

On the Unimolecular Decay and Mechanism of Formation of Si_n^+ Cluster Ions

N. Kh. Dzhemilev, S. F. Kovalenko, S. E. Maksimov, O. F. Tukfatullin, and Sh. T. Khozhiev

Institute of Ion-Plasma and Laser Technologies, Uzbek Academy of Sciences, Tashkent, Uzbekistan

e-mail: maksimov_s@yahoo.com

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Abstract—Dependences of the emission and fragmentation of sputtered Si_n^+ clusters with $n = 1–11$ on the oxygen pressure near the surface are studied using secondary-ion mass spectrometry under Xe^+ -ion bombardment of a silicon surface. It is shown that taking into account the mutual reversibility of reactions of formation and unimolecular decay, the formation of Si_n^+ clusters under ion sputtering can be described within the framework of a mechanism of combinatorial synthesis.

Keywords: cluster mass distribution, fragmentation, silicon, oxygen pressure, cluster formation, combinatorial mechanism

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INTRODUCTION

Under bombardment of the surface of a solid by accelerated ions, the emission of clusters containing from several to hundreds of atoms occurs in the charged or neutral state [1, 2]. Despite considerable interest in clusters in view of challenges of modern technology and secondary-ion mass spectroscopy, the nature of the processes of their formation under ion sputtering still remains unclear even on a qualitative level. In discussions of experimental results, several collective mechanisms were proposed based on the assumption of shockwave formation on the surface of a target in the area of beam incidence [3], assumptions concerning vibrational relaxation in the volume with a high energy density [4] and thermal processes [5]. However, these models, as well as earlier recombination models [6, 7] could not overcome the main difficulty associated with correct description of the mass and energy distributions of sputtered clusters. At the same time, all these mechanisms and models of cluster formation do not take into consideration their unimolecular fragmentation and considerable transformation of the mass and energy spectra of cluster ions from the moment of their formation to the moment of recording via a detector; i.e., these models were developed without relaxation of the internal energy of sputtered clusters after emission.

Recently, a mechanism of the combinatorial synthesis of molecular $\text{Si}_n\text{O}_{2n+1}^-$ clusters was proposed [8], where the ions, atoms and molecules recombine above the surface when they are sputtered independently in individual cascades. According to this mechanism, the

clusters are formed through the successive binding of sputtered particles: Si, O, SiO and SiO_2 (monomers) and active cations O^- and Si^- as a result of pair collisions in the case of their various combinations with each other. In this process, the cluster ion acquires an internal energy sufficient for inverse decay. In the framework of this mechanism, many features in the processes of the unimolecular fragmentation of metal-oxide clusters [9, 10] and the energy spectra of sputtered Si_nO_m^- clusters [11] were successfully explained. This work aims to study the effect of sputtering conditions on the processes of emission and fragmentation of homogeneous Si clusters when oxygen is deposited onto a bombarded surface, as well as the description of regularities obtained within the mechanism [8].

EXPERIMENTAL

Investigation of the processes of the formation, emission and fragmentation of sputtered Si_n^+ clusters was carried out using a secondary-ion mass spectrometer [12] with double focusing in the reverse geometry using a methodology similar to [8–11, 13–15]. Primary Xe^+ ions with an energy of 8.5 keV bombarded silicon targets at an angle of 45° when scanning the surface with a raster size of 1.5×1.5 mm, ion currents of 0.4–0.5 μA and current density of $\approx 10^{-4}$ A cm^{-2} . To study the yield of silicon and silicon-oxide clusters as a factor of the oxygen pressure near the surface, a gas-injection system was used, which allows to change smoothly the pressure in the bombardment chamber from to be changed smoothly from 2×10^{-6} to 5×10^{-3} Pa.

The ion yield was measured with a resolution of $M/\Delta M \sim 300$. The relative error in the secondary-ion yield with oxygen filling the chamber is $\pm 20\text{--}30\%$ and it is caused by the accuracy of measuring the oxygen pressure.

The methodology of studying fragmentation is based on the fact that in a device [12] there are areas in which the direct recording of secondary-ion decay is possible and the latter occurs in various time intervals. The first field-free zone Z_1 enables cluster fragmentation to be recorded in a time interval of $10^{-6}\text{--}10^{-5}$ s after emission. In the second field-free zone Z_2 , the cluster decay processes occur in a time interval of $10^{-5}\text{--}10^{-4}$ s.

