Headrick *et al.*,[5] Bedrossian *et al.*,[6] and Lyo *et al.*[7]

de Frésart *et al.*[2] experimentally studied boron surface segregation on Si(111). Using the Auger electron spectroscopy data, they obtained the value of Gibbs free energy of segregation $G_s = -0.33 \pm 0.02$ eV in the temperature range of $750° \leq T \leq 900°$.

Thibaudau *et al.*[9] investigated boron segregation on Si(111) using scanning tunneling microscopy (STM) in the temperature range of 1045–1245 K. To model the segregation process, they performed Monte Carlo simulations at 1245 K within the framework of a nearest neighbor model. The segregation free energy G_s has been written as a sum of a constant term G_0 and a local term $n_B w$:

$$G_s(n_B) = G_0 + n_B w,$$

where n_B is the number of boron first neighbors surrounding the considered site, and w is an interaction energy. They obtained −0.52 and −0.093 eV for G_0 and w, respectively. In the subsequent paper,[10] these values have been corrected to $G_0 = -0.48\,\text{eV}$ and $w = -0.1\,\text{eV}$ using more sophisticated simulation.

In spite of intensive investigations, there is a lack of quantitative information on the boron energetics near the silicon surface. The segregation theory usually operates with the free energy.[1,11] However, the free energy depends on 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 results of total energy calculations in which temperature effects are not present. To make this comparison, the enthalpy fits better.

The boron segregation enthalpy of −2 eV for the Si(111)–$\sqrt{3}\times\sqrt{3}$-B surface has been found by Thibaudau *et al.*[9] using the STM technique and counting the B-S_5 atoms. It is curious that the authors have obtained this value (−2 eV) from the linear dependence of the Arrhenius plot of $C_s/(1 - C_s)$; however, they mistakenly supposed that it was the free energy (not the enthalpy) and, being surprised of its rather high value, have performed Monte Carlo calculations to find the value of −0.52 eV. The last value was really the free segregation energy, but the origin of the −2 eV value was not discussed at all.[9]

Zavodinsky *et al.*[12,13] performed semiempirical cluster modeling of boron segregation on Si(111). Using large cluster including seven B-S_5 sites (the central B-S_5 site and six surrounding sites), they obtained segregation enthalpies of about −1.8 eV (for isolated boron atom) and −2.1 eV (for boron atom surrounded by six nearest borons in S_5 position). Thus, segregation enthalpy depends on the number of nearest neighbors, which agrees with the STM observations.[9]

Shi *et al.*[14] recently presented modeling of boron segregation on Si(111) using cluster and periodical *ab initio* simulations without taking into account temperature effects. The predicted values of segregation enthalpy are equal to −0.77 eV for periodical and −0.48 eV for cluster calculations. It is difficult to understand, however, why the authors[14] compared calculated values of segregation *enthalpy* with segregation *free energy* found experimentally.[2,9,10] It should be noted that the value of segregation enthalpy was obtained within the framework of periodical slab calculations by using incorrect procedure (we discuss this procedure below).

2. Method of Calculations

To find the segregation enthalpy, we have performed *ab initio* plane-wave total-energy calculations using the fhi96md package[15] in which the Car–Parrinello-type of electronic structure calculation[16] was used. The local density approximation (LDA) after Ceperley–Alder[17] in the Perdew–Zunger parametrization[18] for the exchange and correlation functional was employed. Norm-conserving Hamann[20] (for silicon) and Troullier–Martins[19] (for boron) pseudopotentials were employed. The pseudopotentials were constructed using the fhi98pp package[21] and were verified to avoid ghost states and to describe the basic experimental characteristic of bulk materials.

The surface was simulated by a periodic slab geometry with a $\sqrt{3}\times\sqrt{3}$ surface unit cell containing eight silicon atomic layers. The dangling bonds of the bottom slab layer were saturated by hydrogen atoms. The hydrogen atoms and bottom bilayer silicon atoms were fixed and the rest atoms were free to move. A vacuum region of approximately 9 Å was incorporated within each periodic unit cell to prevent interaction between adjacent surfaces. The energies cutoff E_{cut} of 18, 24, 30, and 40 Ry were applied in calculations presented. A number of simulations were conducted using 24-layer $\sqrt{3}\times\sqrt{3}$ surface unit cell, vacuum gap of 9 Å, and $E_{\text{cut}} = 18\,\text{Ry}$. The silicon bulk was simulated using 64-atomic unit cell. According to previous modeling of boron behavior in bulk silicon,[22] this volume unit cell is large enough to prevent boron interaction.

