PHOTOFRAGMENTATION OF SEMICONDUCTOR POSITIVE CLUSTER IONS

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ABSTRACT

Si, Ge, and GaAs positive cluster ions containing up to sixty atoms have been prepared by laser vaporization and supersonic beam expansion and their laser photofragmentation studied using tandem time-of-flight mass spectrometry. The fragmentation pattern observed for GaAs is very similar to that observed for metal clusters and is consistent with the sequential loss of atoms. Si and Ge clusters appear to fragment by a fission process, Si_n^+ fragments primarily into positive ions in the 6-11 size range with a subsidiary channel corresponding to loss of a single atom. Ge_n^+ also gives clusters in the 6-11 size range at relatively high fluence and has a channel corresponding to loss of a single atom at low fluence. At intermediate fluences, channels corresponding to sequential loss of Ge_{10} and Ge_7 are observed.

INTRODUCTION

Semiconductors are generally covalent solids with sp^3 hybridization having the diamond structure. However, the electronic and geometric structures of semiconductor clusters are expected to be quite different from the bulk because of extensive surface restructuring. The aim of this work is to investigate the properties of semiconductor clusters with the hope of gaining insight into the chemical forces driving surface restructuring.

EXPERIMENTAL

The apparatus has been described elsewhere[1,2]. Briefly, laser vaporization of semiconductor material from a rotating disc takes place in the center of a helium carrier gas pulse. The hot plasma is entrained into a flow tube where clustering and thermalization takes place, and is then cooled to a few K by supersonic expansion into a vacuum. The supersonic jet is skimmed into a molecular beam containing neutral and ionic clusters. Positive clusters are extracted into a field-free flight tube, mass resolved by time-of-flight, and detected by an in-line detector at the end of the tube. In these studies, the maximum cluster size produced was n=80 for Si_n^+, n=50 for Ge_n^+, and x+y=40 for $Ga_xAs_y^+$. Clusters can be mass selected by a timed gate, and fragmented by a probe laser. After interaction with the probe laser, the fragmentation products are accelerated into a perpendicular flight tube, mass-analyzed by time-of-flight, and detected by two microchannel plates.

RESULTS AND DISCUSSION

The mass distributions of the Si, Ge, and GaAs positive cluster ions are smooth for n>20 with no indication of magic numbers. For the discrete near-UV probe laser wavelengths (third and fourth harmonic of the Nd:YAG and ArF and KrF excimer lines) used in these studies there is no qualitative dependence on probe laser wavelength, but the fragmentation patterns do depend strongly upon laser fluence.

Fig. 1 shows a typical fragmentation pattern of a GaAs cluster ion. This pattern strongly resembles those found for the fragmentation of metal cluster ions[3]. It suggests the sequential loss of atoms. However, there is a clear even/odd intensity alternation in the product distribution with the odd fragments being more intense than their even neighbors. A similar intensity alternation has been observed[4] for the fragmentation of GaAs negative cluster ions. These observations suggest that the cluster ions containing an even number of electrons contain no dangling bonds.

The fragmentation patterns of Si and Ge positive cluster ions are very different from GaAs or metal clusters and appear to be dominated by fission processes. Thus for Si_n^+ and Ge_n^+ with n=12 to 29 the observed daughter ions are about half the original size. Similar behavior has been observed[4] for the corresponding negative ions and the patterns are roughly the same for the ions of the same size in the two charge states with a few exceptions. Si_n^+ with n>30 fragment either by loss a single atom or by "explosion" into ions in the 6-11 size range. Intermediate products are not observed. We believe that Si_6^+ - Si_{11}^+ are the largest fragments as the ionization potential is expected to decrease with increasing size and therefore the charge should settle on the largest fragment as particles separate. On the other hand, this fragmentation pattern is observed for Ge_n^+ with n 30-50 only at higher laser fluences. At low fluences Ge_n^+ appears to lose Ge_{10}, and sometimes Ge_7, in a stepwise manner as shown in Fig. 2.

