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Dissociation of Si Clusters Produced by Bombardment of $6keV$ Xe Atoms

I. Arai, H. Sasaki, T. Shimayama and S.-M. Lee
Institute of Physics, University of Tsukuba, Ibaraki 305, Japan
Fax: 81-298-53-6618, e-mail: arai@tac.tsukuba.ac.jp

The dynamics of dissociation in small clusters is expected to give the crucial information on their structure, initial internal temperature and formation machanism. We have measured the dissociation ratios of Si clusters produced by the bombardment of $6keV$ Xe atoms as well as their dissociation patterns. After the bombardment, the clusters were extracted with the potential of $2kV$,$6kV$ or $10kV$ to the free flight region where their dissociations were observed. The monomer evaporation was dominated for the small-sized clusters up to 8 while the fission associated with trimer or tetramer emission was enhanced for the larger-sized clusters. We have calculated the unimolecular dissociation ratios from a modified RRK theory. Given the dissociation energies so far obtained experimentally, the ratios were well reproduced by the theory. As a result, the initial internal temperature was found to be $0.632 \pm 0.090eV$ in k_BT. The residence time of clusters drifting around the bombarded region before the extracttion was found to be $2.90 \pm 0.80 \times 10^{-5}$ s, $3.65 \pm 0.17 \times 10^{-6}$ s and $3.48 \pm 0.17 \times 10^{-6}$ s for the extraction voltages $2kV$, $6kV$ and $10kV$, respectively. The observed strong dependence on the extraction voltage suggests that the clusters are actually drifting in the gaseous circumstance around the bombarded region. This observation favours the model of cluster emission as a whole particle from the surface of bombarded material.
Key words: Cluster, Dissociation, Si, Sputtering

1. INTRODUCTION

The sputtering, i.e., the particle emission from the surface of bulk material bombarded by an energetic atomic particle, has long been studied. However, most of the published works on the sputtering have focused mainly on the measurement of the total sputtering yield while the study of the phenomenon such as cluster emission remains as one of the least understood field. Even the basic mechanism of the cluster formation has not been established yet[1].

In the earlier stage of study, the cluster formation in the sputtering was perceived as the emission of a whole particle from the bulk surface of bombarded material. Now, one believes on the statistical agglomeriation processes of individual sputtered atoms. With aid of the conventionally used statistical theory[2], the measurement of the dissociation of clusters leads us into the insight on both their internal temperature at the very early stage and their residence time around the bulk surface before the extraction [3]. In other words, the dynamics of dissociation of the clusters produced by the sputtering is expected to give the crucial information on the fundamental cluster formation process.

2. EXPERIMENT

In the present study, we have measured the dissociation ratios of Si clusters, which were produced by the bombardment of $6keV$ Xe atoms, as well as their dissociation patterns. After the bombardment, the

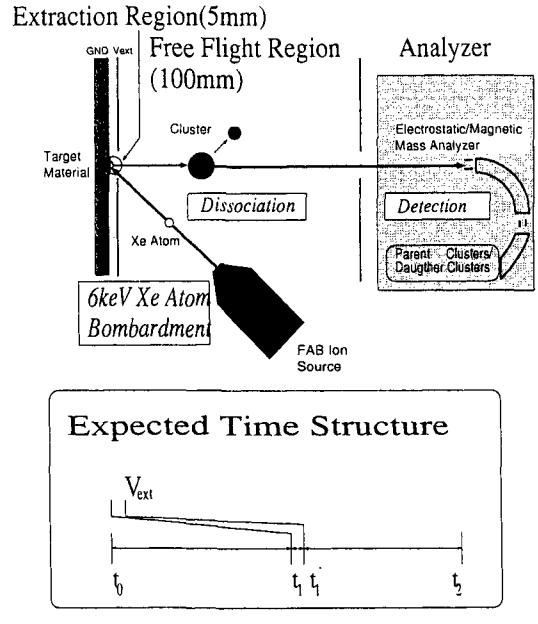

Figure 1. Experimental Setup.

clusters were extracted to the extraction gap of 5 mm length applied with the electrostatic potential of $2kV$, $6kV$ *or* 10 kV. The accelerated clusters were guided to the free flight region of 100 mm length where their dissociations were observed. Finally, both the parent clusters and the daughter clusters were iden-

tified by the electrostatic/magnetic mass analyzer(see Figure 1).

