A Theoretical Study on Hydrogenation of Small Silicon Clusters

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Density-functional calculations in the generalized gradient approximation were performed for the structures and energetics of small hydrogenated silicon clusters: Si_6H_x ($0 \leq x \leq 14$). We found that hydrogenation causes the Si_6 cluster undergo an abrupt structural change from compact ($x \leq 6$) to open ($x \geq 8$) geometries. Relative stabilities of the Si_6H_x clusters are discussed based on calculated formation energies.

1. Introduction

The structures of small silicon clusters (Si_n) are well known to favor compact forms whose bonding characters are qualitatively different from a tetrahedral bonding network in a bulk diamond structure [1,2]. However, those of the hydrogenated clusters (Si_nH_x) have been little understood except some cases of hydrogen-saturated ones [3,4], because partial hydrogenation of the Si_n clusters provides much more complicated structures than the pure silicon counterpart.

Hydrogenated silicon clusters have been known as byproducts during chemical vapor deposition of silicon in a silane plasma. Mandich et al. [5] and Raghavachari [6] studied the reaction of $Si_nH_x^+$ clusters (n up to ~4) with SiH_4, and found that they are grown incrementally such that $Si_{n-1}H_x^+ + SiH_4 \rightarrow Si_nH_y^+ + H_2$. Murakami and Kanayama [7] used hydrosilicon radicals instead of SiH_4 to produce larger clusters with n up to 10. The latter case showed that stabilities of those clusters are very sensitive to the coverage of the hydrogen atoms.

The hydrogenated silicon clusters have been also regarded as a model of porous silicon [8]. However, most theoretical studies along this line have been limited to fragments of a bulk silicon crystals with dangling bonds fully saturated with H [3,4].

The purpose of this study is to investigate the effect of hydrogenation on the structure of small silicon clusters. Our primary interest is in the structure evolution of a silicon cluster as a function of the coverage of hydrogen atoms. We consider neutral Si_nH_x clusters with $n = 6$ and allow x to vary in a wide range, $x = 2, 4, 6, 8, 10, 12$ and 14.

2. Method of calculation

The calculations were performed using the density functional theory in its plane-wave pseudopotential formulation [9] and generalized gradient approximation (GGA-PW'91) [10]. We adopted the Vanderbilt ultrasoft pseudopotential [11] for the $1s$ state of H and the Troullier-Martin-type of pseudopotential [12] for Si. The wave functions were expanded with a cutoff of $E_{PW}=12.25Ry$. In all the optimizations the clusters were placed in a cubic cell with edge length of 16Å and structure optimization was symmetry unrestricted. Test calculations for a Si_2H_6 molecule reproduced the experimental bond lengths as well as angles with relative errors less than 0.5%.

3. Results and discussion

Before proceeding to the result of hydrogenated silicon clusters, we compare the structure of the Si_6 cluster obtained in the present study (see Fig.1(a) and Table I) with those pre-

viously calculated [1,2]. First of all, we confirmed that the use of the current plane-wave basis set gave accurate atomic positions, because they were essentially the same as those optimized by using the localized orbitals, except isotropic shrinkage of the cluster by ~0.02 Å.

Our structure is an edge-capped trigonal bipyramid, similar to that obtained at the HF/6-31G* level of theory [1]. A major difference is that the bond distances of the atoms 1 and 3 from the atoms 5 and 6 are much shorter than those from the atom 2 in our calculation while the length ordering is opposite in the HF/6-31G* structure. This bond-length ordering becomes the same as our DFT results if the second-order Møller-Plesset perturbation is taken into account [2].

We now turn to investigation of calculated structures of Si_6H_x clusters. The minimum-energy configurations obtained in this study for Si_6H_{0-6} and Si_6H_{8-14} are illustrated in Fig.1 and Fig.2, respectively. The structures of the Si_6H_x clusters with $x \leq 6$, shown in Fig.1, have a common aspect that the basic skeleton of silicon atoms is that of Si_6.

Attachment of hydrogen atoms is systematic in the sense that each apex of the bare Si_6 cluster is terminated one after another.