3. Results and Discussion

First we have carried out test energy calculations of the Si(111)$\sqrt{3}\times\sqrt{3}$-B system using the slab periodic cell. We substituted silicon atoms by boron atoms layer-by-layer. The energies in relation to the system with boron in T_4 position are shown in Table 1. A number of cutoff energies employed to study the influence of plane-wave basis set on the total energy. Results of Shi *et al.* are included in Table 1 for comparison.

Table 1. Relative energies (in eV) of the Si(111) ($\sqrt{3}\times\sqrt{3}$)R30°-B system for a boron atom occupying sites in different layers for a number of E_{cut}.

	Ref. 14	Present results			
Layer	18 Ry	18 Ry	24 Ry	30 Ry	40 Ry
0 (T_4)	0.00	0.00	0.00	0.00	0.00
1	−0.09	−0.11	−0.13	−0.14	−0.15
2 (S_5)	−1.04	−1.12	−1.18	−1.20	−1.21
3	−0.62	−0.63	−0.66	−0.68	−0.68
4	−0.27	−0.30	−0.34	−0.36	−0.37

One can see that the results of Shi *et al.* are close to ours. That is predictable, since we employed essentially the same code, the same approximation (LDA), and the same unit cell. Insignificant distinctions can be explained by differences in parametrization of pseudopotentials.

Difference in energy of B-S_5 and B-T_4 configurations was calculated by a number of authors. According to early simulations with cutoff energy of 12 Ry by Bedrossian *et al.*[6] and Lyo *et al.*,[7] the relative energy of B-S_5 equals −0.93 and −1.0 eV, respectively. Kaxiras *et al.*[8] demonstrated that B-S_5 relative energy changes from −0.4 to −1.0 eV when the cutoff energy increases from 6 to 12 Ry. According to our calculations, weak dependence of relative energy on E_{cut} is at least observed up to 30 Ry. Test calculations for 24-layer silicon slab show that the dependence of relative energies (for boron atoms in 1–4 layer) on the depth of the $\sqrt{3} \times \sqrt{3}$ surface unit cell is negligible.

To obtain the segregation energy (enthalpy), we should compare the energies of boron atom in bulk silicon and in S_5 position of Si(111)$\sqrt{3} \times \sqrt{3}$-B system. Using the cluster approach, we can substitute single silicon atom by boron layer-by-layer. It is obvious that at the appropriate depth of boron atom its position can be considered as a bulk one.

That was the approach employed by Zavodinsky *et al.*[12,13] for cluster systems. The obtained segregation enthalpies of −1.8 eV (for isolated boron atom) and −2.1 eV (for boron atom surrounded by six nearest borons in S_5 positions) are in good agreement with the experimental data of Thibaudau *et al.*[9] Moreover, segregation enthalpy depends on the number of nearest neighbors, which agrees with the STM observations.[9]

The same method was employed by Shi *et al.*[14] to find the segregation energy within the framework of periodical slab calculations. The authors[14] calculated the total energy of system with boron atom placed in subsurface layers. However, using this method within the framework of periodical calculations leads to the artificial $\sqrt{3} \times \sqrt{3}$ periodicity in (111) plane in the depth of crystal. Physically it looks like the displacement of ideal boron-doped δ-layer and makes no sense in finite-temperature bulk systems.

Again, method of segregation energy calculation used by Shi *et al.*[14] is applicable for cluster simulations only, in which a single atom can be displaced.

