Structural Transitions in Size-Selected Germanium Cluster Ions

J. M. Hunter, J. L. Fye, and M. F. Jarrold
Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

J. E. Bower
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 19 May 1994)

Injected ion drift tube techniques have been used to probe the geometries of germanium cluster ions. Clusters with ~(10–40) atoms appear to follow a one-dimensional growth sequence to give prolate geometries. At ~40 atoms the clusters stop following this growth sequence, and clusters with ~(40–70) atoms appear to retain roughly the same aspect ratio. At ~70 atoms the clusters abruptly reconstruct to a more spherical geometry. Dissociation energies, measured for the germanium clusters, suggest that clusters with $n < 70$ can be thought of as loosely bound assemblies of small strongly bound fragments (such as Ge_7 and Ge_{10}). It appears that the structural transition at ~70 atoms may reflect a change to a more bulklike bonding arrangement.

PACS numbers: 61.50.Lt, 36.40.+d

How the properties of semiconductors are modified as dimensions approach interatomic distances is currently a topic of great scientific interest and technological importance [1]. Nanocrystalline materials, with dimensions >10 nm, can be viewed as small pieces of the bulk material. But as dimensions shrink to approach interatomic distances (<1 nm), little is known about what happens to the geometric structure. Recent studies have shown that small silicon clusters follow a one-dimensional growth sequence up to ~27 atoms at which point they reconstruct to a more spherical geometry [2]. The structure and the bonding of bulk germanium are very similar to that of bulk silicon, and the bulk surfaces show similar (but not identical) reconstructions [3]. Thus germanium clusters might be expected to adopt the same geometries as silicon clusters. However, the results presented here reveal an unforeseen variety in the geometries adopted by germanium clusters. Small silicon and germanium clusters appear to have similar geometries, but the larger ones are fundamentally different.

The germanium cluster ions were generated by pulsed laser vaporization, size selected with a quadrupole mass spectrometer, and then injected at various energies into a drift tube containing helium (or neon). Mobilities were measured by injecting a short pulse of clusters into the drift tube and recording their arrival time distribution at the detector. Clusters with compact geometries have large mobilities and travel across the drift tube more rapidly than those with less compact geometries [4]. Figure 1 shows a plot of the relative mobilities of germanium clusters containing 7–54 atoms. The relative mobilities were obtained by dividing the measured mobilities by the mobility of a sphere with the density of bulk germanium. This procedure removes the systematic variations in the mobilities due to the change in the number of atoms in the cluster. The results shown in the figure are an average of at least two independent measurements which generally agree to within 1%. Starting at around Ge_{10}^+, the mobilities systematically decrease with increasing cluster size. The line in Fig. 1 shows the mobilities predicted if clusters with more than 10 atoms follow a one-dimensional growth sequence to give prolate or elongated geometries [2]. Here the clusters are represented by cylinders of variable length l and fixed diameter d_c. We assume $d_c = l$ for $n = 10$, thus the aspect ratios (l/d_c) predicted by this simple model are, for example, two for a 20 atom cluster and four for 40 atom cluster. The mobilities of germanium clusters containing up to ~35 atoms closely follow the predictions of this model. For clusters with more than 35 atoms the mobilities start to systematically diverge from the line, indicating that the clusters are no longer following a one-dimensional growth sequence. Assuming that the geometries remain relatively compact [5], a two-dimensional growth sequence to give oblate geometries is a plausible alternative to the one-dimensional model considered above. However, the mobilities for a two-dimensional growth model decrease

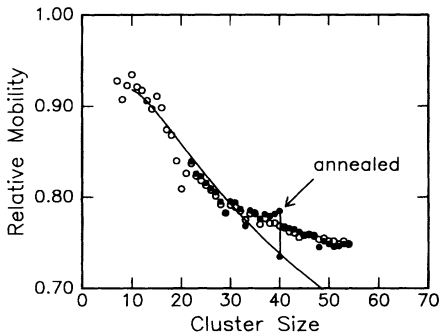

FIG. 1. Plot of the relative mobilities of Ge_n^+. The open points are for unannealed clusters (50 eV injection energy) and the filled points are for annealed clusters (200 eV injection energy). The line shows the prediction of a one-dimensional growth model (see text).