The electrostatic/magnetic mass analyzer was operated in 'link-scan' mode, in which the mass spectrum of clusters was measured under the condition of fixed velocity v_{ANA}. It should be noted that only parent clusters and daughter clusters can be observed in the same velocity , i.e.,

$$v_{ANA} = \sqrt{\frac{2eV_{ext}}{m_n}} \quad (1)$$

determined by the mass of parent cluster m_n and the extraction voltage V_{ext}.

Figure 2 shows a typical mass spectrum measured in 'normal' mode, i. e., non-biased mode. The Si clusters of the size up to 10 are clearly identified in it. Figure 3 shows a typical mass spectrum measured in 'link-scan' mode. As expected, only the parent(Si_8) and daughter(Si_7) clusters are observed in it.

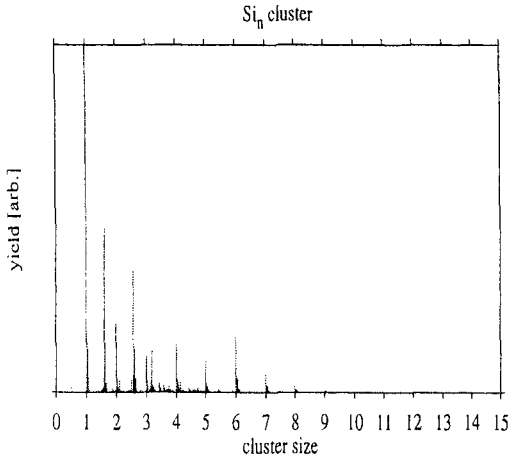

Figure 2. Mass Spectrum of Si Clusters Measured in Normal Mode.

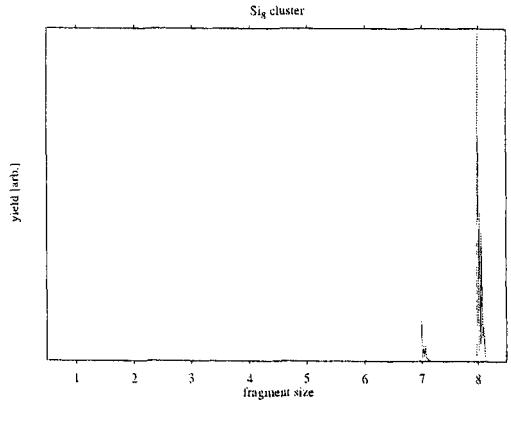

Figure 3. Mass Spectrum of Si Clusters Measured in Link-Scan Mode.

The decay ratio is defined as

$$R_{decay} = \frac{Number\ of\ Daughters}{Number\ of\ Parents} \quad (2)$$

We have measured the systematic data of R_{decay} for Si clusters with the size n from 3 up to 11. As a result, the characteristic dissociation patterns designated by the number of the emitted neutral fragments were observed. Furthermore, the decay ratios into the monomer evaporation, i.e., the decay associated with one neutral fragment, were examined at the various extraction voltage.

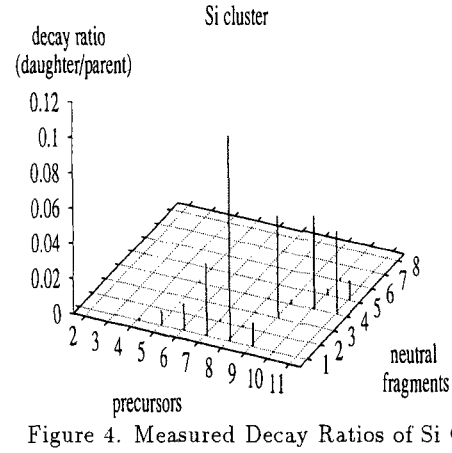

Figure 4. Measured Decay Ratios of Si Clusters.