If we represent the decay reaction in the second field-free zone Z_2 in the form



where M_n^\pm , m^\pm , and m_0 are the masses of the parent ion and the charged and neutral fragments, respectively, then the kinetic energy E_f of a charged fragment formed in zone Z_2 is given by

$$E_f = \frac{m^\pm}{M_n^\pm} eU_0, \quad (2)$$

where U_0 is the acceleration voltage applied to the sample (5000 V, usually).

The fragmented ions formed in reaction (1) in the first field-free zone Z_1 can be recorded by tuning the mass-analyzer to the transmission of ions with the effective mass [12]

$$M^* = \frac{(m^\pm)^2}{M_n^\pm} \quad (3)$$

and by tuning the energy analyzer to the energy E_f determined by Eq. (2).

RESULTS AND DISCUSSION

When silicon is sputtered with Xe^+ ions without the inlet of oxygen to the bombarded surface at a residual pressure of no more than $P = 2 \times 10^{-6}$ Pa, the mass distribution of Si_n^+ is characterized by monotonically decreasing intensities with increasing yield of Si_4^+ and Si_6^+ clusters. Moreover, the emission of Si_n^+ clusters with $n > 11$ is not observed, as was previously noted in [16]. When the chamber with the sample is filled with oxygen, the mass spectrum of Si_n^+ varies considerably with increasing pressure (Fig. 1): the yield of monomers monotonically increases, but contrary to that, the yields of Si_n^+ clusters with $n \geq 7$ decreased, and poorly defined maxima are present in the spectra of Si_n^+ clusters with $n = 2\text{--}7$. Moreover, the yield of oxygen ions and heteronuclear Si_nO_m^+ clusters increases

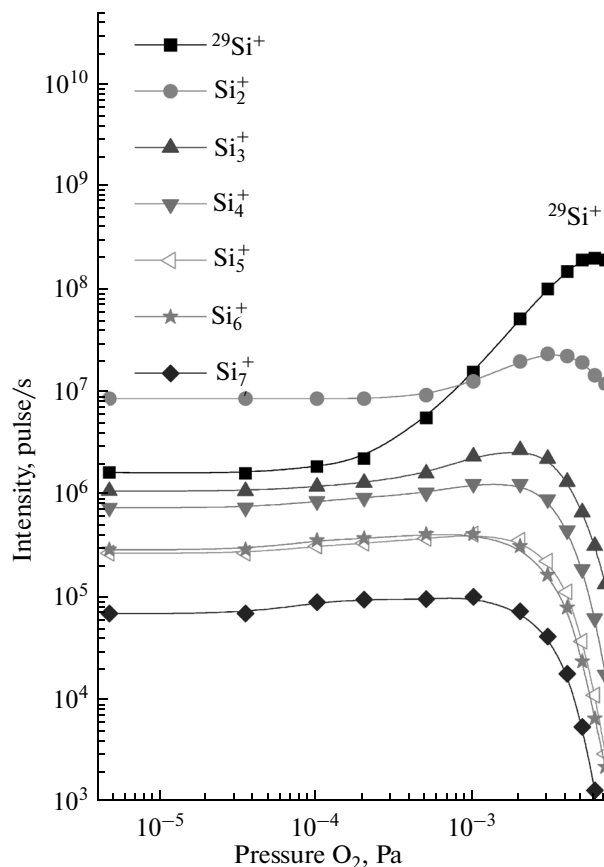
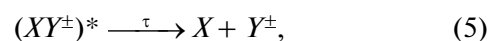
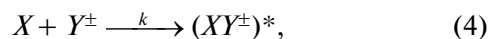


Fig. 1. Dependence of the yields of Si_n^+ -cluster ions on the oxygen pressure in the chamber of bombardment.

with increasing pressure. These regularities in the dependences of the Si_n^+ and Si_nO_m^+ yields on the pressure of O_2 near the target agree with the data [17] obtained when silicon is sputtered with argon ions. When the oxygen pressure reaches the value $P = 5 \times 10^{-3}$ Pa, the sputtering of Si_n^+ and Si_nO_m^+ corresponds to that previously described in [14].

