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Low-energy surface collision induced dissociation of Ge and Sn cluster ions

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Abstract. Fragmentation of germanium and tin cluster ions (Ge_x^+, Sn_x^+: $x = 4{\sim}20$) in the low-energy collisions with a Si surface has been investigated by means of a tandem time-of-flight mass spectrometer. At low incident energies, smaller clusters fragmented by an atom loss process, whereas larger clusters decayed by fission. The favored fragmentation paths for both cluster ions were similar to those for Si cluster ions. The results support the structural similarities among Si, Ge, and Sn clusters in the present size range. For tin cluster ions, low-energy fragmentation patterns were compared with those obtained from theoretical calculations using generalized gradient approximation (GGA) and the B3PW91 exchange-correlation functional. It has been found that the B3PW91 hybrid functional results are consistent with the experimental observations.

PACS. 31.15.Ew Density-functional theory – 36.40.Qv Stability and fragmentation of clusters – 36.40.-c Atomic and molecular clusters

1 Introduction

Structure and stability of semiconductor clusters have been the subjects of intensive research because of their importance in both basic science and technologies. Nowadays, the trend of downsizing electronic devices makes the research on the subjects even more important than ever.

In the group-14 elements, both Si and Ge take the tetrahedral structure in the bulk. This leads to a speculation that Si_x and Ge_x clusters also have the same geometry. In fact, this elementary idea is valid for small cluster ions (x up to ≈30). [1] In the size range of 13∼30, these clusters take the prolate structure based on the tricapped trigonal prism (TTP) [2–5], although the detailed structures are not totally the same [6]

Tin is unique in that it has two allotropes, semiconducting α-Sn and metallic β-Sn in the bulk, and the phase transition occurs below room temperature ($T_c = 286$ K): the metallic phase is more stable at room temperature. However, interestingly, tin clusters also take the prolate type geometries like Si and Ge clusters for x up to ≈35 [7,8]. Thus, in small clusters with x up to ≈30 transition from covalent to metallic bonding seems to occur between tin and lead [1].

Thermal fragmentation of clusters gives prospects on size-dependent stability of clusters and hence, some information on geometries. In accordance with recent progress in theoretical calculations on the cluster geometries and energies, fragmentation patterns can now be used as a reliability check for calculated results [9,10]. We have been studying the structure and size-dependent stability of group-14 clusters by surface induced dissociation (SID) experiments and theoretical calculations. In this paper, we will show the results we have obtained for Ge and Sn clusters, and discuss structural similarities and difference.

2 Experimental methods

The experiments were performed by means of a home-designed tandem time-of-flight (TOF) mass spectrometer. The details of the experimental setup have been reported elsewhere, and are described here briefly [11,12]. Clusters were produced by the laser vaporization method [13]. Positive ions from the cluster source were extracted by the Wiley-Mclaren's accelerator [14]. For the SID experiments, mass selection was performed by applying a pulsed high voltage (pulse width ≈ 2 μs) to a 90° ion mirror [15,16]. The mass-selected ions were decelerated and allowed to collide with a Si surface. Scattered positive ions were then extracted back by the electric field with which the incident ions were decelerated, and were detected by a tandem microchannel plate. The collision energy was varied by changing a bias voltage applied to the substrate. The incident energy spread of the primary ion beam was estimated to be 80 eV (FWHM). In this paper, an incident energy (E_i) stands for the difference between the

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mean kinetic energy of the projectile ions and the substrate potential.

The experiment was carried out under UHV conditions: the base pressure in the scattering chamber was on the order of 10^{-9} torr. During the experiments, the substrate was maintained at 150 °C to avoid physisorption of residual gases in the vacuum chamber.

3 Computational methods

Computational approaches have been made for neutral and cationic tin clusters [8,10,17]. The ground state geometries of the neutral and charged clusters have been obtained using the ultrasoft pseudopotential method [18,19] with a plane wave basis and GGA [20] for the exchange-correlation energy. For clusters, we used a simple cubic supercell of side 20 Å and Γ point for the Brillouin zone integrations. A large number of structures, including those reported for Si [3] and Ge [6] clusters, were optimized [8]. It has been observed that hybrid exchange-correlation functional [21] like B3PW91 shows better agreement with experimental results [17]. Therefore, the lowest energy structures obtained from GGA were reoptimized with B3PW91 exchange-correlation functionals using the Gaussian method [22].