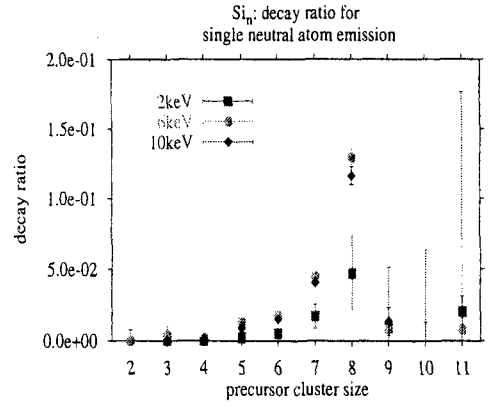

Figure 5. Measured Decay Ratios of Si Clusters into Monomer Evaporation.

Figure 4 shows the measured decay ratios of Si clusters into each pattern. It is observed that the monomer evaporation is dominated for the small-sized clusters up to 8 while the fission-like decay associated with trimer or tetramer emission is enhanced for the larger-sized clusters. Figure 5 shows the measured decay ratios of Si clusters into the monomer evaporation at the various extraction voltage. One can see their strong dependence on the extraction voltage.

3. STATISTICAL MODEL

For further understanding, we have analyzed the unimolecular dissociation ratios of the clusters with the size n from 5 to 8 with use of the statistical model, i.e., a modified RRK theory.

The RRK theory was originally developed by O.K.Rice, H.G.Ramsperger and L.S.Kassel[4,5,6]. Recently, it was modified and successfully applied to the photoninduced evaporation of charged clusters by P.C. Engelking[7]. C. Bréchignac et al. also successfully used the modified RRK theory to analyze the dynamics of unimolecular dissociation of sodium cluster ions[3].

In the modified RRK theory, the evaporation of Si_n^+ cluster anion is described as follows. At first, the Si_n^+ cluster anion is in its metastable state with the internal energy E^* and the dissociation energy D_n^+. The state is a quasiequilibrium state in which E^* is randomly distributed among $s = 3n-6$ internal modes. Then, the cluster is going to evaporate a monomer in the case of localizing enough internal energy($\geq D_n^+$) in single mode. The evaporation rate of Si_n^+ cluster is given as

$$k_n = \nu^3(s-1)8\pi\mu g S\frac{(E^*-D_n^+)^{s-2}}{(E^*)^{s-1}} \tag{3}$$

E^* : *Internal Energy*
D_n^+ : *DissociationEnergy*
ν : *Phonon Frequency*
μ : *Reduced Mass*
g : *Channel Degeneracy*
s : *Degree of Freedom*$(3n-6)$
S : *Cluster Cross Section*

In the present case, the decay ratio of Si_n^+ cluster anion is calculated under the following assumptions(refer also Figure 1);

(1)The dissociation energy D_n^+ so far obtained experimentally is given[8].

(2)The internal energy of the cluster follows a gaussian distribution of the temperature T_0 at the time $t_0 = 0$, i.e., the instant just after its formation.

(3)After some residence time t_1, the cluster arives at the extraction region.

(4)The cluster is accelerated during the time period $(t_1' - t_1)$ to the entrance of the free flight regionn.

(5)The cluster passes the free flight region during the time period $(t_2 - t_1')$.

(6)The parameters to be fixed are the initial internal temperature T_0 and the residence time t_1 before the extraction.