One of the main provisions of the model [8] is the mutual reversibility of reactions of the formation of sputtered clusters and their unimolecular decay. In this case the process of cluster-ion evolution can be divided into two stages. In the first stage, the formation of clusters with simultaneous activation occurs, and in the second stage, their spontaneous decay



where k and τ are the constant of the formation reaction of an activated cluster and its lifetime until decay, respectively. Unimolecular fragmentation of cluster ions is considered as the second stage of the bimolecular chemical reaction (5). Thus, according to [8], the

Channels and probabilities of decay $P(\%)$ for Si_m^+ ($m = 2-8$) clusters in the first zero-field zone Z_1 , sputtered from the surface of silicon with Xe^+ ions with oxygen inflow up to a pressure of $P(\text{O}_2) = 4 \times 10^{-3}$ Pa

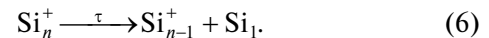
Ion	Decay channel	$P, \%$
Si_2^+	$\text{Si}^+ + \text{Si}$	5.3×10^{-2}
Si_3^+	$\text{Si}_2^+ + \text{Si}$	0.15
	$\text{Si}^+ + \text{Si}_2$	2×10^{-2}
Si_4^+	$\text{Si}^+ + \text{Si}_3$	1.7×10^{-2}
	$\text{Si}_2^+ + \text{Si}_2$	0.15
	$\text{Si}_3^+ + \text{Si}$	0.26
Si_5^+	$\text{Si}^+ + \text{Si}_4$	3×10^{-3}
	$\text{Si}_2^+ + \text{Si}_3$	2.5×10^{-2}
	$\text{Si}_3^+ + \text{Si}_2$	8×10^{-2}
	$\text{Si}_4^+ + \text{Si}$	2.0
Si_6^+	$\text{Si}^+ + \text{Si}_5$	2×10^{-3}
	$\text{Si}_2^+ + \text{Si}_4$	1×10^{-2}
	$\text{Si}_3^+ + \text{Si}_3$	3×10^{-2}
	$\text{Si}_4^+ + \text{Si}_2$	0.1
	$\text{Si}_5^+ + \text{Si}$	2.2
Si_7^+	$\text{Si}^+ + \text{Si}_6$	2×10^{-3}
	$\text{Si}_2^+ + \text{Si}_5$	6×10^{-3}
	$\text{Si}_3^+ + \text{Si}_4$	2×10^{-2}
	$\text{Si}_4^+ + \text{Si}_3$	5.5×10^{-2}
	$\text{Si}_5^+ + \text{Si}_2$	0.2
	$\text{Si}_6^+ + \text{Si}$	5.0
Si_8^+	$\text{Si}^+ + \text{Si}_7$	6×10^{-3}
	$\text{Si}_2^+ + \text{Si}_6$	7×10^{-3}
	$\text{Si}_3^+ + \text{Si}_5$	1×10^{-2}
	$\text{Si}_4^+ + \text{Si}_4$	6.7
	$\text{Si}_5^+ + \text{Si}_3$	4×10^{-2}
	$\text{Si}_6^+ + \text{Si}_2$	0.1
	$\text{Si}_7^+ + \text{Si}$	9.1

channels of cluster decay are indicative of the initial clusters from which a certain cluster ion is formed. By comparing the yields of cluster ions XY^\pm , initial cluster ions Y^\pm and fragmented XY_D^\pm ions which are formed in

field-free zones Z_1 and Z_2 of the device, we can describe the formation of different groups of cluster Si_n^+ ions within the framework of [8].

To solve this problem, the channels of Si_n^+ fragmentation were studied (see table) in all possible stoichiometric directions, which are reversed channels relative to the formation channels, as was noted. As was shown previously [16], for most Si_n^+ clusters the presence of several fragmentation channels is characteristic. This reflects the combinatorial character of the cluster formation process: Si_n^+ synthesis occurs simultaneously and parallel in several chain reactions corresponding to various channels. So, for example, for the Si_4^+ cluster we observe decays with different lifetimes with the formation of fragmented Si_1^+ , Si_2^+ , and Si_3^+ ions. For all Si_n^+ clusters, one direction of the decay is dominant in most cases: for Si_n^+ with $n = 1-8$, decay with the emission of a neutral Si atom is the main one. At the same time, the intensities of Si_n^+ decay with the formation of an atomic Si^+ ion are small and they are at the sensitivity limit of the experimental technique.