It appears unlikely that these clusters are loosely bound aggregates as the fragmentation of Si_{60}^+ to Si_{10}^+ is at least quadratic in ArF fluence as shown in Fig. 3 indicating that this fragmentation is a two-photon process. Thus the loss of Ge_{10} and Ge_7 seems to indicate that these neutral clusters are exceptionally stable or there is a natural cleavage process giving rise to these fragments.

ACKNOWLEDGMENT

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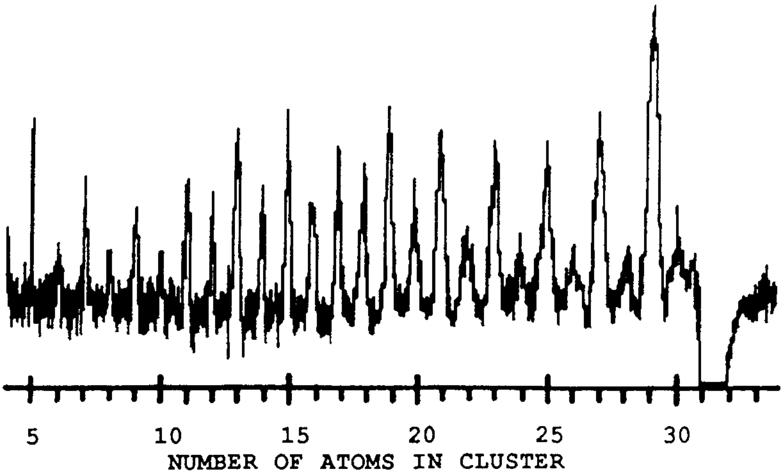

Fig. 1. Fragmentation of GaxAsy+ with x+y=31 with 27 mJ/cm^2 355 nm laser. The results were obtained by subtracting two data sets: one with laser on, and the other with laser off.

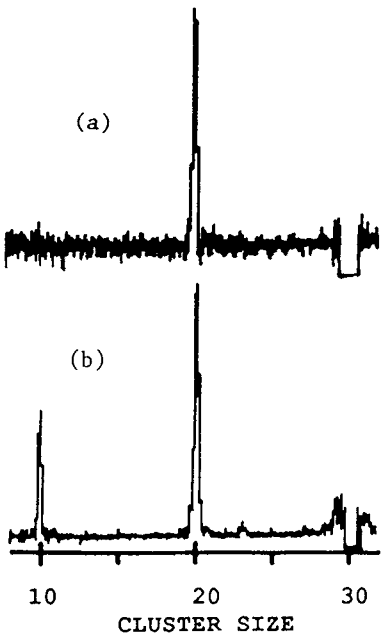

Fig. 2. Fragmentation of Ge_{30}^+ with (a): 1 mJ, and (b): 5 mJ 532 nm laser.

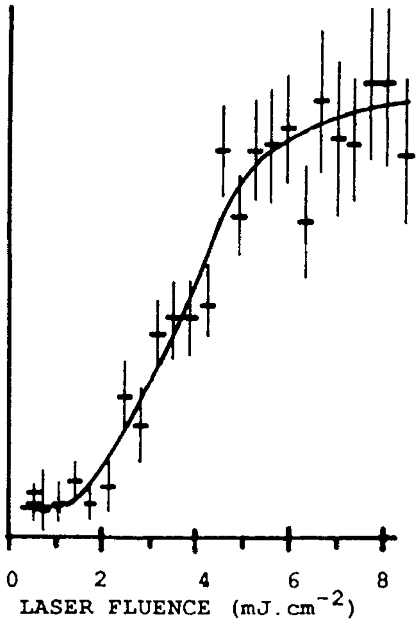

Fig. 3. Fluence dependence of Si_{10}^+ signal intensities produced from Si_{60}^+ with 193 nm laser.