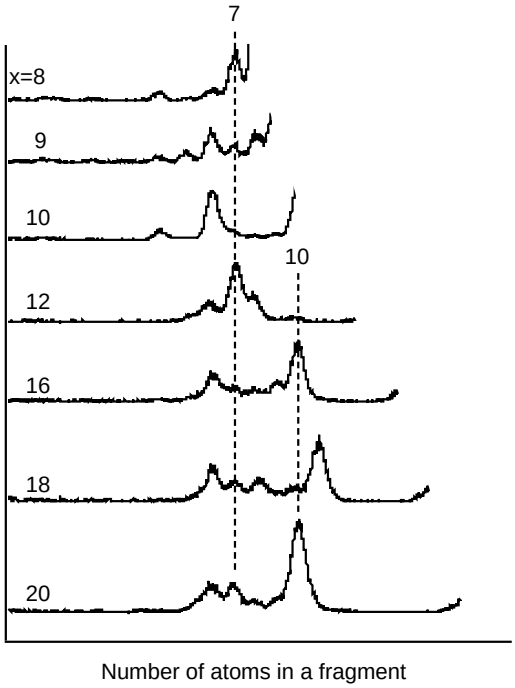

Fig. 1. Mass spectra for fragment ions generated in the collisions of Ge_x^+ (x = 8, 9, 10, 14, 16, 18, 20) with a Si surface.

4 Results and discussion

4.1 Ge clusters

Figure 1 shows the fragmentation mass spectra for Ge_x^+ (x = 8, 9, 10, 14, 16, 18, 20) in collision with a Si surface at nominal 0 eV [23]. Up to $x = 9$, Ge_x^+ decayed by atom loss, while, for x larger than this value, they tend to decay into halves, which is consistent with former gas-phase collision-induced dissociation (CID) results [4]. Among the fission paths, those producing Ge_7, Ge_{10}, Ge_6^+, Ge_7^+, and Ge_{10}^+ were dominant, which results are similar to those reported for the low-energy CID of Si_x^+ [24] and Ge_x^+ clusters [4]. Although the structures of Si and Ge clusters diverge from $x \approx 13$ [6], they are still similar in that they consist of stacked or fused subunits of identical sizes, and thus, it is understandable that favored fragmentations give rise to the stable subunit clusters rather than Ge_{x-1}^+ and an atom. It is noteworthy that from dissociation energy measurements, Hunter *et al.* [4] have proposed that Ge_x clusters are weakly bound aggregates of small units such as Ge_7 and Ge_{10}.

4.2 Sn clusters

The fragmentation pattern drastically changes between Sn_{11}^+ and Sn_{12}^+: Sn_6^+, and Sn_7^+ fragments were dominant for the Sn_{12}^+ and Sn_{13}^+ incidences, while fragments such as Sn_{x-1}^+, Sn_{x-2}^+, ... were the major species for the Sn_x^+ (x = 4∼11) incidences. The transition from the fission type to the atom loss type decay has been observed in the CID patterns for Si_x^+ [24] and Ge_x^+ [4], and is also apparent in Figure 1.

In Figure 2, low-energy SID patterns for Sn_x^+ (x = 14∼20) are shown. Surprisingly, the decay patterns were very similar to those of Ge_x^+ except at $x = 16$. In this size regime, the proposed ground state structures of Sn clusters consist of fused or stacked two subunits as Si and Ge clusters [8]. Thus, again the fission process is intuitively understandable. Moreover, the sizes of the most intense fragment ions observed for Sn_x^+ were almost the same as those for the corresponding Si cluster ions [24]. All the neutral Si, Ge and Sn heptamers and decamers are at local minima in the second order difference of the total energy ($\Delta E_2 = 2E(x) - E(x+1) - E(x-1)$) [5,8,25]. It is also predicted by the present calculation that ΔE_2 is minimal at Sn_7^+, and Sn_{10}^+ [17].

When the fragmentation patterns of Ge_x^+ and Sn_x^+ (x = 14∼20) are compared, it can be seen that relative intensity of heptamer with respect to hexamer is high for Sn_x^+ fragmentations. This result is consistent with fragmentation energy of these species. We have calculated the fragmentation energy, $E_f(x^+) = E(x^+) - E(y^+) - E(z)$, of an x-atom cation cluster decaying into a y-cation and a z-neutral cluster product ($x = y + z$), assuming that fragmentation occurs along the lowest energy pathways with no activation barrier. From the calculation, it was found that E_f for Sn_6^+ and Sn_7^+ are almost the same [10]. In contrast, the dissociation energy for Ge_6^+ obtained from the CID experiment is considerably larger than that of Ge_7^+ [4].