TABLE I. Structure parameters (in Å) of Si_6 in Fig.1(a).

atom pair	DFT1[a]	DFT2[b]	HF[c]	MP2[d]
1-2	2.63	2.61	2.364	2.73
1-5	2.38	2.37	2.442	2.36
2-3	2.52	2.50	–	2.73
2-5	2.42	2.40	2.435	2.36
4-5	2.36	2.34	2.323	2.36
5-6	2.70	2.68	2.651	2.69

[a]This work. [b]Calculated with LCAO [19]. [c]Ref. [1]. The basis set used is 6-31G*. [d]These bond lengths were reproduced in this study by using the 6-31G* basis set [18], because they are not shown in Ref. [2]. Note that the MP2/6-31G* optimized structure has D_{4h} symmetry about the bond between the atoms 5 and 6.
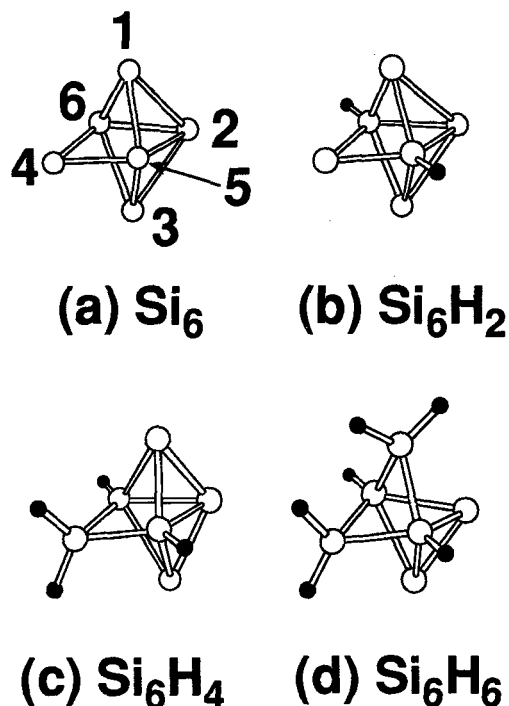

(a) Si_6 (b) Si_6H_2

(c) Si_6H_4 (d) Si_6H_6

FIG. 1. Ball-stick models of the structures of Si_6H_{0-6} clusters optimized in this study. Open and closed circles represent Si and H atoms, respectively.

In the case of Si_6H_4 (Fig.1(c)) and Si_6H_6 (Fig.1(d)), SiH_2 units with the sp^3-like configuration are formed. However, formation of SiH_2 in Si_6H_2 is unfavorable, total energy of a structure containing one SiH_2 unit being ~0.1 eV higher than that of the structure shown in Fig.1(b). We also found that a geometry of Si_6H_2 in which two hydrogen atoms are attached to $Si(1)$ and $Si(3)$ is 0.55 eV higher in energy than the one in Fig.1(b).

It is interesting to compare our optimized structures with those previously considered. Quantum chemical calculations [13,14] have suggested that hexasilaprismane may be energetically favorable. We found that the structure in Fig.1(d), which has not been investigated previously, is 0.34 eV lower in energy than hexasilaprismane. Hexasilabenzene, a silicon analogue of benzene (C_6H_6) [15], has in our calculation higher energy by 0.69 eV than that of hexasilaprismane, in reasonable agreement with the value 0.412eV [13] or 0.581eV [16], obtained in quantum chemical calculations.
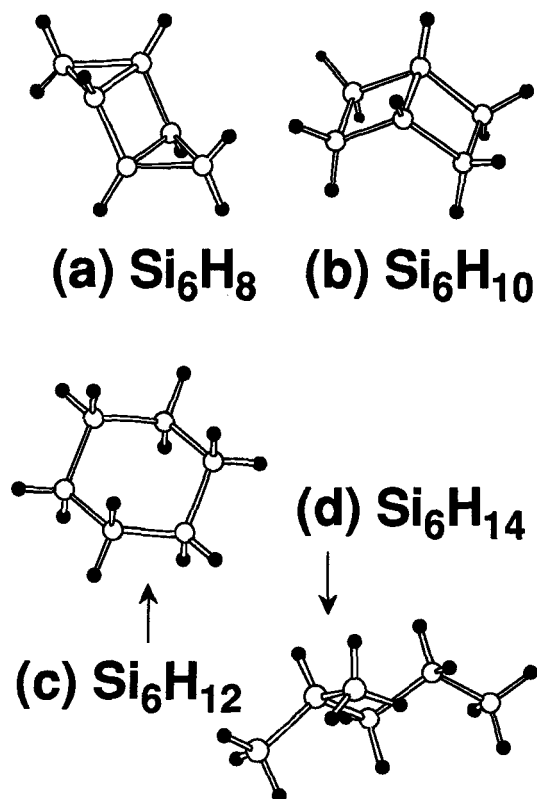
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(a) Si_6H_8 (b) Si_6H_{10}

(d) Si_6H_{14}

(c) Si_6H_{12}

FIG. 2. The structures of Si_6H_{8-14} clusters optimized in this study.

