

Theoretical Studies on Molecular and Electronic Structures for Hydrogenated Si and Ge Clusters

Norihisa Oyama, Toshiaki Takano, Eiji Ohta, Kyozauro Takeda^a and Kenji Shiraishi^b

*Department of Instrumentation Engineering, Faculty of Science and Technology,
Keio University, Hiyoshi, Kohoku-ku, Yokohama, Kanagawa, 223 Japan*

^a*Department of Materials Science and Engineering, School of Science and Engineering,
Waseda University, Ohkubo, Shinjuku-ku, Tokyo, 169 Japan*

^b*NTT Basic Research Laboratories, Morinosato-Wakamiya, Atsugi-si, Kanagawa, 243-01 Japan*

Recently, several Si fine clusters were synthesized under ultra-high vacuum conditions. Although magic numbers of these naked Si clusters have already been reported theoretically, few works have been studied on the effect of hydrogenation on these clusters. We performed the first-principles electronic calculations on the hydrogenated as well as the naked Si clusters, and here, discuss their electronic and molecular structures, including Si and Ge numbers from 1 to 10. Based on the calculated total energies, naked clusters including 6, 7, and 10 Si atoms can only exist without H passivation, but the other clusters tend to be hydrogenated forms rather than naked forms. Similar features were also found in the Ge cluster system.

1 Introduction

Recently, Murakami and Kanayama synthesized hydrogenated Si microclusters in the ion trap method[1]. The electronic and optical properties of these microclusters are expected to be very different from those of the bulk Si crystal. Many theoretical studies reveal the electronic and optical characteristics of these Si microclusters. The existence of the magic numbers were also predicted theoretically[2-5]. However, these theoretical studies were limited to the naked Si clusters. Most of the synthesized Si clusters are hydrogenated because they are synthesized by decomposing the silane (SiH₄) gas. Therefore, the theoretical studies on those hydrogenated microclusters should be investigated.

Here, we perform the first-principles calculations on the hydrogenated as well as the naked Si clusters, and investigate how the hydrogenation changes the cluster formation and the electronic structures. By comparing the calculated total energies, we also try to find the most energetically stable species. Further, we expand these theoretical calculations to the Ge clusters and discuss the electronic difference between the Si and Ge

microclusters.

2 Computational Details

We used the first-principles pseudopotential approach with a local density approximation (LDA) scheme to calculate the electronic and molecular structures. The wave functions were expanded in plane waves. The norm-conserving pseudopotentials[6] were used and the non-local parts of the pseudopotential were approximated by the separable forms[7]. The cutoff radii of the potentials were carefully chosen so as not to produce ghost bands. The energy cutoff was 9.00 Ry for the Si atom and 10.24 Ry for the Ge atom, respectively. This cutoff condition reproduced the optimized bond lengths within an error of 0.6% for the Si-Si bond, 1.1% for the Si-H bond, 1.1% for the Ge-Ge band, and 1.0% for the G-H bond.

We considered three types of the basic Si (Ge) skeleton forms. Figure 1 shows these three types of clusters:(a) chain-type clusters, (b) ring-type clusters and (c) a bulky form. For the ring-type clusters, we further considered the planar form (b-1) and corrugated form (b-2). An ex-

ample of the bulky form, which is called an octasilacubane, is shown in Fig. 1 (c). For these three types of clusters, we have carried out the first-principles energy calculations on the hydrogenated as well as the naked Si (Ge) clusters.

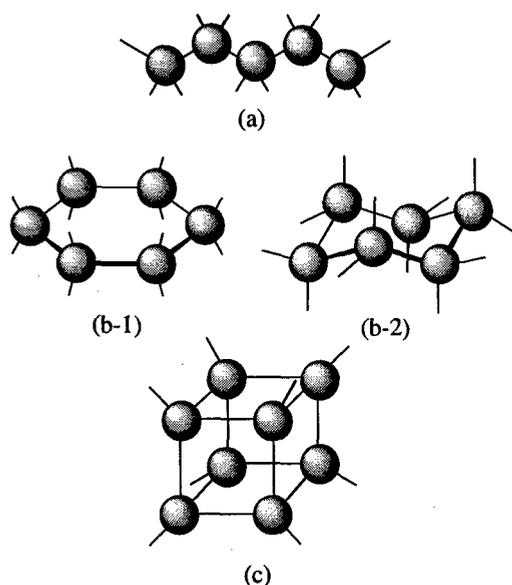


Figure 1: Illustration of the three types microclusters considered in this work.