0031-9007/94/73(15)/2063(4)$06.00

much less rapidly than for the one-dimensional growth model [2], and they are not in agreement with the measured mobilities for clusters with 10–40 atoms.

A pulsed laser vaporization source provides a nonequilibrium environment for cluster growth and may not generate the lowest energy structural isomer [6]. The clusters can be annealed by increasing the injection energy so that they undergo a rapid transient heating cycle as they enter the drift tube [7]. The relative mobilities of annealed germanium clusters are shown in Fig. 1 along with the data for the unannealed clusters [8]. Annealing causes a detectable geometry change for only one cluster: Ge_{40}^{+}. As can be seen from Fig. 2, when Ge_{40}^{+} is annealed a second isomer emerges with a lower mobility than the isomer coming directly from the source. After annealing the relative abundances of these two isomers are comparable, which suggests that they have similar stabilities. Note that the relative mobility of the Ge_{40}^{+} isomer that appears after annealing falls on the line for one-dimensional growth, indicating that this highly elongated geometry is relatively stable for Ge_{40}^{+}, while slightly smaller clusters have departed from the one-dimensional growth sequence.

Because of the limited mass range of quadrupole mass spectrometers, Ge_{54}^{+} is the largest singly charged germanium cluster that we are able to examine. However, measuring the mobilities of doubly charged Ge_n^{++} provides a way to study clusters with more than 54 atoms (the Ge_n^{++} were generated by injecting a 2 kV electron beam into the buffer gas flow ~1 cm from where the clusters exit the source). The relative mobilities [9] of even numbered Ge_n^{++} with $n = 44$–86 are plotted in Fig. 3, along with the results for the singly charged clusters. The solid line in Fig. 3 shows the prediction of the one-dimensional growth model, and the dashed lines show aspect ratios for prolate geometries (with variable d_c). In the region of overlap, from $n = 44$ to 54, Ge_n^{+} and Ge_n^{++} have nearly

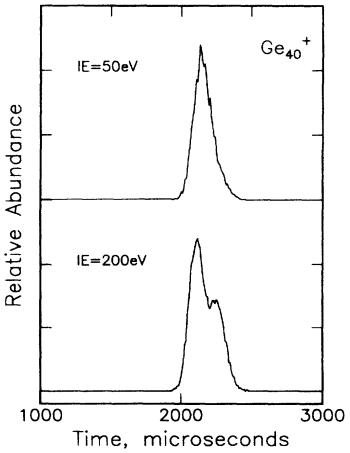

FIG. 2. Drift time distributions recorded for Ge_{40}^{+} with injection energies of 50 and 200 eV. At the higher injection energy the clusters are annealed and a second isomer appears at longer times in the drift time distribution.

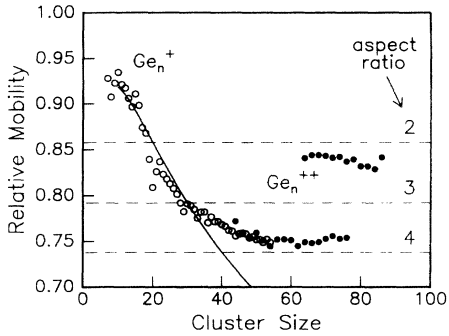

FIG. 3. The relative mobilities of Ge_n^{+} (open circles), and Ge_n^{++} (filled circles) plotted against cluster size. The points are the experimental data and the line is the predictions of a one-dimensional growth model (see text). The dashed lines give the aspect ratios assuming that the clusters remain prolate.

identical relative mobilities. As can be seen from Fig. 3, the relative mobilities of germanium clusters with more than around 45 atoms have stopped decreasing and have leveled off at a value of around 0.75. This corresponds to an aspect ratio of ~4 (assuming the clusters remain prolate). Clusters with ~40–70 atoms appear to retain an approximately constant aspect ratio. But then for clusters with ~70 atoms an abrupt structural transition occurs. A new isomer, with a larger relative mobility, first appears in the drift time distribution for Ge_{64}^{++}. The two isomers coexist up to Ge_{76}^{++}, and then for larger clusters only the isomer with the larger relative mobility remains. Note that this reconstruction does not take the clusters all the way to a spherical geometry. The new isomer has an aspect ratio of ~2 (assuming a prolate geometry).

