Stability and fragmentation of multiply ionized Si_N^M clusters

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Abstract. The stability of neutral, singly and multiply ionized silicon clusters, Si_N^M ($N = 2-7$, $M = 0$, ± 1, ± 2, ± 3), has been investigated using an *ab initio* density functional method. We show that the fragmentation effect significantly affects the structure of mass-spectra of multiply ionized silicon clusters. For Si_N^{2+} clusters, the clusters with a large fragmentation energy are found to correspond to the high peaks at $N = 4$ and 6 in mass-spectra. For Si_N^{2-} clusters, a peak at $N = 5$ in mass-spectra has been predicted to be especially high.

PACS. 36.40.Qv Stability and fragmentation of clusters – 36.40.Wa Charged clusters

1 Introduction

In recent years there has been a wide interest in the theoretical and experimental investigations of clusters of atoms and molecules. Since a cluster is expected to be the smallest device unit, it is very important to know the electronic and atomic structure of stable clusters. Experimentally, the stability of the clusters has been studied mainly from mass-spectra. Peaks in such mass-spectra are considered to represent (1) initial structure which can be desorbed easily from a target, (2) the cohesive energy of the clusters, (3) an incremental binding energy, or (4) a fragmentation energy [1].

Mass-spectra of silicon clusters, which are significant clusters in industry, have been obtained experimentally, and were explained as follows. For neutral clusters the peaks represent those having low cohesive energies [2,3], or small incremental binding energies [3,4]. Mass-spectra of a singly ionized silicon cation cluster were explained as the incremental binding energy effect [5], and a singly ionized silicon anion cluster as the cohesive energy (electron affinity) effect [6].

Multiply ionized silicon clusters especially attract our interest, because the clusters can fragment into daughter clusters due to strong coulomb repulsion [7,8]. Tsong obtained mass-spectra for doubly ionized silicon cation clusters, and insisted that the peaks at $N = 4$, 5 and 6 were closely related to their initial structures [9]. However we think that the result should rather be understood as the fragmentation energy effect. Since his experiment was performed under a non-equilibrium condition, clusters could only fragment without being combined. Therefore

we considered that such a fragmentation effect became more dominant. In this paper, we calculate total energies of neutral, singly and multiply ionized Si clusters Si_N^M ($N = 2-7$, $M = 0$, ± 1, ± 2, ± 3) to evaluate fragmentation energies using an *ab initio* density functional method. We further discuss the peaks of doubly ionized cation/anion silicon clusters in mass spectra in terms of the fragmentation energy.

2 Calculation details

Our calculation was based on the spin density functional method with the 6−31G* basis set. Electron exchange and correlation effects were included using Becke's exchange functional [10] and Lee, Yang, and Parr's correlation functional [11]. We used the spin-unrestricted calculation. We then calculated the total energy $E(N, M)$ of the most stable structure for each silicon cluster, Si_N^M ($N = 2-7$, $M = 0$, ± 1, ± 2, ± 3).

Although it is impossible to compute the accuracy of our calculation for general-sized clusters, we can only guess the accuracy, for example, by comparing electron affinities for a Si_2 (and Si_2^-) molecule for two basis sets; 6−31G* (present basis) and 6−311+G** (more accurate basis). The calculated result was −1.713 eV (3.943 eV) for 6−31G* and −1.869 eV (3.599 eV) for 6−311+G*, the energy differences being less than 0.35 eV in this case.

3 Results and discussion

In this section, we describe the calculated total energies for the most stable Si_N^M clusters ($N = 2-7$, $M = 0$, ± 1,

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±2, ±3). We then calculate the incremental binding energies E_{inc} of Si_N and Si_N^+. Finally, we calculate the fragmentation energies E_{fr} for Si_N^M, and discuss the stability of the doubly ionized Si cation clusters observed in the experiment and then of the anion ones.

