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KINETIC ENERGY AND MASS ANALYSIS OF COVALENT GROUP IV CLUSTER IONS IN PULSED-LASER STIMULATED FIELD EVAPORATION

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Abstract - Multiply charged cluster ions of silicon and carbon can be formed in pulsed-laser stimulated field evaporation. In general, the signal intensity decreases monotonically with the cluster size. However, a few cluster ion species stand out; these are species of greater stability. For Si, they are $\text{Si}_4^{2+}$ and $\text{Si}_6^{2+}$, and for C they are $\text{C}_3^+$ and $\text{C}_5^+$. While Si field evaporates mostly as $2^+$ cluster ions, C field evaporates mostly as $1^+$ cluster ions. There is, however, a small fraction of $2^+$ and $3^+$ C-cluster ions. For $3^+$ C-cluster ions, the intensity is smaller for smaller cluster ion species, indicating the occurrence of Coulomb repulsive dissociation. The different stabilities observed for Si and C clusters are in good agreement with theoretical calculations.

I. INTRODUCTION

In low temperature field evaporation, ions formed are almost always atomic ions. A very small fraction of cluster ions has been occasionally observed in the atom-probe, especially in field evaporation of compound semiconductors, but the number is too small to make a good scientific study of their formation. Only with the advent of the pulsed laser atom-probe that a significant fraction of cluster ions can be formed.

Properties of atomic clusters and cluster ions are subjects of considerable scientific and technological interest. It is realized that powder and particles are one of the most common forms of raw materials from which it is relatively easy to manufacture end products with good uniformity. Small particles are also known to be chemically and catalytically much more active. From scientific point of view, small atomic clusters represents another form of matter which is intermediate between condensed states and atomic and molecular states. There are many subjects of interest, these include the magic numbers, the critical numbers, the ionization energies, the binding energy of atom in clusters, the structure and electronic levels of clusters and chemical properties etc. Recently, there have been many experimental and theoretical investigations of properties of covalent bond clusters. In particular, detailed calculations show that for Si, the most stable clusters with regard to fragmentation reaction, $\text{Si}_n \rightarrow \text{Si}_{(n-1)} + \text{Si}$, are $\text{Si}_4$, $\text{Si}_6$ and $\text{Si}_{12}$. On the other hand, even though C is a covalent bond material of the same valency, the more stable clusters are the odd-numbered clusters such as 3 and 5-atom clusters. We are able to observe these differences in pulsed-laser stimulated field desorption, thus providing a valuable confirmation of the validity of these cluster calculations.

II. EXPERIMENTAL RESULT AND DISCUSSIONS

II.1 Sizes and Charge States of Cluster Ions

Mass spectra and ion energy distributions are obtained with a pulsed-laser time-of-
flight atom-probe which has now being improved with the installation of electronic timers of 156 ps time resolution and a high voltage power supply of 2 parts in 10^6 per hour stability. The flight path has also been lengthened to ~778 cm. This system has been accurately calibrated with the onset flight times of pulsed-laser field desorbed inert gas ions, and it is now capable of achieving a precision and accuracy of one part in 100,000 in both ion mass and kinetic energy analyses.

Silicon and carbon cluster ions of up to about 10 atom size can be formed by pulsed-laser stimulated field desorption of silicon and graphite tips. These tips can be prepared from electrochemical etching of silicon whiskers and graphite rods. In pulsed-laser stimulated field evaporation, if the laser power is big enough, then atoms can be continuously supplied from the tip shank by a temperature and field gradient induced surface diffusion and the pulsed-laser stimulated field evaporation can be maintained almost indefinitely without changing the tip voltage. Thus a spectrum containing a few ten-thousand ions can be obtained. In Fig. 1 and Fig. 2, portions of spectra containing cluster ions are shown for both Si and C. Their relative intensities are listed in Table I according to the charge states of the ions. Using a multinomial expansion coefficient analysis of the isotope-mixed mass lines, it is concluded that Si_{2+} mass lines contain few 1+ Si-cluster ions, and those C_{n+} mass lines contain few 2+ C-cluster ions.

A few interesting features of the mass spectra are summarized below:

1). In pulsed-laser stimulated field desorption, in general, the intensities of cluster ions decrease monotonically with the cluster sizes. However, there are some cluster ion species standing out. These are ions species with a greater stability, as reflected both in the desorption process, and in resisting fragmentation. For Si, in
general, even-numbered cluster ion species more abundant, and the most abundant cluster ion species are \( \text{Si}_6^{2+} \) and \( \text{Si}_8^{2+} \). In contrast, for C, the odd-numbered cluster ion species are more abundant, with \( \text{C}_3^+ \) and \( \text{C}_5^+ \) showing greatest relative intensities. This result is in good agreement with the theoretical result of Raghavachari,\textsuperscript{5} which is reproduced in Fig. 3. In this figure, the solid line represents the fragmentation energy in the dissociation reaction \( \text{C}_n^+ \rightarrow \text{C}_{n-1}^+ + \text{C} \) as a function of \( n \), and the dashed line represents the fragmentation energy in the reaction \( \text{Si}_n^+ \rightarrow \text{Si}_{n-1}^+ + \text{Si} \) as a function of \( n \).