Similar studies for silicon clusters have suggested that small silicon clusters also follow a one-dimensional growth sequence to give elongated geometries [2]. However, silicon clusters with around 27 atoms reconstruct to give nearly spherical geometries. The origin of this structural transition and the structural characteristics of the different types of silicon cluster geometries have been the subject of several recent theoretical studies [10,11]. The structural transition that occurs for silicon clusters with around 27 atoms appears to result from a change in the structure from geometries with the atoms arranged on a single shell to geometries with internal atoms, where the atoms are arranged in two shells. The absence of a similar structural transition for germanium clusters in the same size regime may result from the lower surface energy of germanium [12].

Further insight into the nature of the different geometries observed for germanium clusters can be obtained from studies of their dissociation. At high injection energies the cluster ions can be heated to the point where they fragment as they enter the drift tube. The larger germanium clusters fragment predominantly by sequential loss of Ge_{10} units (and in a few cases Ge_7) [13,14]. Results presented below will show that these are particularly stable clusters. Estimates of the dissociation energies can be obtained from

detailed analysis of the injection energy thresholds for dissociation using a modified impulsive collision model to estimate the degree of collisional excitation that occurs as the clusters enter the drift tube and a statistical model to describe the subsequent fragmentation of the heated clusters [15]. This approach does not provide a rigorous measurement of the dissociation energies because of uncertainties in the model used to estimate the degree of collisional excitation. However, measurements with different buffer gases (helium and neon) yield nearly identical dissociation energies, and dissociation energies determined for the smaller clusters are in reasonable agreement with previous measurements [16]. The dissociation energies determined for the germanium clusters are shown in Fig. 4. The cohesive energy of bulk germanium is 3.85 eV/atom, and the dissociation energies of clusters with up to ~10 atoms are comparable to the bulk cohesive energy. For clusters with more than 11 atoms, the dissociation energies drop precipitously and remain at ~1.2 eV. Note that this behavior is entirely different from the behavior of large silicon clusters where the dissociation energies smoothly approach the bulk cohesive energy [15]. In view of the large dissociation energies of the small germanium clusters ($n < 12$) and the small dissociation energies of the larger clusters, it is reasonable to consider the larger germanium clusters as weakly bound aggregates of small stable germanium clusters such as Ge_7 and Ge_{10}. This aggregate exists because the small germanium clusters are not bulk fragments. The large number of dangling bonds associated with small bulk fragments drives a reconstruction to more highly coordinated geometries as predicted [17] and recently observed [18] for small silicon clusters. The reconstruction of the small germanium fragments is so successful (they are so stable) that formation of roughly spherical close-packed geometries for larger clusters is energetically unfavorable.

Figure 5 shows a plot of the cohesive energies deduced from the dissociation energies. The cohesive energies rise sharply up to Ge_{10} and then abruptly level off. The dashed line is a fit based on the premise that the larger clusters consist of a loosely bound assembly of small stable clusters [19]. The solid line gives the cohesive energies expected for spherical clusters with bulk properties:

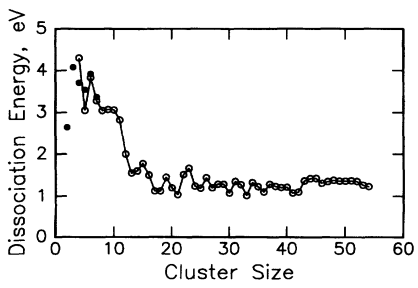

FIG. 4. Dissociation energies for Ge_n^+. The results of previous measurements [16] of the dissociation energies of small Ge_n clusters (●) are shown for comparison.