3.1 Total energy and stable structure of Si_N^M

The total energies for the Si_N^M clusters are shown in Table 1. The most stable structure of each singly, doubly and triply ionized Si_N^M cluster ($M = \pm1, \pm2, \pm3$) was found to be similar to that of the neutral one. The most stable structures for Si_N and $\text{Si}_N^\pm$ agree well with the results reported in the previous works [1–6].

Si_2^M ($M = 0, \pm1, \pm2$): Bond lengths were as follows: Si_2^{2+}, 0.306 nm; Si_2^+, 0.234 nm; Si_2, 0.220 nm; Si_2^-, 0.214 nm; and Si_2^{2-}, 0.220 nm. These bond lengths, except that of Si_2^{2+} were shorter than that of silicon crystal, 0.235 nm.

Si_3^M ($M = 0, \pm1, \pm2$): Stable structure for Si_3 was an isosceles triangle with an open angle of 85.4° and with the sides of 0.221 nm. For the ionized clusters, Si_3^{2+}, Si_3^+, Si_3^- and Si_3^{2-}, stable structures were also isosceles triangles, where the angles (the bond lengths) were Si_3^{2+}, 87.8° (0.244 nm); Si_3^+, 71.4° (0.225 nm); Si_3^-, 66.1° (0.229 nm); and Si_3^{2-}, 60.0° (0.239 nm).

Si_4^M ($M = 0, \pm1, \pm2$): Each Si_4^M cluster had a flat rhombus structure. Their diagonal bond angles (side lengths) were Si_4^{2+}, 90.0° (0.234 nm); Si_4^+, 71.6° (0.233 nm); Si_4, 63.0° (0.236 nm); Si_4^-, 60.9° (0.237 nm); and Si_4^{2-}, 59.0° (0.239 nm).

Si_5^M ($M = 0, \pm1, \pm2, -3$): Stable structures for Si_5^M were trigonal bipyramids: Si_5^{2+}, Si_5^+, Si_5, Si_5^- and Si_5^{3-} had C_{2v} symmetry and Si_5^{2-} had D_{3h} symmetry.

Si_6^M ($M = 0, \pm1, \pm2, \pm3$): Calculated stable structures for Si_6^M were tetragonal bipyramids. The base square planes for Si_6, Si_6^- and Si_6^{2-} had bond lengths of Si_6, 0.280 nm; Si_6^-, 0.265 nm; and Si_6^{2-}, 0.254 nm. The cap bond lengths were Si_6, 0.241 nm; Si_6^-, 0.246 nm; and Si_6^{2-}, 0.254 nm. Si_6^{2-} had the highest class of symmetry and is O_h symmetric. Mulliken population analysis showed that electron charge in Si_6^{2-} was distributed into six atoms evenly ($-2e/6$ for each atom). The base planes for Si_6^+, Si_6^{2+}, Si_6^{3+} and Si_6^{3-} were oblong, and their bond lengths of the long (short) sides were Si_6^+, 0.278 (0.268) nm; Si_6^{2+}, 0.275 (0.259) nm; Si_6^{3+}, 0.265 (0.258) nm; and Si_6^{3-}, 0.284 (0.243) nm. The cap bond lengths were Si_6^+, 0.242 nm; Si_6^{2+}, 0.245 nm; Si_6^{3+}, 0.250 nm; and Si_6^{3-}, 0.259 nm.

Si_7^M ($M = 0, \pm1, \pm2, \pm3$): The optimized structures for Si_7^M were pentagonal bipyramids (five atoms form a pentagon and the other two atoms cap). Si_7, Si_7^- and Si_7^{2-} had D_{5h} symmetry and their bond lengths of the base pentagons were Si_7, 0.254 nm; Si_7^-, 0.249 nm; and Si_7^{2-}, 0.245 nm. Si_7^+ and Si_7^{2+} had C_{2v} symmetry, because base pentagons were distorted from C_{5h} symmetry. The lengths between the two cap atoms were Si_7^{2+}, 0.312 nm;

Table 1. Total energies (Hartree) for Si_N^M ($N = 1-7$).