For $x \geq 8$ (Fig.2), the structures of Si_6H_x clusters are drastically different from those for $x \leq 6$. All silicon atoms in the clusters in this regime are fourfold coordinated and terminated with either one or two hydrogen atoms. Figure 2(a) shows the structure of a Si_6H_8 cluster with the lowest possible energy in our calculation. For $x=10$, bicyclo[2.2.0]hexasilane in Fig.2(b) was found to be the lowest-energy isomer, in agreement with the calculation by Nagase et al [17]. For $x=12$, cyclohexasilane (Fig.2(c)) has the lowest energy, as expected.

We further studied relative energetics between a fully saturated chain-like structures of Si_6H_{14} and Si_6H_{12} (cyclohexasilane, Fig.2(c)). For this purpose we used a $16\text{Å}\times16\text{Å}\times24\text{Å}$ supercell and performed the structure optimizations of both clusters. The total energy of Si_6H_{14} is 0.1eV lower than that of cyclohexasilane with a H_2 molecule. However, contributions of zero-point energies of H atoms reverse the energy ordering:

the latter becomes lower in energy than the former by about 0.05eV. We also found that the chain-like structures of Si_6H_{14} are nearly degenerated within the energy range of $\sim$0.1eV irrespective of the number and position of the side chains.

Finally, we show the results of relative stability of the clusters. Figure 4 shows the formation energy of the optimized Si_6H_x clusters. We took a mixture of the optimized Si_6 cluster and H_2 molecules as a reference of the formation energy.

Obviously, formation of Si_6H_x clusters with larger coverages of hydrogen is more favorable. However, formation of Si_6H_{14} is slightly unfavorable against formation of a mixture of cyclohexasilane and H_2, as described above. Although we have not calculated the formation energies of the Si_6H_x clusters with $x \geq 16$, it is highly expected that further hydrogenation would lead to insertion of H atoms in the Si-Si bonds, whose formation is no longer energetically favorable.

There is yet another aspect of the formation energy curve. In the range $2 \leq x \leq 10$, they are always above the straight line connecting the formation energies at $x=0$ and $x=12$ (dotted line in Fig.5) although the one for $x = 2$ deviates only slightly. Since this straight dotted line represents the formation energy of a system where Si_6 and Si_6H_{12} clusters coexist, defined as $E_{form}^{coexist}(x) = \frac{(12-x)E_{form}(x=0)+xE_{form}(x=12)}{12}$, we can say that creation of Si_6H_x clusters ($4 \leq x \leq 10$) is energetically less favorable than coexistence of Si_6, Si_6H_{12} and perhaps Si_6H_2 clusters. Although this feature is specific to the situation in which neutral Si_6H_x clusters are in equilibrium with a reservoir of H_2 molecules, it may provide an interesting insight into the relative stabilities of these clusters.

If one attempts to make the theoretical considerations more realistic, then it would be at least necessary to extend the present calculation to ionized clusters. Investigations of transition states during the incremental growth should also be important. Moreover, some dynamical aspects, such as effects of hydrogen abstraction, collision of rare-gas buffer, and AC acceleration on electronic and geometric structures of the clusters might be key factors to govern the observed mass populations [7].
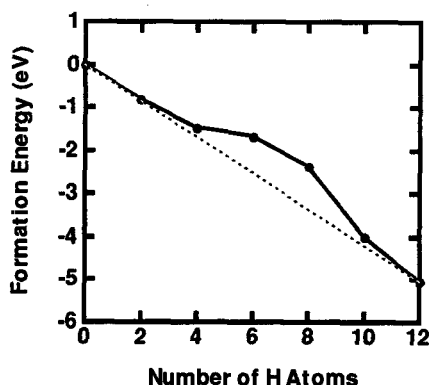
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FIG. 3. Calculated ormation energy of Si_6H_x clusters as a function of x.

4. Conclusions

In conclusion, we performed first-principles calculations on stable structures and energetics for hydrogenated silicon clusters: Si_6H_x. Hydrogenation of silicon clusters categorizes their structures into two distinct families. In the low-coverage cases ($x \leq 6$), the structures essentially belong to a family characterized by a compact geometry of a Si_6 cluster. On the other hand, in the cases of higher coverages ($x \geq 8$), the clusters are transformed into more open structures. Calculated formation energies suggest coexistence of low-coverage (Si_6, Si_6H_2) and hydrogen-saturated (Si_6H_{12}) clusters in the atomsphere of H_2 molecules.

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