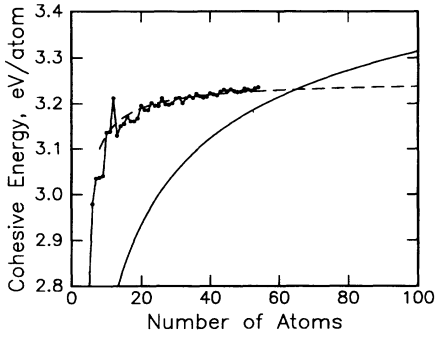

FIG. 5. Cohesive energies (in eV/atom) plotted against cluster size. The points are the experimental results. The dashed line is a fit to the data based on the premise that the larger clusters ($n > 11$) consist of a loosely bound assembly of smaller strongly bound clusters such as Ge_7 and Ge_{10}. The solid line gives the cohesive energies expected for spherical clusters with bulk properties (see text).

$$E_{\mathrm{coh}}(n) = E_{\mathrm{coh}}(\infty) - \left[\frac{27\pi V_a^2\gamma^3}{n}\right]^{1/3}, \qquad (1)$$

where $E_{\mathrm{coh}}(\infty)$ is the bulk cohesive energy/atom, V_a is the bulk atomic volume, and γ is the bulk surface energy. The measured cohesive energies for a variety of metal clusters have been found to rapidly approach the prediction of this model [20]. For small germanium clusters the cohesive energies predicted for the loosely bound assembly are larger than the cohesive energies given by the bulk sphere model. However, with increasing cluster size the cohesive energies predicted by the bulk sphere model increase more rapidly and eventually exceed those expected for the loosely bound assembly. At this point it becomes energetically favorable to rearrange the loosely bound assembly to a bulk sphere. The crossover appears to occur at around 65 atoms. This is approximately the size regime where an abrupt structural transition is observed in the mobility measurements. Thus these results suggest that the structural transition observed at around 70 atoms may result in a fundamental change in the nature of the cluster from a loose assembly of smaller fragments to a more compact (bulklike) bonding arrangement. The dissociation energies should increase at this point, but we are not able to perform measurements for clusters larger than Ge_{54}^+ because of instrumental limitations. Measurements of the dissociation energies of Ge_n^{++} could not be performed because of their low abundances. The models employed above are relatively simple, and so the good agreement between the location of the predicted structural transition in Fig. 5 and the structural transition in the mobilities could be fortuitous. The location of the transition in Fig. 5 is very sensitive to the surface energy. A value of 1.03 $\mathrm{J\,m^{-2}}$ (taken from the work of Miedema [10]) was employed here. There is little information available on the surface energies of bulk germanium surfaces, and how the surface energy of a

germanium cluster is related to the surface energy of the bulk surfaces is not known.

The results presented above suggest that germanium clusters with up to ~70 atoms can be viewed as weakly bound assemblies of small stable fragments such as Ge_7 and Ge_{10}. Clusters with up to ~40 atoms probably consist of a stack of these fragments. At ~40 atoms where the mobilities stop decreasing, the stack presumably stops growing longer, and clusters with up to ~70 atoms appear to retain approximately the same aspect ratio. For one cluster in the transition region (Ge_{40}^+), a highly elongated isomer and a slightly more compact isomer appear to have similar energies. The elongated isomer for Ge_{40}^+ probably consists of a stack of four Ge_{10} units, and the high stability of the Ge_{10} unit presumably accounts for the existence of this isomer. A loose assembly of small stable fragments naturally leads to prolate geometries for smaller clusters (up to ~20 atoms). But the persistence of the one-dimensional growth sequence to larger cluster sizes indicates a definite preference for forming elongated geometries. This preference could arise from the optimum binding sites being on opposite sides of the small fragments (as for example in the capped trigonal prism which has been proposed as a building block for small silicon clusters [2]). The reason for the departure from the one-dimensional growth sequence at ~35 atoms is not entirely clear. The surface energy of the elongated geometries may play a role in destabilizing them relative to slightly more compact arrangements. While geometries consisting of weakly bound assemblies of small strongly bound germanium fragments appear to be the lowest energy geometry for these clusters, this cannot persist indefinitely: as the cluster size increases, reconstruction to a more compact (bulklike) bonding arrangement eventually becomes energetically favorable. This structural transition appears to occur at around 70 atoms. The geometries found here for the larger germanium clusters are fundamentally different from those found for silicon clusters. The origin of this remarkable difference is not clear at this time, and detailed theoretical studies appear necessary to resolve this issue.