Cluster Si_N^M (N, M)	Total Energy (Hartree) $E(N, M)$
$(1, +2)$	-288.46661
$(1, +1)$	-289.06438
$(1, 0)$	-289.35567
$(1, -1)$	-289.38302
$(1, -2)$	-289.12836
$(2, +2)$	-578.02885
$(2, +1)$	-578.54719
$(2, 0)$	-578.82578
$(2, -1)$	-578.88872
$(2, -2)$	-578.74303
$(3, +2)$	-867.52958
$(3, +1)$	-868.03397
$(3, 0)$	-868.32429
$(3, -1)$	-868.39155
$(3, -2)$	-868.26135
$(4, +2)$	-1157.08819
$(4, +1)$	-1157.55466
$(4, 0)$	-1157.83248
$(4, -1)$	-1157.89656
$(4, -2)$	-1157.26135
$(5, +2)$	-1446.56183
$(5, +1)$	-1447.02820
$(5, 0)$	-1447.31468
$(5, -1)$	-1447.38797
$(5, -2)$	-1447.30593
$(5, -3)$	-1446.99995
$(6, +2)$	-1736.07217
$(6, +1)$	-1736.53159
$(6, 0)$	-1736.80503
$(6, -1)$	-1736.86865
$(6, -2)$	-1736.78578
$(6, -3)$	-1736.49731
$(7, +3)$	-2025.00306
$(7, +2)$	-2025.59627
$(7, +1)$	-2026.02192
$(7, 0)$	-2026.29686
$(7, -1)$	-2026.35802
$(7, -2)$	-2026.27399

Si_7^+, 0.292 nm; Si_7, 0.276 nm; Si_7^-, 0.320 nm; and Si_7^{2-}, 0.352 nm. Si_7^{3+} had no symmetry. The optimized structure for Si_7^{3+} was a strongly distorted pentagonal bipyramid.

3.2 Incremental binding energy

The incremental binding energy is defined as the difference between the cohesive energies of Si_{N-1}^M and Si_N^M clusters,

$$E_{\text{inc}}(N, M) \equiv E_{\text{coh}}(N - 1, M) - E_{\text{coh}}(N, M). \quad (1)$$
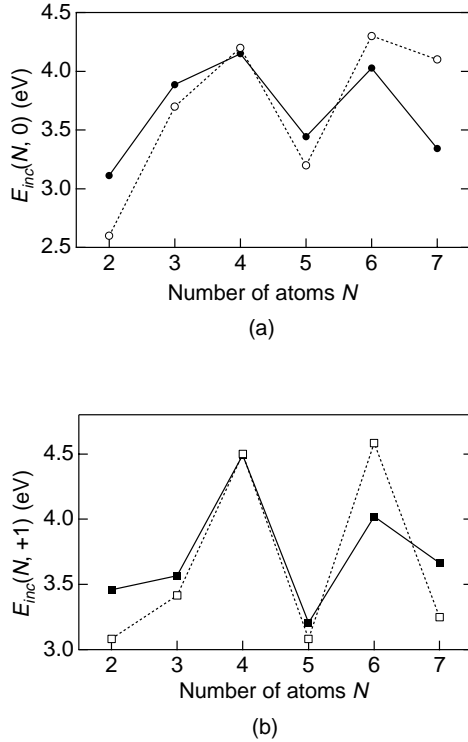
(a)

(b)

Fig. 1. Incremental binding energies E_{inc} (eV) for Si_N (a) and Si_N^+ (b) clusters as a function of number of atoms N. Dots for the present work, and circles for previous theoretical work [3,5].

Fig. 2. Fragmentation energies E_{fr} (eV) for Si_N^M clusters as a function of number of atoms N.

Since the cohesive energy $E_{coh}(N, M)$ is defined as

$$E_{coh}(N, M) \equiv E(N, M) - N E(1, 0), \qquad (2)$$

by the total energies $E(N, M)$ of a Si_N^M cluster and of a neutral Si atom. We evaluate $E_{inc}(N, M)$ from the calculated results of $E(N, M)$.

