Surface Segregation Behavior of B, Ga, Sb, and As Dopant Atoms on Ge(100) and Ge(111) Examined with a First-principles Method

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Abstract. To understand surface segregation behaviour of B, Ga, As, and Sb dopant atoms on Ge (100) and Ge (111) surfaces, the potential energies of these dopant atoms in the five top layers of the surfaces were evaluated by first-principles molecular orbital calculations of model clusters. The obtained potential energy curves of these dopant atoms for Ge (100) closely resemble those for Si (100) surface. On the other hand, Ge (111) surface exhibits different potential profiles as compared with Ge (100) surface. The thermal activation energy between the adsorbed state and sub-surface state was also evaluated for each dopant atom. These energy data determining the driving force and dynamical property of dopant segregation help us to understand the difference in dopant surface segregation phenomena on Ge(100) and Ge(111) surfaces from an atomistic point of view.

1. Introduction

Molecular beam epitaxy (MBE) is an established crystal growth method for forming sharp doping profile and abrupt heterointerfaces. However, many elements have been shown to segregate to the epitaxial surface during MBE growth process. It is known that B, Ga, Sb, and Ge show different behaviors in surface segregation during Si MBE [1-3]. We previously examined these segregation behaviors on Si (100) surface with calculations using a first-principles method and showed that the trend of surface segregation is primarily prospected by seeing the bond energy difference between the dopant-Si and Si-Si bonds [4]. Aggressive downscaling of high-performance metal-oxide semiconductor field effect transistors (MOSFET) is bringing about the revival of Ge as a promising candidate material for high mobility complementary MOS (CMOS). One of the crucial problems associated with the fabrication of aggressively scaled Ge channel CMOS is the formation of n-type ultrashallow junctions with ion implantation techniques [5-6]. It was recently reported that the formation of ultrashallow ohmic contacts for n-type Ge was made possible by Sb δ-doping followed by Ge homoepitaxial growth [7]. It was also shown that the segregation effect of Sb on Ge (111) surface is lower than that on Ge (100) surface. Unfortunately, there are very few experimental data with regard to the dopant surface segregation phenomena on Ge surface. Judging from the importance of Ge channel as a promising electronic material and δ-doping process as an appropriate formation technique for ultrashallow junctions/contacts, a first-principles study to reveal atomistic mechanism of...
the dopant surface segregation on Ge surfaces is indispensable for design and improvement of the δ-doping process with Ge homoepitaxial growth. Hence, we investigate the surface segregation behaviors of B, Ga, As, and Sb on Ge (100) and Ge (111) surfaces with a first-principles method and compare them with the previously reported segregation behavior on Si (100) surface.

2. Calculation details

The behavior of a dopant atom incorporated into semiconductor crystal can be explained by a two-state model with an appropriate potential for a dopant atom [8]. A schematic energy diagram is shown in Figure 1. The jumping rate for surface segregation is determined by the potential barrier, so-called activation energy $E_a$, and the driving force of surface segregation is the energy difference between the surface (adsorbed) and subsurface (incorporated) states, $\Delta G_{seg}$. We evaluated the potential energies of B, Ga, As, and Sb dopant atoms in the five top layers of Ge (100) and Ge (111) surfaces and also the activation energy of each dopant atom between the adsorbed state and the incorporated state at the first subsurface by using a first-principles molecular orbital program with model clusters in this study. For the calculation, we used a Ge$_{17}$H$_{25}$ cluster and a Ge$_{16}$H$_{29}$ cluster as a Ge (100) surface model and a Ge (111) surface model, respectively (see Figure 2). No surface reconstruction was explicitly considered as a first approximation for both surfaces in this study because there remains no reconstructed structures in the MBE grown epitaxial layer. The Ge (100) surface model has the same surface configuration as modeled in our previous paper for Si (100) calculations and the bridge site was taken as the adsorption site for Ge (100) surface due to its largest adsorption energy for B dopant on Si (100) surface [4]. For the Ge (111) surface model, the adsorption site was assumed to be a T4 site with 3-fold symmetry located on the top of a Ge atom in the second layer. The T4 site on Si (111) surface was reported to give the largest adsorption energies for group IIIA metals among various adsorption sites [9].