To find the correct value of segregation energy, we have to calculate energies of bulk ($E_{\text{bulk,Si}}$) and surface ($E_{\text{surf,Si}}$) silicon systems without dopant atom and those ($E_{\text{bulk,B}}$ and $E_{\text{surf,Si}}$) with B atom in substitutional positions. Then segregation energy E_s is defined as

$$E_s = (E_{\text{bulk,Si}} + E_{\text{surf,B}}) - (E_{\text{bulk,B}} + E_{\text{surf,Si}}).$$

The calculated value of segregation energy does not depend on the cutoff energy (in the range of 18–40 Ry) and is equal to −1.91 eV. The dependence of E_s on the unit cell depth is negligible, for 24-layer slab and $E_{\text{cut}} = 18$ Ry the segregation energy does not essentially change ($E_s = -1.93$ eV).

The obtained segregation energy (enthalpy) of about −1.9 eV is close to published data of experimental studies (−1.93 eV)[9] and cluster semiempirical calculations (−1.83 and −2.1 eV).[12,13]

4. Conclusion

Segregation of boron on Si(111)($\sqrt{3} \times \sqrt{3}$)R30° surface has been studied using the periodical calculations within the LDA. The obtained segregation energy (enthalpy) of about −1.9 eV is close to the published data of experimental studies and cluster semiempirical calculations. The influence of plane-wave basis set cutoff energy and the unit cell depth on the value of segregation energy has been investigated.

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References

1. D. McLean, *Grain Boundaries in Metals* (Oxford University Press, London, 1957).
2. E. de Frésart, K. L. Wang and S. S. Rhee, *Appl. Phys. Lett.* **53** (1988) 48.
3. H. Jorke and H. Kibbel, *Appl. Phys. Lett.* **57** (1990) 1763.
4. M. R. Sardela Jr, W.-X. Ni, J. O. Ekberg, J.-E. Sundgren and G. V. Hansson, *Mater. Res. Soc. Symp. Proc.* **220** (1991) 109.
5. R. L. Headrick, I. K. Robinson, E. Vlieg and L. C. Feldman, *Phys. Rev. Lett.* **63** (1989) 1253.
6. P. Bedrossian, R. D. Meade, K. Mortensen, D. M. Chen, J. A. Golovchenko and D. Vanderbilt, *Phys. Rev. Lett.* **63** (1989) 1257.
7. I.-W. Lyo, E. Kaxiras and Ph. Avouris, *Phys. Rev. Lett.* **63** (1989) 1261.
8. E. Kaxiras, K. C. Pandey, F. J. Himpsel and R. M. Tromp, *Phys. Rev. B* **41** (1990) 1262.
9. F. Thibaudau, T. P. Roge, Ph. Mathiez, Ph. Dumas and F. Salvan, *Europhys. Lett.* **25** (1994) 353.
10. D. Gandolfo, J. Ruiz, F. Thibaudau and V. A. Zagrebnov, *Europhys. Lett.* **30** (1995) 145.
11. S. Hofmann and J. Erlewein, *Surf. Sci.* **77** (1978) 591.
12. V. G. Zavodinsky, E. N. Chukurov and I. A. Kuyanov, *Surf. Rev. Lett.* **6** (1999) 127.
13. V. G. Zavodinsky, I. A. Kuyanov and E. N. Chukurov, *J. Vac. Sci. Technol. A* **17** (1999) 2709.
14. H. Q. Shi, M. W. Radny and P. V. Smith, *Surf. Rev. Lett.* **10** (2003) 201.
15. M. Bockstedte, A. Kley, J. Neugebauer and M. Sheffler, *Comput. Phys. Commun.* **107** (1997) 187.
16. R. Car and M. Parrinello, *Phys. Rev. Lett.* **55** (1985) 2471.
17. D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45** (1980) 567.
18. J. P. Perdew and A. Zunger, *Phys. Rev. B* **23** (1981) 5048.
19. N. Troullier and J. L. Martins, *Phys. Rev. B* **43** (1991) 1993.
20. D. R. Hamann, *Phys. Rev. B* **40** (1989) 2980.
21. M. Fuchs and M. Sheffler, *Comput. Phys. Commun.* **119** (1999) 67.
22. J. Zhu, T. D. dela Rubia, L. H. Yang, C. Mailhiot and G. H. Gilmer, *Phys. Rev. B* **54** (1996) 4741.