We gratefully acknowledge partial support of this work by the National Science Foundation (CHE-9306900).

[1] See, for example, L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990); J. R. Heath, Science **258**, 1131 (1991); W. L. Wilson, P. F. Szajowski, and L. E. Brus, Science **262**, 1242 (1993); L. E. Brus, J. Phys. Chem. **98**, 3575 (1994).

[2] M. F. Jarrold and V. A. Constant, Phys. Rev. Lett. **67**, 2994 (1992).

[3] See, for example, J. P. LaFemina, Surf. Sci. Rep. **16**, 133 (1992).

[4] D. F. Hagen, Anal. Chem. **51**, 870 (1979); G. von Helden *et al.*, J. Chem. Phys. **95**, 3615 (1991).

[5] Theoretical studies show that compact three-dimensional geometries emerge for small germanium clusters. See, for example, G. Pacchioni and J. Koutecky, J. Chem. Phys. **84**, 3301 (1986).

[6] S. Maruyama, L. R. Anderson, and R. E. Smalley, J. Chem. Phys. **93**, 5349 (1990).

[7] M. F. Jarrold and E. C. Honea, J. Am. Chem. Soc. **114**, 459 (1992).

[8] The relative mobilities of the annealed clusters shown in Fig. 1 have been reduced by 2% to account for penetration of the injected clusters into the drift tube.

[9] The relative mobilities of the doubly charged clusters shown in Fig. 3 have been divided by 2 to remove the effect of the additional charge.

[10] E. Kaxiras and K. Jackson, Phys. Rev. Lett. **71**, 727 (1993).

[11] U. Rothlisberger, W. Andreoni, and M. Parrinello, Phys. Rev. Lett. **72**, 665 (1994).

[12] A. R. Miedema, Z. Metallkde **69**, 287 (1978).

[13] Germanium clusters with 4–9 atoms dissociate by loss of a neutral atom. The dominant fragments observed for Ge_{10}^+–Ge_{18}^+ are $6^+ + 4$, $7^+ + 4$, $6^+ + 6$, $6^+ + 7$ and $7^+ + 6$, $7^+ + 7$, $8^+ + 7$, $10^+ + 6$, $10^+ + 7$, and $11^+ + 7$, respectively. With a few exceptions the larger clusters dissociate by losing a neutral Ge_{10} species. The exceptions are Ge_{22}^+, Ge_{23}^+, Ge_{27}^+, and Ge_{38}^+, and the products are $15^+ + 7$, $16^+ + 7$, $20^+ + 7$, and $31^+ + 7$, respectively.

[14] Q.-L. Zhang *et al.*, J. Chem. Phys. **88**, 1670 (1988).

[15] M. F. Jarrold and E. C. Honea, J. Phys. Chem. **95**, 9181 (1991).

[16] A. Kant and B. H. Strauss, J. Chem. Phys. **45**, 822 (1966); J. E. Kincade, U. V. Choudary, and K. A. Gingerich, Inorg. Chem. **11**, 3094 (1979).

[17] K. Raghavachari, Phase Transitions **24–26**, 61 (1990); P. Ballone *et al.*, Phys. Rev. Lett. **60**, 271 (1988); D. Tomanek and M. Schluter, Phys. Rev. B **36**, 1208 (1987).

[18] E. C. Honea *et al.*, Nature (London) **366**, 42 (1993).

[19] The cohesive energy (per atom) of a loose assembly of Ge_{10} units is given by

$$E_{\mathrm{coh}}(n) = 3.13 + \frac{1.2}{n}\left(\frac{n-10}{10}\right),$$

where the cohesive energy of Ge_{10} is 3.13 eV and 1.2 eV is the binding energy of the Ge_{10} fragments.

[20] U. Ray *et al.*, J. Chem. Phys. **91**, 2912 (1989); C.-X. Su, D. A. Hales, and P. B. Armentrout, J. Chem. Phys. **99**, 6613 (1993); P. B. Armentrout, D. A. Hales, and L. Lian, in "Advances in Metal and Semiconductor Clusters," edited by M. A. Duncan (JAI, Greenwich, CT, to be published), Vol. II.