The potential energy for each dopant atom was obtained taking into account the structural relaxation of the Ge lattice by optimizing the both positions of the dopant atom and the nearest Ge atoms around the adsorbed or incorporated dopant atom. And all the hydrogen atoms terminating the cluster models were fixed throughout the structural optimization. All calculations were performed using the first-principles molecular orbital program package “Gaussian 03” [10]. QST3 keyword option for structural optimization routine of Gaussian 03 program was thoroughly employed in exploration for the transition states in this study. Density functional calculations were carried out using B3LYP hybrid functional and the DGDZVP basis set (double-ζ valence plus polarization) [11,12].

![Figure 1](image1.png)  
**Figure 1.** A two-state model to describe dopant exchange process between surface and subsurface states.

![Figure 2](image2.png)  
**Figure 2.** Cluster models used to calculate $\Delta G_{seg}$ and $E_a$: (a) Ge (100) surface model (Ge$_{17}$H$_{25}$) and (b) Ge (111) surface model (Ge$_{16}$H$_{29}$). The actual locations of the dopant atoms are shown by the arrows.
3. Results and discussion

The obtained adsorption energies for B, Ga, As, and Sb dopant atoms on the Ge (100) and Ge (111) surfaces are listed in Table 1. The calculated adsorption energies on Si (100) and Si (111) surfaces are also tabulated for comparison [4, 9]. B atom has the largest adsorption energies for both Ge (100) and Ge (111) surfaces due to its largest bonding energy to Ge atom. Sb has the second largest adsorption energies. The same tendency in the adsorption energy is observed for the dopant adsorption on Si (100) surface.

| Surface  | B   | Ga  | As  | Sb  |
|----------|-----|-----|-----|-----|
| Ge(100)  | 4.26| 2.56| 2.99| 3.20|
| Ge(111)  | 3.50| 2.92| 3.08| 3.42|
| Si (100) | 7.35| 4.56| ----| 5.28|
| Si (111) | 4.83| 2.53| ----| ----|
| Dopant-Ge| 3.49| 2.80| 2.54| 2.34|

a), b): reported values in [4] and [9], respectively.
c) Calculated for the bonds in $\text{H}_2\text{B}-\text{GeH}_3$, $\text{H}_2\text{Ga}-\text{GeH}_3$, $\text{H}_2\text{As}-\text{GeH}_3$, and $\text{H}_2\text{Sb}-\text{GeH}_3$.

The adsorption structures of these dopant atoms on the Ge (100) surface were very similar to those reported for Si (100) surface [4]. The adsorption structures at T4 site on Ge (111) surface are shown in Figure 3. All the dopant atoms except B atom make four bonds with three Ge atoms on the top surface and one Ge atom in the second layer as shown in Figure 3. The average of bond lengths between the dopant atom and the Ge atoms are 2.10 Å for B, 2.78 Å for Ga, 2.89 Å for As, and 2.99 Å for Sb. The average of the bond lengths for Ga, As, and Sb atoms are longer by 0.4 Å than the sum of atomic covalent radii of dopant and Ge atoms while the averaged B-Ge bond length is only longer by 0.07 Å than the sum of atomic covalent radii. And it is clearly seen in Figure 3 that the adsorption site of B atom is very close to the top surface layer. From these results it can be expected that B atom will distort Ge lattice structure near Ge top surface much more than other dopant atoms due to its small covalent radius and strong preference for trivalent coordination.

![Figure 3](image-url)  
*Figure 3. The adsorption structures of B, Ga, As, and Sb dopant atoms at T4 site on Ge (111) surface. The number denotes bond length (in Å) between a dopant atom and a Ge atom. The deeper layer than the fifth layer is omitted and the terminating hydrogen atoms are also omitted for clarity.*