Figures 1a and b show the calculated incremental binding energies $E_{inc}(N, M)$ for $M = 0$ and $M = +1$. Our results are shown by dots. Since our results agree well with the previous results shown by circles [3,5] (*i.e.* within about 1 eV), we think that our calculation is valid enough to evaluate the stability for Si_N^M ($M = 0, +1$) clusters.

3.3 Fragmentation energy

The stability of doubly or multiply ionized clusters can not simply be discussed in terms of the incremental binding energy. We must consider several fragmentation channels of a cluster Si_N^M into small clusters of different charges:

$$Si_N^M \rightarrow Si_a^p + Si_b^q + ..., (a + b + ... = N, p + q + ... = M). \qquad (3)$$

When any of the above fragmentation channels is exoergic, the Si_N^M cluster can dissociate into daughter clusters provided that the activation energy for such a dissociation process is negligibly small or is ignored. Fragmentation
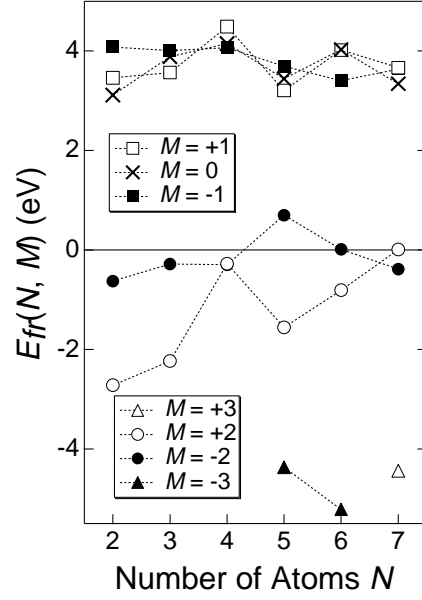
probability is large for a channel which has a larger exoergic energy. We calculate latent heats for all the fragmentation channels, and determine the most probable fragmentation channel that has the lowest fragmentation energy $E_{fr}(N, M)$ defined as

$$E_{fr}(N, M) \equiv [E(a, p) + E(b, q) + ...] - E(N, M). \qquad (4)$$

In Figure 2, we plot the calculated fragmentation energies $E_{fr}(N, M)$ for Si_N^M ($N = 2$–7, $M = -1, \pm 2, \pm 3$). The plots of $E_{fr}(N, 0)$ (shown by crosses) agree with the $E_{inc}(N, 0)$ in Figure 1a, $E_{fr}(N, +1)$ (shown by open squares) in Figure 2 agree with $E_{inc}(N, +1)$ in Figure 1b. Furthermore $E_{fr}(N, -1)$ for singly ionized anion clusters was found to be the same as $E_{inc}(N, -1)$. These results indicate that the most probable fragmentation of the neutral and/or singly ionized clusters is the evaporation process;

$$Si_N^M \rightarrow Si_{N-1}^M + Si^0 (M = 0, \pm 1). \qquad (5)$$
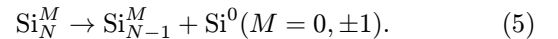
The most probable exoergic fragmentation channels (and products) for doubly (and multiply) ionized clusters are shown in Table 2.

3.3.1 Cation clusters

Mass-spectra of the doubly ionized cation silicon clusters were observed by the pulsed-laser-stimulated field desorption of silicon emitters [9]. The peaks of the mass-spectra had the following features. The intensity ordering of the Si_N^M was $I(Si_4^{2+}) > I(Si_6^{2+}) > I(Si_5^{2+}) > I(Si_3^{2+}) \gg I(Si_2^{2+}) \approx 0$, where $I(Si_N^M)$ represents a peak intensity of the Si_N^M cluster. In addition, only Si_4^+ was detected as a sharp and high peak among singly ionized cation clusters Si_N^+. Tsong insisted that the features were caused by an

Table 2. The lowest fragmentation channels and fragmentation energies (eV) for parent Si_N^M clusters. The clusters whose fragmentation channel is exoergic are listed.