We observe the following main channel of Si_n^+ cluster decay

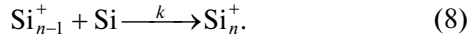


From (6) it follows that due to the reversibility of the formation and decay reactions, the change in the yield of Si_n^+ clusters with increasing oxygen pressure must depend on the concentration of charged Si_{n-k}^+ and neutral Si_k particles. At the same time, as was noted in [18], if the concentration of one component in the reaction is much higher than the concentration of another component, then the concentration of the final reaction product is proportional to the concentration of the minor component, i.e., the concentration is described by a linear equation. It is known [1, 2] that atomic ions give the main contribution to the sputtered-ion component, as a rule, and the probability of the ionization of sputtered atomic particles has a value on the order of 10^{-3} in most cases [19]. Consequently, under the used experimental conditions, neutral Si atoms give the main contribution to the products of sputtering. Correspondingly, the yields of cluster Si_n^+ ions should be proportional to the yields of positively charged Si_{n-1}^+ and fragmented $\text{Si}_{(n-1)D}^+$ ions which are the main decay products of Si_n^+ clusters at $n = 1-8$.

$$[\text{Si}_n^+] = q(n)[\text{Si}_{n-1}^+][\text{Si}], \quad (7)$$

where the left side (in square brackets) describes the yield of a certain type of particles, $q(n)$ is the proportionality coefficient for the given reaction.

The results in Fig. 1 show that for Si_n^+ clusters with $n > 3$ variations in the yield with oxygen pressure are well described by Eq. (7), which determines the yield variations in the “primary” Si_{n-1}^+ clusters. Therefore, the formation of Si_n^+ really occurs (according to [8]) through opposite reactions relative to (6)



The observed differences in the yield dependences of Si_n^+ ions with $n = 1-3$ on the oxygen pressure are caused by the fact that cluster ions are formed in the excited state [8]. For dimers and trimers, vibrational degrees of freedom which are necessary for accumulating excess energy are lacking, and the decay of most Si_2^+ and Si_3^+ ions proceeds in times comparable to the period of the atomic vibration. Only a part of the charged dimers and trimers with an excitation energy insufficient for decay may initiate the following reactions of Si_n^+ synthesis through different parallel channels or reach the detector in the form of “stable” ions. Qualitatively this conclusion is confirmed by the data on Si_2^+ and Si_3^+ -cluster fragmentation. So, intensity maxima of Si_{2D}^+ clusters formed in regions of zero field upon the fragmentation of Si_3^+ clusters (Fig. 2) are observed at the same oxygen pressures as the maxima of Si_2^+ , but these pressures are higher than those corresponding to the maxima of Si_3^+ . This is due to the fact that the decay of excited Si_3^+ clusters with small lifetimes, the number of which is proportional to the yield of primary Si_2^+ clusters (according to (7)), occurs in the field-free zones Z_1 and Z_2 . Similarly to that, the yield of Si_D^+ fragments upon the decay of Si_2^+ dimers continuously increases with pressure proportionally to the growth of the Si^+ yield shown in Fig. 1, in field-free zones and in both time intervals.

With increasing Si_n^+ -cluster size n , the number of vibrational degrees of freedom in which the excitation energy is accumulated increases. The decay of such clusters is described within the Rice–Ramsperger–Kassel theory of unimolecular reactions [20]

$$\tau = \tau_0/[1 - E_d/E_{\text{ex}}]^{s-1}, \quad (9)$$

where $\tau_0 \approx 10^{-13}$ s is the average atomic vibration period of a cluster. Figure 3 shows the characteristic dependence of the peak values of Si_n^+ , Si_{n-1}^+ , and fragmented $\text{Si}_{(n-1)D}^+$ ions on the oxygen pressure during the process of Si_n^+ decay. Figures 3a and 3b correspond to $n = 4$ and $n = 7$, respectively. As one can see from this figure, the probabilities of the unimolecular decay of Si_n^+ clusters is independent of their yield intensities when the oxygen pressure varies in the chamber. These

