

## Surface Segregation Behaviors of B, Ga, and Sb during Si-MBE: Calculation Using a First-Principle Method

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### 1. Introduction

Molecular beam epitaxy (MBE) has been expected to become a powerful tool for forming sharp doping profiles because of its low-temperature growth process. However, many dopants have been shown to segregate to the epitaxial surface during MBE growth. This surface segregation phenomenon inhibits the formation of sharp doping profiles.

It is known that B, Ga, and Sb show different behaviors in surface segregation during Si-MBE. Though B and Ga are both group III elements, B is an exceptional dopant that hardly segregates to the Si surface while Ga segregates easily. Sb has less of a tendency to segregate than Ga, but segregates much more easily than B. We believe an analysis of these completely different behaviors of B, Ga, and Sb can help clarify the origin of surface segregation.

Surface segregation is essentially a dynamic process in which a dopant atom jumps from a subsurface to a surface. The behavior of the dopant can be explained by the two-state model [1, 2] with an appropriate potential for the dopant. A schematic potential energy curve is illustrated in Fig. 1 as a function of the dopant's depth in the crystal. Here the jumping rate for surface segregation is determined by the potential barrier, and the driving force of surface segregation is the energy difference between the surface and subsurface states. Quantitative studies of the potential energy of dopants in crystals are indispensable for understanding the different behaviors of various dopants.

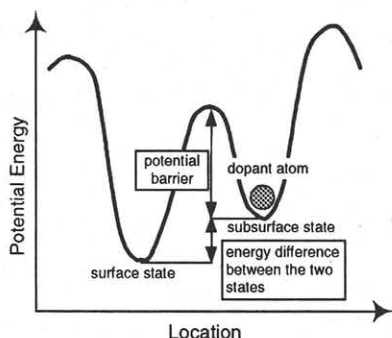


Fig. 1 Schematic energy diagram of the two-state model.

In this paper, we evaluate the potential energies of B, Ga, and Sb atoms in the top three layers of a Si(100) surface using accurate density functional calculations and describe the origin of the different segregation behaviors of B, Ga, and Sb.

### 2. Calculation Details

First, we determined the adsorption sites of the B, Ga, and Sb atoms on the Si(100) surface. We calculated the four possible adsorption sites (the bridge, hollow, antibridge, and on-top sites) on a surface modeled with a Si cluster ( $\text{Si}_9\text{H}_{12}$  or  $\text{Si}_9\text{H}_{16}$ ) and searched for the most stable adsorption site by changing the height of the dopant atom from the surface. The H atoms were used to terminate the dangling bonds of the Si atoms at the boundaries of the clusters.

To evaluate the energy difference between the two states described in Fig. 1, we calculated for each dopant the adsorption state and the three incorporated states into the first to third Si layers using a larger Si cluster,  $\text{Si}_{12}\text{H}_{16}$  shown in Fig. 2. The structures of the incorporated states were generated by the exchange of an adsorbed dopant atom and a Si atom in one of the three surface Si layers. Structural relaxation of the Si lattice was taken into account by optimizing the positions of the nearest Si atoms around the adsorbed or incorporated dopant atoms.

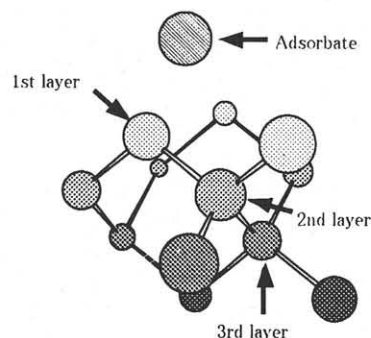


Fig. 2 Cluster model (the dopant atom +  $\text{Si}_{12}\text{H}_{16}$ ) used to calculate the potential energy of the B, Ga, and Sb atoms on or in the Si(100) surface layers. The four locations, each of which corresponds to the adsorption state and the three incorporated states, are indicated by the arrows.

To evaluate the potential energy barrier in Fig. 1, we divided the linear transfer path of the dopant atom from the adsorption site to the incorporated site in the first Si layer into five parts of equal length. At each dividing point the total energy was calculated while optimizing the positions of the nearest Si atoms.

We performed all the calculations using the linear combination of Gaussian-type orbitals-model core potential-density functional theory (LCGTO-MCP-DFT) program deMon [3].

### 3. Results and Discussion

The calculated potential energies of each dopant atom are shown in Fig. 3, where the adsorption state energy is taken as zero.

