Electronic and Structural Theory of Group-IV Microclusters

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The non-spherical model-potential study on group-IV, sp³-hybridized microclusters has revealed that there are two different series for sp³ clusters, crystalline series and amorphous series. Starting from the model potential structures, we have investigated electronic states of several typical silicon clusters based on the Bond-Orbital Model and the LCAO-Xα method. The Bond-Orbital-Model study shows that surface-dangling-bond states concentrate on the Fermi level in every cluster. This may cause the reconstructions of the silicon clusters from the sp³ structures. LCAO-Xα-force calculations on Si₆ and Si₁₀ of crystalline series have shown the presence of the common reconstruction mechanism named "triangle contraction." On the other hand, the structural deviations of Si₆ and Si₁₀ of amorphous series are found to be small as long as their symmetries are conserved.

1. Introduction

In recent years, several interesting experimental [1-5] and theoretical [6-11] studies on group-IV, silicon clusters have been done. Time-of-flight and photofragmentation experiments have shown the relative abundances of small silicon clusters [1-4], and Si₆ and Si₁₀ are found to be relatively stable. Since silicon atoms are bound with covalent bonds which have mutually related orientations, the observed relative abundances are expected to reflect cluster geometries. There are some theoretical studies on silicon cluster geometries calculating their electronic structures [6-9]. Another theoretical approach, using the model potential for silicon atoms, has been also adopted [10,11].

In our previous work [12], a non-spherical model potential for sp³-hybridized atoms was introduced and the cluster geometries and magic numbers were discussed. The obtained structures tend to have ring structures and have been classified into two groups and named "crystalline series" and "amorphous series" after their pair-distance distribution. The crystalline-series and amorphous-series clusters mainly consist of six- and five-membered rings, respectively.

In this paper, electronic structures of several typical clusters of both series are studied for the case of silicon clusters. The selected clusters from crystalline series are Si₆ and Si₁₀, and from amorphous series Si₅ and Si₂₀ (Fig. 1). Si₆ is, of course, the smallest cluster among those consisting of six-membered rings. Si₁₀ has a three-dimensional cage structure made up of four six-membered rings. Both are magic-number clusters. Similarly, Si₅ and Si₂₀ are typical two- and three-dimensional magic-number clusters of only five-membered rings. Electronic states of these clusters are calculated using a simple tight-binding-approximation method, i.e., Bond-Orbital Model [13], and the Linear-Combination-of-Atomic-Orbitals

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The Bond-Orbital Model (BOM), which has been introduced for the bulk materials with tetrahedral bonds, is simple but very useful to understand their physical properties. Hence, in order to know the general properties of sp$^3$-hybridized silicon clusters, BOM is applied for crystalline-series Si$_6$ and Si$_{10}$, and for amorphous-series Si$_{18}$ and Si$_{20}$. For transfer parameters between various orbital pairs, $V_2-V_6$ [13], the values for silicon bulk are used. ($V_6$ is known to be very small and ignored in the present calculation.) In the case of amorphous-series clusters, however, the transfer parameters only between orbitals which correspond to the bulk geometries are used. Calculated electronic energy levels for Si$_6$, Si$_{10}$, Si$_{18}$, and Si$_{20}$ are shown in Fig. 2 with Gaussian-broadened density of states (DOS) for the schematic comprehension. It has been found from components of eigen states that dangling-bond states are concentrating near the Fermi level, $E_F$. Therefore, orbital energies for these clusters are expected to be very sensitive to the deformations, and the deformation can easily occur. Especially, the deformation which induces changes in transfers between dangling-bond orbitals is most preferable, since the levels near $E_F$ are dangling-bond states. In other words, dangling-bond interactions cause deformations of the clusters.

In order to know the sensitivities of levels near $E_F$ in regard to the transfer between dangling bonds, electronic states for clusters with additional transfer parameters between dangling bonds have been calculated tentatively (Fig. 3). For every cluster, new transfers (-0.6 eV) are introduced into the nearest pair of dangling bonds which have no transfers in BOM. In the case of Si$_{18}$ and Si$_{10}$, the additional transfer is introduced not only into the above dangling-bond pairs but also into the corresponding pair of bonding orbitals, because the distance between the pair orbitals is relatively short. It can be seen from the differences between Fig. 2 and