3 Result and Discussion

3.1 Molecular Structures

Let us discuss the geometrical structures of Si and Ge microclusters. Figure 2 (a) shows the initial and optimized structures of the Si_{10} clusters (a) and Ge_6 clusters (b). The energy optimization changes the geometrical structure very differently from the initial adamantane form: The tetrahedral Si bonds assumed in the Si_{10} naked cluster are completely destroyed during the geometrical optimization. The present *ab initio* total energy calculations result in the tetrahedron stable form for the Si_{10} microcluster.

On the other hand, few reconstructions were found in the fully hydrogenated cluster having the same adamantane skeletal form. In the latter cluster, the hydrogenation of the Si's dan-

gling bond (DB) conserves the tetrahedral skeletal bonds. The naked DB state is unstable because this state is half-filled by electrons. The hydrogenation terminates this DB state and stabilizes energetically by saturating it with electrons. In the naked clusters, however, there is no way except for the geometrical reconstruction to quench these DB states. This is one reason why the naked Si skeleton reconstructs significantly but the hydrogenation does not induce such a geometrical reconstruction.

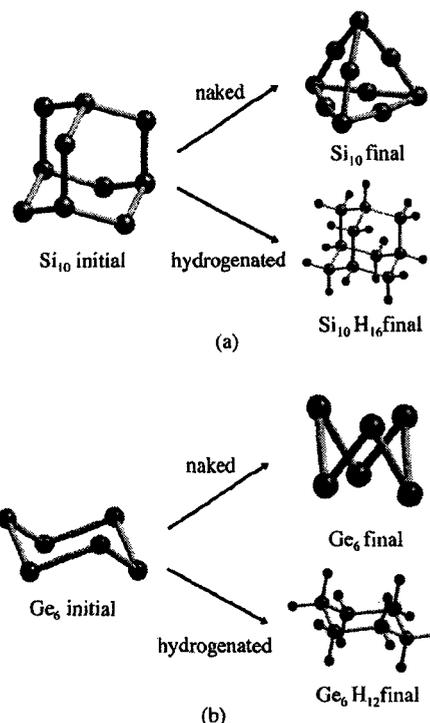


Figure 2: Comparison of the optimized geometrical structures with their initial tetrahedrally bonded structures; (a) Si_{10} bulky form and (b) Ge_6 ring-cluster.

For naked clusters, the larger structural reconstructions occur with increasing skeleton atom numbers, up to 10 atoms. These features are similarly found in the Ge cluster systems as shown in Fig.2 (b).

3.2 Electronic Structures

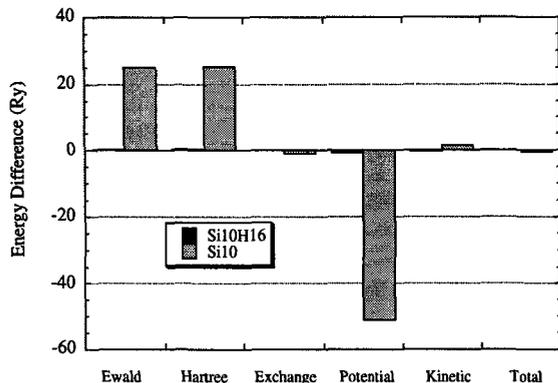


Figure 3: Contribution of the lattice repulsive energy (Ewald), Hartree repulsive energy, core-electron attractive potential, kinetic energy, and the exchange-correlation energy to reconstruct the optimized structures of the naked Si_{10} and the hydrogenated $\text{Si}_{10}\text{H}_{16}$ clusters. The individual energy contribution is shown by the energy difference between those of the initial and optimized structure of the naked Si_{10} and the hydrogenated $\text{Si}_{10}\text{H}_{16}$ clusters, respectively.

Let us investigate how the hydrogenation functions electronically. For this purpose, we focus on the Si_{10} naked cluster, and compare its electronic structure with that of the $\text{Si}_{10}\text{H}_{16}$ hydrogenated cluster. For the Si_{10} cluster, geometrical reconstruction due to total energy stabilization decreases the effective volume of the cluster. This decrease in the cluster volume shortens the interatomic lengths, and increases the Ewald and Hartree repulsive-energy contributions. However the ion-electron attractive potential energy overcomes the above repulsive contributions. As a result, a stabilization energy of about 0.05 Ry is obtained by this geometrical reconstruction as shown in Fig. 3.