The calculated total energies of the clusters as functions of the locations of the dopant atoms – that is, the potential energies for the dopant atoms – are shown in Figure 4. The location of a dopant atom is denoted by the layer number of the layer where the dopant atom is located. As can be seen in...
Figure 4, B and As atoms have more energetically stable incorporated states than the adsorbed states in the subsurface layers of Ge (100). On the other hand, all the energies of the incorporated states of Ga and Sb atoms are higher than those of the adsorbed states. The incorporated-state energies for both Ga and Sb atoms increase monotonically as they go deeper from the adsorption site to the fifth Ge layer. These potential energy curves for B, Ga, and Sb atoms on Ge (100) surface are very close to those obtained for Si (100) surface [4]. This simply implies that surface segregation behavior on Ge(100) surface for these four dopant atoms is expected to be similar to that on Si (100) surface; B and As atoms will not segregate to the Ge (100) surface during MBE process, but Ga and Sb will do. Although the potential energy for Ge (111) surface changes quite differently as compared with the potential energy curve obtained for Ge (100) for all the four dopant atoms, both B and As dopant atoms have more stable states than the adsorbed states in the incorporated layers, the second and fourth layers for B atom and second layer for As atom, respectively.

To compare more intensively the surface segregation behavior on Ge (100) with that on Ge (111) surfaces and to draw informative conclusions, it is necessary for us to examine both segregation energy $\Delta G_{seg}$ and thermal activation energy $E_a$. The two-state model tells that a surface segregation process is controlled by a segregation energy for the case of growth at high temperatures and at relatively slow growth-rates while it is controlled by a thermal activation energy for the case of growth at lower temperatures or faster growth rates. Here, we summarize the calculated segregation energies and thermal activation energies for B, Ga, As, and Sb dopant atoms on Ge (100) and Ge (111) surfaces in Table 2.

| Surface | $\Delta G_{seg}$ / $E_a$ | B | Ga | As | Sb |
|---------|------------------------|---|----|----|----|
| Ge(100) | $\Delta G_{seg}$       | -0.39 | 0.33 | -0.18 | 0.26 |
|         | $E_a$                  | 0.98  | 0.96 | 0.56 | 1.20 |
| Ge(111) | $\Delta G_{seg}$       | 0.09  | 1.36 | -0.17 | 0.16 |
|         | $E_a$                  | 1.17  | 1.54 | 2.28 | 3.00 |

Figure 4. Total energies of the Ge surface cluster model with dopant atoms of B, Ga, As, and Sb in the five surface layers of the Ge surfaces: (a) Ge (100) and (b) Ge(111). The adsorbed state energy is taken as zero. The actual locations of the dopant atoms are depicted by the arrows in Figure 2.
Considering the magnitude of the activation energies listed in Table 2, we can expect less surface segregation effects on Ge (111) surface than Ge (100) surface for δ-doping process of all the four dopant atoms followed by the homoepitaxial growth at lower temperatures or faster growth rates. It is also expected that B and As dopant atoms will not segregate to Ge surfaces due to the existence of their stable positions in the subsurface layers while Ga and Sb dopant atoms will segregate to the surface. As for the surface segregation of Sb dopant atom on Ge (100) surface, it was estimated that the segregation energy was around 0.4eV and the thermal activation energy was around 1.4 eV based on the temperature dependence of the segregation length in the temperature range from 100 °C to 500 °C [13]. Our computational results agree well with these values. It was also stated in the report that the shift of the temperature dependence curve of the segregation length toward lower temperature region is well explained by the decrease of the thermal activation energy rather than by the increase of the segregation energy within the framework of the two-state model. The lower thermal activation energy calculated for Ge (100) than that for Ge (111) corresponds directly to the experimentally observed temperature dependence curve for Ge (100) in the lower temperature region as compared with that for Ge (111) [7]. Unfortunately there are very few experimental data on surface segregation behaviors of other dopant atoms on Ge (100) and Ge (111) surfaces, we cannot compare our computational results directly with the experimental data. We are hoping that our first-principles calculation results will accelerate the development of δ-doping process as an appropriate formation technique for ultrashallow junctions/contacts.

4. Summary
The surface segregation process for B, Ga, As, and Sb dopant atoms on Ge (100) and Ge (111) surfaces were investigated with a theoretical approach using accurate first-principles method. Segregation energy, ΔGseg, and activation energy, Ea, were quantitatively evaluated with appropriate density functional and basis functions. Based on the computational results, we can expect less surface segregation effects on Ge (111) surface than Ge (100) surface for δ-doping process of all the four dopant atoms followed by the homoepitaxial growth at lower temperatures or faster growth rates. The expected behavior of Sb surface segregation on Ge (100) and Ge (111) surfaces is in agreement with experimentally observed behavior.

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