**TABLE I. RELATIVE ABUNDANCE**

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>( + )</td>
<td>( 2+ )</td>
</tr>
<tr>
<td>( \text{C}_3(1.00) )</td>
<td>( \text{C}_3(0.18) )</td>
</tr>
<tr>
<td>( \text{C}_2(0.33) )</td>
<td>( \text{C}_5(0.09) )</td>
</tr>
<tr>
<td>( \text{C}_5(0.25) )</td>
<td>( \text{C}_7(0.05) )</td>
</tr>
<tr>
<td>( \text{C}_6(0.18) )</td>
<td>( \text{C}_11(&lt;0.01) )</td>
</tr>
<tr>
<td>( \text{C}_7(0.03) )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}_6(0.03) )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}_9(0.01) )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}_8(&lt;0.01) )</td>
<td></td>
</tr>
</tbody>
</table>
2). No 3+ cluster ions are found for Si, but 3+ cluster ions of up to 10-atoms are found for C. The cluster-size dependence of the intensities of 3+ C-cluster ions is reversed from those of the other charge states. 10-atom cluster is found to be most abundant, followed by 7-atom cluster and then 5-atom cluster. This reversed behavior of the size dependence clearly indicates the occurrence of Coulomb repulsive dissociation, or known as Coulomb explosion, of small 3+ C-cluster ions. We find C$_{10}^{3+}$ is the most stable 3+ C-cluster ions, again, in good agreement with the calculations.

3). For Si, most cluster ion species formed are doubly charged, whereas for C, the most abundant charge state is the singly charged state.

4). Cluster sizes are much smaller in pulsed-laser stimulated field evaporation than those found in other techniques. In field evaporation, cluster ions are formed directly in the field evaporation process, whereas in other techniques, most of the clusters are formed by further condensation of atoms and small clusters into larger ones. It is found that in a nozzle expansion technique, there are two modes of cluster size distributions. The first mode is very similar to what we have observed. We therefore conclude that this mode is related directly to the desorption process, while the second mode is related to the condensation process.

5). In both cases, the smallest 2+ cluster ion species are Si$_2^{2+}$ and C$_3^{2+}$. Thus the critical number for both the doubly charged C and Si cluster ions is 3.

II.2 Photo-Excitation in Pulsed-Laser Stimulated Field Evaporation

It is found that ions formed in laser stimulated field evaporation by very intense laser light exhibit a high energy tail of up to a few hundred eV in excess energy. In Figs. 4 and 5, two examples are shown for carbon ions. $\tau_2$ indicates where the theoretical onset flight time, or the flight time of the most energetic ions and therefore the shortest flight time, should be if there were no photo-excitation in the field evaporation
process. With our system, this time can be predicted to better than ±1 ns. Thus we are able to establish the existence of a very large high energy tail in every one of these ion energy distributions. The excess energy of some of these ions exceeds 340 eV. This literally means that some of these ions are ejected out of the surface with an initial kinetic energy of up to ~340 eV by the intense laser irradiation of the surface.

For atomic ions, the high energy tail cannot come from dissociative reactions of cluster ions. This can be understood from the following example. Consider that a $C_n^{+}$ ion is formed right at the surface. After it is accelerated to an intermediate potential $V_{int}$ it is dissociated into a $C^{+}$ and a $C_{n-1}^{+}$. The final kinetic energy of the $C^{+}$ ion is $eV_0 - eV_{int}(1 - 2/n)$ where $V_0$ is the accelerating voltage. For $n>2$, this energy is smaller than $eV_0$. For $n=2$, it is $eV_0$. Thus $C^{+}$ ions in this and other dissociation reactions can only suffer from additional energy deficit. On the other hand, the final kinetic energy of $C_{n-1}^{+}$ is $eV_0 - eV_{int}(1 - 2(n-1)/n)$ which is greater than $eV_0$ if $n>2$, equal to $eV_0$ if $n=2$, and smaller than $eV_0$ if $n<2$. Thus these $C_{n-1}^{+}$ ions can appear in the high energy tail as well as the low energy tail of the $C_{n-1}^{+}$ mass line. Atomic ions in the high energy tail can come only from photon-exciations. We therefore rule out the possibility of a high energy tail of atomic ions by dissociation reactions of cluster ions. We must conclude that the high energy tail of atomic ions is either due to photo-exciations, or a heating effect. A heating effect cannot produce an ion of a few hundred eV excess energy. It must be due to a photo-excitation effect. With the photon energy of only 3.68 eV, direct core level excitation is highly unlikely since it will require a near 100-photon excitation. A more likely mechanism is that conduction band electrons are excited in cascade to energy levels up to a few hundreds eV above the Fermi level. When these electrons de-excite to the Fermi level, their energies are directly transferred to an evaporating ion, similar to an Auger process.

![Fig. 4](image1.png)

![Fig. 5](image2.png)
II.3 Dissociation Reactions

From the ion energy distributions, we can also find the dominant dissociation channels of cluster ions. Ions in the tail can only be produced way above the surface, or from some dissociation reactions. For both Si and C, the mass lines of the singly charged atomic-ions have the most prominent low energy tails. This shows clearly that most of the cluster ions dissociate by emitting either a neutral atom or a singly charged atomic ion. In our spectra the low energy tail of $\text{C}_2^+$ is not unusually large, thus fragmentation by emitting a $\text{C}_2$ cluster or ion cannot be an important dissociation channel in our case. Such a dissociation channel has been observed to be the most prominent one in photon-induced dissociation of large cluster ions. In our case, the dissociation occurs most probably by the Coulomb repulsive force existing in multiply charged cluster ions.

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References