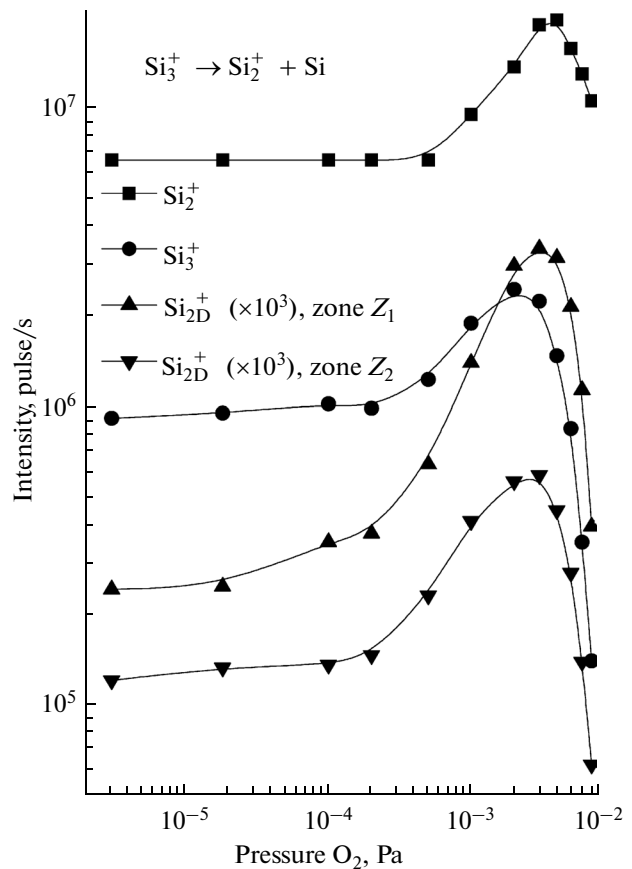


Fig. 2. Same as in Fig. 1 for Si_3^+ and Si_2^+ ions and the yield of fragmented Si_{2D}^+ ions upon the decay of Si_3^+ in zero-field zones Z_1 and Z_2 .

regularities are observed for all Si_n^+ clusters at $n = 4-7$. As concerns the fragmentation probabilities of Si_n^+ clusters with $n = 8-11$, depending on the O_2 pressure, there is an experimental difficulty due to the mass superposition of homonuclear Si_n^+ and heteronuclear Si_nO_m^+ ion peaks [14]. At the same time, in the range of small pressures $P < 10^{-4}$ Pa when the number of Si_nO_m^+ clusters is small, the dependences of the yield for Si_n^+ , Si_{n-1}^+ and fragmented $\text{Si}_{(n-1)D}^+$ ions are also similar.

The results concerning the independence of the probabilities of the unimolecular fragmentation of homogeneous Si_n^+ ($n = 4-11$) clusters of the sputtering conditions also confirm the statistical nature of the processes of their formation [8]. In reality, according to (9), the constancy of the Si_n^+ fragmentation times with a certain number n of atoms is indicative of the same excitation energy E_{ex} of these clusters at varying oxygen pressure near the surface. At the same time,