Parent Cluster Si_N^M (N, M)	Fragmentation Channel	Fragmentation Energy (eV)
$(2, +2)$	$(1, +1) + (1, +1)$	-2.719
$(3, +2)$	$(2, +1) + (1, +1)$	-2.231
$(4, +2)$	$(3, +1) + (1, +1)$	-0.277
$(5, +2)$	$(4, +1) + (1, +1)$	-1.557
$(6, +2)$	$(4, +1) + (2, +1)$	-0.808
$(7, +3)$	$(4, +1) + (2, +1) + (1, +1)$	-4.440
$(2, -2)$	$(1, -1) + (1, -1)$	-0.626
$(3, -2)$	$(2, -1) + (1, -1)$	-0.283
$(4, -2)$	$(2, -1) + (2, -1)$	-0.297
$(7, -2)$	$(5, -1) + (2, -1)$	-0.384
$(5, -3)$	$(2, -1) + (2, -1) + (1, -1)$	-4.368
$(6, -3)$	$(5, -2) + (1, -1)$	-5.215

initial structure effect; highly symmetric atomic structures which contained 4, 5 and 6 Si atoms were easily desorbed from the Si surface.

The features of the observed mass-spectra can also be explained in terms of the fragmentation energy. The ordering of the fragmentation energies of the doubly ionized Si cation cluster, shown in Figure 2, is $E_{\mathrm{fr}}(7, +2) > E_{\mathrm{fr}}(4, +2) > E_{\mathrm{fr}}(6, +2) > E_{\mathrm{fr}}(5, +2) > E_{\mathrm{fr}}(3, +2) > E_{\mathrm{fr}}(2, +2)$. Thus the ordering for $N = 4, 6, 5, 3$ and 2 is the same as the intensity ordering of the mass spectra. Since a process with large exoergic energy has a large fragmentation probability, the Si_2^{2+} clusters can easily dissociate to have a low peak intensity in the observed mass-spectra. In contrast, Si_4^{2+} and Si_6^{2+} clusters which have high exoergic fragmentation energies can remain so long as they give high peaks in the mass-spectra. Although our calculation predicts the peak for the Si_7^{2+} clusters will be the highest one, it was extremely low in the experiment [9]. We think that the Si_7^{2+} clusters were merely desorbed from the silicon surface for some reason.

Such dissociations of Si_N^{2+} clusters may result in the increase of the mass peaks of their products. In Table 2, we notice that Si_4^+ clusters are produced as a result of dissociation of Si_5^{2+} and Si_6^{2+}. The Si_4^+ clusters, once they have formed, are considered to be unable to fragment because they have a negative fragmentation energy.

3.3.2 Anion clusters

We can make a similar argument for silicon anion clusters. As shown in Figure 2, the ordering of fragmentation energies $E_{\mathrm{fr}}(N, -2)$ is $E_{\mathrm{fr}}(5, -2) > E_{\mathrm{fr}}(6, -2) > E_{\mathrm{fr}}(3, -2) > E_{\mathrm{fr}}(4, -2) > E_{\mathrm{fr}}(7, -2) > E_{\mathrm{fr}}(2, -2)$. Therefore, a high peak of the mass-spectra for Si_N^{2-} is expected to be present at cluster size $N = 5$. For singly ionized Si anion cluster, Si_2^- is expected to have a high peak, because Si_2^- appears frequently in the lowest fragmentation channels of Si_N^{2-} clusters, as shown in Table 2.

4 Conclusion

The most stable structures and their fragmentation energies of neutral, singly and multiply ionized silicon clusters Si_N^M ($N = 2$–7, $M = 0, \pm1, \pm2, \pm3$) were calculated by an *ab initio* density functional method. As a result of our calculation, we found mass-spectra of the multiply ionized silicon clusters to be affected mainly by fragmentation of the clusters. For Si_N^{2+} clusters, the clusters which have large fragmentation energy are found to correspond to the high peaks at $N = 4$ and 6 in mass-spectra. For Si_N^{2-} clusters, a peak at $N = 5$ in the mass-spectrum has been predicted to be especially high.

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