Although the corresponding energy parts of the $\text{Si}_{10}\text{H}_{16}$ hydrogenated adamantane cluster contribute similarly in the total energy stabilization, the energy difference of the individual energy parts is not significant (Fig. 3). The reason is that the hydrogenation hardly decreases the effective volume (only by 0.48 %). The kinetic part plays an important role in forming the stable structure of the hydrogenated $\text{Si}_{10}\text{H}_{16}$ cluster,

while the potential energy part controls the total energy in the naked Si_{10} cluster.

3.3 Stable Chemical Species

Based on the calculated total energies for the present microclusters, we looked for the most energetically stable forms. In Fig.4, we show the chemical species having three Si (Ge) atoms in the order of the calculated total energies. For the comparison of the total energies, we considered the stoichiometrical species in which the total numbers of Si (Ge) and H atoms are equalized.

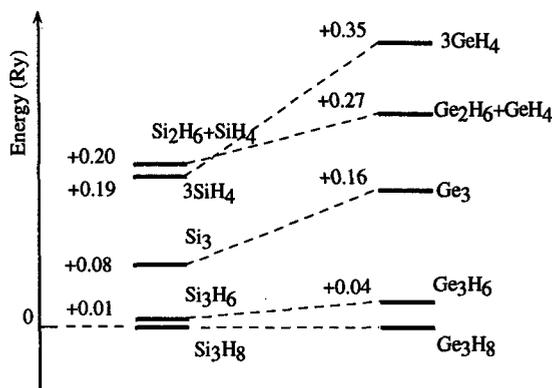


Figure 4: Comparison of the calculated total energies for Si_3 and Ge_3 microclusters. Here, five candidates having three skeleton atoms are considered. For the comparison of the total energy, we consider the stoichiometrical species in which the total numbers of Si (Ge) and H atom are equalized.

According to Fig. 4, the present calculation concludes that the chain-type structure (Si_3H_8 or Ge_3H_8) is the most stable specie in the Si_3 and Ge_3 systems, respectively. The second stable specie is the ring-type structure for Si and Ge systems. And the energy difference from the chain-type structure is only 0.01 Ry for Si_3H_8 but 0.04 Ry for Ge_3H_6 , respectively. Therefore, two hydrogenated microclusters of Si_3H_8 and Si_3H_6 are produced, but Ge_3H_6 is slightly difficult to be formed. It is also a common feature that the naked Si_3 and Ge_3 ring-clusters are energetically unstable and do not appear.

We summarized the other chemical species in Table 1. The clusters represented by bold characters are the most energetically stable species among the clusters including the same Si (Ge) atom number. According to Table 1, the chain-type forms become a stable species when the cluster has less than three Si or Ge atoms. By increasing the number of Si (Ge) atoms in the cluster, the stable form changes from the chain-type to the ring-type, and finally to the bulky type. Among these stable chemical species, the naked Si_6 and Ge_6 clusters having the puckered ring-form are most remarkable, while the clusters which include the nine Si (Ge) atoms are energetically unstable in the present calculation.

Table 1: Predicted energetically stable species for Si and Ge micro-clusters.

m	Si	Ge
1	SiH₄	GeH₄
2	Si₂H₆ , SiH ₄	Ge₂H₆ , GeH ₄
3	Si₃H₈ , Si ₃ H ₆	Ge₃H₈ , Ge ₃ H ₆
4	Si₄H₈ , Si ₄	Ge₄H₈ , Ge ₄
5	Si₅H₁₀ , Si ₅ H ₁₂	Ge₅H₁₀ , Ge ₅ H ₁₂
6	Si₆ , Si ₆ H ₁₂ (D _{3d})	Ge₆ , Si ₆ H ₁₂ (D _{3d})
7	Si ₇ , Si ₇ H ₁₆	Si ₇ , Ge ₇ H ₁₄
8	Si₈H₈	Ge₈H₈
9	None	None
10	Si ₁₀ H ₁₆ , Si ₁₀	Ge ₁₀ H ₁₆ , Ge ₁₀

4 Summary

First-principles electronic calculations were performed on Si and Ge microclusters. The hydrogenation in these clusters saturates the unpaired DB states, and stabilizes their electronic states energetically. This electronic stabilization causes less reconstruction, whereas a large amount of reconstruction occurs when the naked DBs are conserved in the clusters. The similarity found in both the molecular and electronic structures of the Si and Ge clusters is caused by the similarity in the wave functions of the valence electrons in the Si and Ge atom.

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