The probability to have the internal energy E^* at the time t_0 is given by

$$P_n^0(t_0, E^*) = N_0 \exp\left(\frac{-(E^* - sk_BT)^2}{2\sigma^2}\right) \tag{4}$$

$$\sigma = \frac{2k_BT}{3} \tag{5}$$

During the residence time t_1, the fast evaporative cooling occurs. The probability finding the Si_n^+ cluster anion with the internal energy E^* after the time t_1 is given by

$$P_n(t_1, E^*) = P_{n+1}^0(t_0, E^* + D_{n+1}^+) \times \int_0^{t_1}(1-\exp\{-k_{n+1}[E^*+D_{n+1}^+]t\}) \times \exp\{-k_n(E^*)(t_1-t)\}dt \tag{6}$$

Then, the slow sequential evaporation occurs during the extraction and the free flight. The probability to find the Si_n^+ cluster anion with the internal energy E^* at t_2 is given by

$$Q_n(t_2, E^*) = P_n(t_1', E^*)\exp\{-k_n(E^*)[t_2 - t_1']\} \tag{7}$$

Finally, the decay ratio R_{decay} is calculated as

$$R_{decay} = \frac{\int_0^\infty [P_n(t_1', E^*) - Q_n(t_2, E^*)]dE^*}{\int_0^\infty Q_n(t_2, E^*)dE^*} \tag{8}$$

4. RESULTS AND DISCUSSIONS

At first, the observed decay ratios are well reproduced by the modified RRK theory as shown in Figure 6, Figure 7 and Figure 8. Thus, it is found that such a statistical picture works well enough to describe the dissociation of Si clusters produced by the sputtering. Especially, it is used as a powerful tool to reduce more essential parameters under the physical process such as the initial internal temperature and the residence time before the extraction.

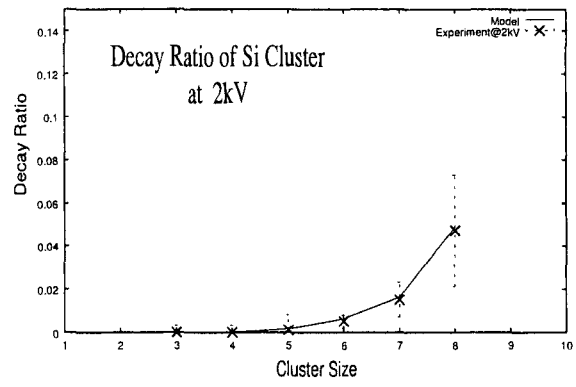

Figure 6. Calculation Based on modified RRK Theory: $V_{ext} = 2kV$.

Secondly, the initial internal temperature was found to be $0.632 \pm 0.090eV$ in k_BT. If we assume that the cluster was formed in quasiequilibrium, it should be also the freeze-out temperature of the cluster formation in the bombarded region and provide an essentially new information on the unknown dynamics of heat conductance around the bombarded region which leads to the sputtering of atoms and clusters after the bombardment of energetic atom. The temperature is more than twice larger than the boiling temperature of bulk material. However, because of the rather large dissociation energy of the Si_n^+ cluster anion, the considerable amount of them get rid of the dissociation

when passing the free flight region.

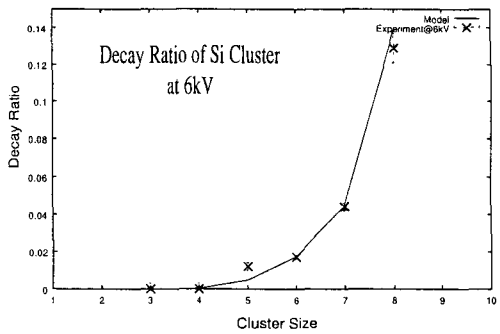

Figure 7. Calculation Based on modified RRK Theory: $V_{ext} = 6kV$.