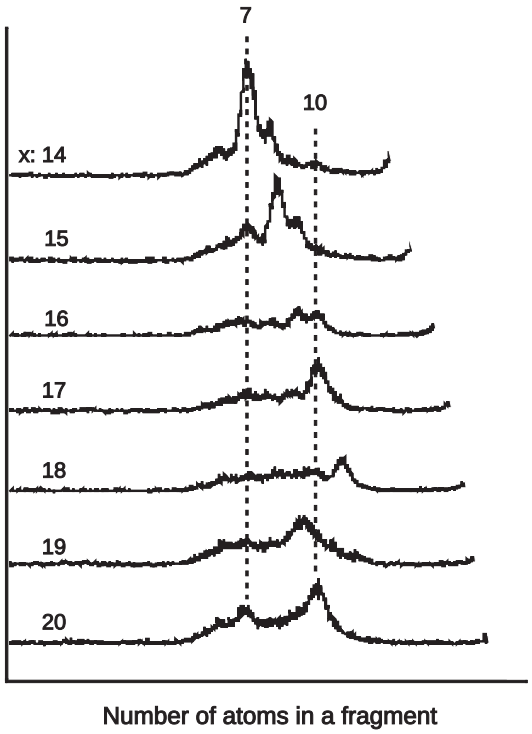

Fig. 2. Mass spectra for fragment ions generated in the collisions of Sn_x^+ ($x = 14\sim20$) with a Si surface.

Table 1 gives a comparison of the observed fragmentation paths with a few lowest energy fragmentation channels obtained from the B3PW91 calculations. As shown in Table 1, the agreement between the experimental and the calculated results are excellent. The present B3PW91 results are in better agreement as compared to the earlier results where only neutral clusters were considered [8]. The calculated results also show that in all the cases Sn_x^+ clusters with $x \leq 11$ favor monomer evaporation, while for larger clusters, the fission type fragmentation is more favorable. For Sn_{12}^+, the monomer loss process was more favored in calculation than the fission to Sn_6^+ and Sn_6. However, the fragmentation energy difference between the two processes was as small as 0.2∼0.3 eV. This is consistent with the experimental result that Sn_{12}^+ are at the border between the two types of decay.

It should be noted that the present calculation using B3PW91 functionals predict that the charge should be on the heavier fragment in the monomer loss processes, which is consistent with the experiment as shown in Table 1. However, in GGA, charge was predicted to be on monomers, and it is only for the heavier parent ions that GGA results were in agreement with experiment. This is due to a better prediction of the IPs calculated by using B3PW91 functional [17].

5 Summary

Fragmentation profiles in the low-energy collisions of Ge_x^+ and Sn_x^+ with a Si surface have been investigated. The favored fragmentation paths for both cluster ions ($x = 12\sim20$) were similar to those for Si cluster ions in the CID studies [24]. The result supports the structural similarities among Si, Ge, and Sn clusters in this size range.

The low-energy SID patterns of Sn_x^+ were in excellent agreement with the fragmentation patterns predicted using B3PW91 hybrid functionals,while GGA failed to reproduce the experimental results in the smaller size range. This is probably because electron correlation is more important for smaller size range and metallic nature of bonding emerges for clusters with larger sizes [17].

Table 1. Comparison of favored fragmentation channels obtained from the calculation and the experiment.

x	Calculation	Experiment
3	(2, 1)	-
4	(3, 1)	(3, 1)
5	(4, 1)	(3, 1), (3, 2)
6	(5, 1)	(5, 1)
7	(6, 1)	(6, 1)
8	(7, 1)	(7, 1)
9	(8, 1)	(8, 1) (7, 2)
10	(9, 1)	(9, 1) (8, 2) (7, 3)
11	(10, 1)	(10, 1) (7, 4) (6, 5)
12	(11, 1) (7, 5) (6, 6)	(6, 6)
13	(7, 6) (6, 7)	(7, 6) (6, 7)
14	(7, 7)	(7, 7)
15	(8, 7) (9, 6)	(8, 7) (9, 6) (7, 8)
16	(9, 7) (10, 6)	(9, 7) (10, 6)
17	(10, 7)	(10, 7)
18	(11, 7) (8, 10)	(11, 7)
19	(10, 9)	(9, 10) (10, 9)
20	(10, 10)	(10, 10)

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