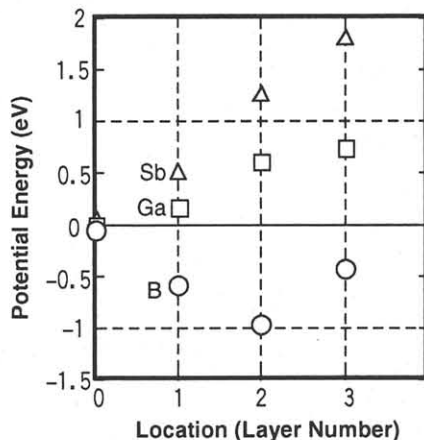


Fig. 3 Potential energies of B, Ga, and Sb in the three surface layers of the Si(100) surface.

As can be seen, the incorporated states for B within the three surface Si layers are more stable than the adsorption state and the incorporated state for B in the second surface layer is the most stable. On the other hand, all the incorporated states of Ga and Sb are less stable than their surface states. The incorporated-state energies for both Ga and Sb increase monotonously as they go deeper from the first to the third Si layers. These results clearly show that the surface segregation of B hardly occurs, but Ga and Sb readily segregate to the Si surface in a thermodynamic sense. This agrees with the experimental observations. Although Sb is less stable than Ga in the Si crystal, the weaker tendency of Sb to segregate compared to that of Ga can be explained by the smaller jumping rate of Sb due to its larger potential barrier as described below.

We will now discuss the origin of these potential energies for the dopants. When the dopant incorporation takes place, dissociation and formation of the dopant-Si and Si-Si bonds occur. If the bond energy of the dopant-Si bond is higher than that of the Si-Si bond, the incorporated state of the dopant in the first layer should be more stable than the surface state, i.e., surface segregation should be difficult.

The single-bond energies of the B-Si, Ga-Si, Sb-Si, and Si-Si bonds were obtained from the calculations for  $\text{H}_2\text{B-SiH}_3$ ,  $\text{H}_2\text{Ga-SiH}_3$ ,  $\text{H}_2\text{Sb-SiH}_3$ , and  $\text{H}_3\text{Si-SiH}_3$ . The bond energy of B-Si (4.32 eV) is higher than that of Si-Si (3.73 eV), but those of Ga-Si (3.42 eV) and Sb-Si (3.11 eV) are lower. The difference between the B-Si and Ga-Si bond energies must be the primary cause of the completely different behaviors of B and Ga in surface segregation. When the dopant goes from the adsorption site to the second layer, the number of nearest Si atoms increases. As a result, B becomes more stable, while Ga and Sb become less stable corresponding to the difference between the dopant-Si and Si-Si bond energies.

The incorporated state of B in the second layer is the most

stable (Fig. 3). In that layer, the B atom is planarly threefold coordinated by the nearest Si atoms. In the third layer, the coordination around the B atom becomes more tetrahedral in nature. Moreover, the B-Si bond length increases and becomes closer to the Si-Si bond length in the crystal (2.35 Å). The change in the bond length is about 0.1 Å. This change causes structural strain, which is the main reason for the energy rise in the third layer compared with the second layer. The energy rise for Ga and Sb in the third layer is also attributed to the same cause.

The potential energies of B, Ga, and Sb between the adsorption site and the incorporated site in the first layer are shown in more detail in Fig. 4. The potential barriers for the dopants are about 0.7 eV, 0.2 eV, and 0.6 eV for B, Ga, and Sb respectively. The smaller barrier of Ga compared with that of Sb allows Ga to jump from the subsurface state to the surface state more frequently. This makes it easier for Ga to segregate to the surface kinetically.

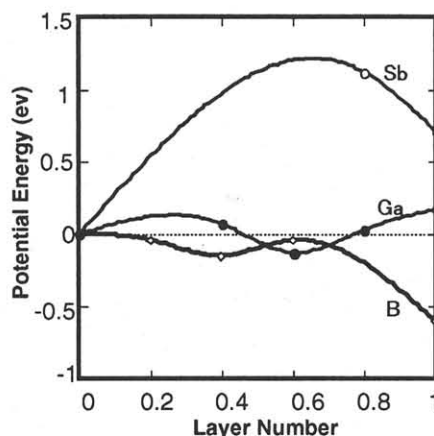


Fig. 4 Detailed potential energies of B, Ga, and Sb between the adsorption site and the incorporated site in the first layer.

### 4. Conclusions

Based on our first-principle calculations, we have shown for the first time that the different behaviors of B, Ga, and Sb in surface segregation can be understood by considering the bond energy of the dopant-Si bond as the driving force for surface segregation. The smaller potential barrier between the surface and subsurface states for Ga compared to that for Sb clearly explains the stronger tendency of Ga to segregate to the Si surface.

### References

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