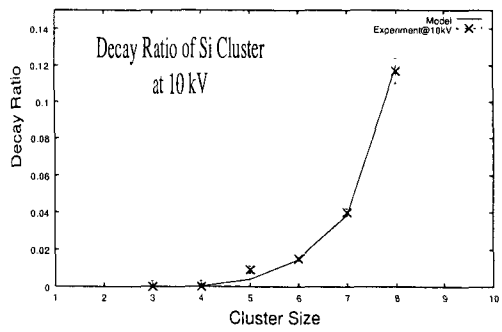

Figure 8. Calculation Based on modified RRK Theory: $V_{ext} = 10kV$.

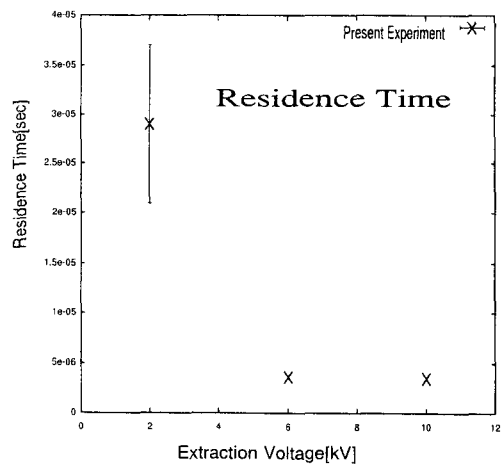

Figure 9. Extraction Voltage Dependence of Residence Time.

Thirdly, the residence time of clusters drifting around the bombarded region before the extracttion was found to be $2.90 \pm 0.80 \times 10^{-5}$ s, $3.65 \pm 0.17 \times 10^{-6}$ s and $3.48 \pm 0.17 \times 10^{-6}$ s for the extraction voltages $2kV$, $6kV$ and $10kV$, respectively. It seems that the residence time has no significant dependence on the cluster size n while it has a strong dependence on the extraction voltage as shown in Figure 9. This observation suggests that the preformed clusters actually drift in the gaseous circumstance around the sputtered region. Indeed, the drift time may be slightly dependent on the cluster size n, but the dependence is expected to be proportional to $n^{1/3}$ from the Stokes' law and negligibly small in comparison with the strong dependence on the extraction voltage which is expected to be proportional to V_{ext}^{-1}. Furthermore, if the cluster is formed throuh the statistical agglomeriation in such gaseous circumstance, there should be more apparent cluster size dependence because the cluster with the larger size is formed at the later time in the agglomeriation process. However, this is not the case. These considerations strongly suggest that the picture of cluster formation as the emission of a whole particle from the bulk surface of bombarded material is favoured in the present case.

5. SUMMARY

In summary, the dissociation of Si clusters produced by the bombardment of $6keV$ Xe atoms has been measured for the extraction voltage of $2kV$, $6kV$ and $10kV$ applied on the bombarded region. The systematic data of decay ratios have been obtained for the clusters with the size n from 3 up to 11 and the characteristic dissociation patterns, i.e., the monomer evaporation and the fission-like trimer/tetramer emission, have been observed. As for the monomer evaporation, the dissociation ratios appear to be strongly dependent on the extraction voltage. To understand further, we have calculated the dissociation ratios from a modified RRK theory. Given the dissociation energies so far obtained experimentally and assuming an initial internal temperature and a residence time of the clusters drifting around the bombarded region before the extraction as adjustable parameters, the dissociation ratios have been reproduced well by the theory. The initial internal temperature was found to be $0.632 \pm 0.090eV$ in k_BT while the residence time was found to be $2.90 \pm 0.80 \times 10^{-5}$ s, $3.65 \pm 0.17 \times 10^{-6}$ s and $3.48 \pm 0.17 \times 10^{-6}$ s for the extraction voltages $2kV$, $6kV$ and $10kV$, respectively. The observed strong dependence on the extraction voltage suggests that the clusters are actually drifting in the gaseous circumstance around the bombarded region. This observation favours the model of cluster emission as a whole particle from the surface of bombarded material.

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