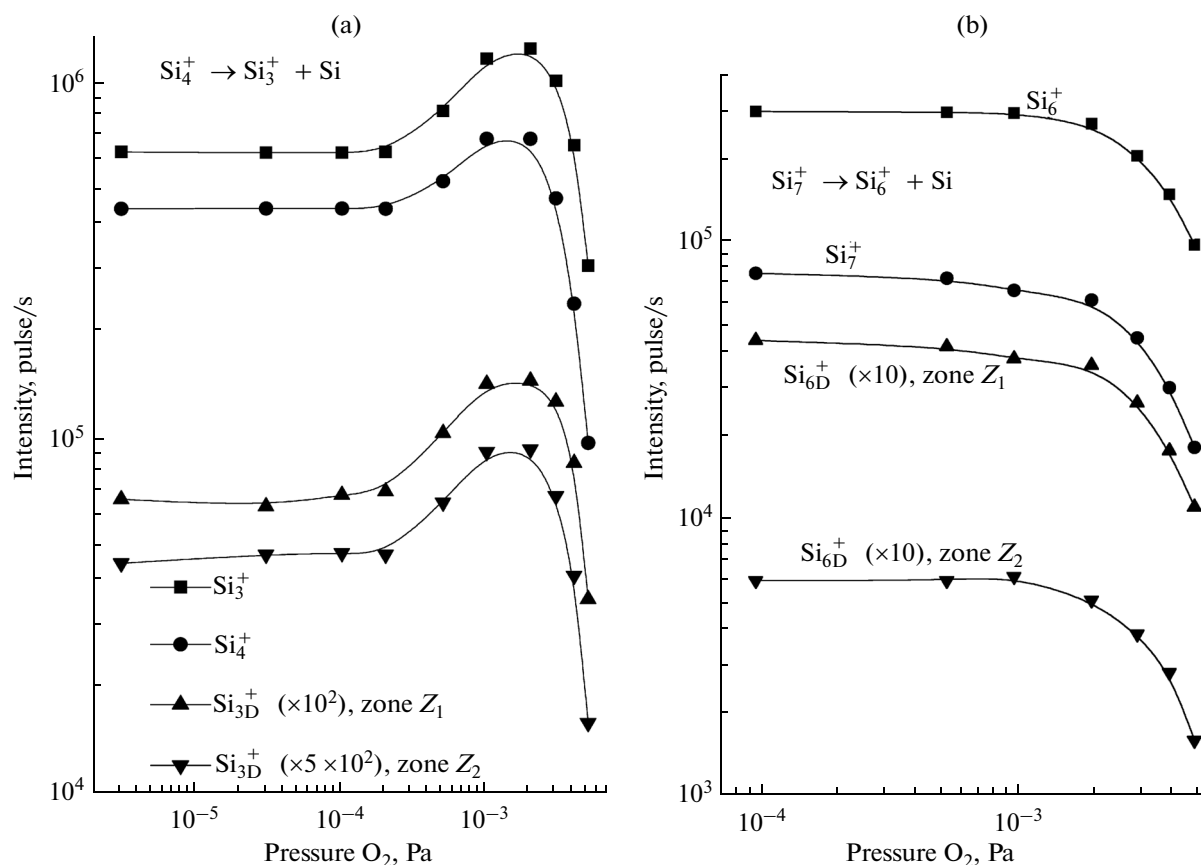
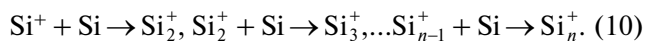


Fig. 3. Same as in Fig. 1 for Si_n^+ and Si_{n-1}^+ ions and the yield of fragmented $\text{Si}_{(n-1)D}^+$ ions upon the decay of Si_n^+ in the zero-field zones: (a) $n = 4$; (b) $n = 7$.

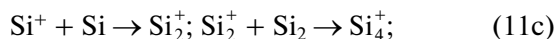
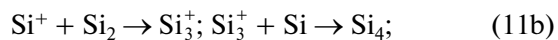
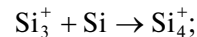
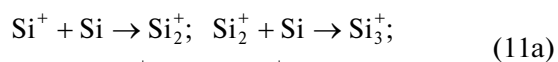
within the framework of collective mechanisms [3–5], the clusters are formed in some excited region where the energy density changes depending on the experimental conditions. Since the emitted clusters are a fragment of this region, their excitation energy E_{ex} and, consequently, the lifetime τ until decay and the probabilities of decay in this fixed time interval must also vary, which is not observed in the experiment. But within statistical mechanism [8] a change in the conditions of cluster sputtering leads only to variations in the probabilities of cluster formation in the processes of recombination above the surface. However, their excitation energy remains the same giving rise to the constant decomposition probability of Si_n^+ clusters (Fig. 3).

So, according to [8], the process of Si_n^+ -cluster formation can be described in the following way. The main channel of cluster synthesis is the chain of successive reactions with the binding of a neutral Si atom



The formation of Si_n^+ also occurs via other parallel reactions which are inverse to the decay reactions (see

the table). Thus, for example, the plurality of the reaction chains for Si_4^+ can be represented in the following form



Similar chains of parallel reactions of cluster synthesis can also be written for other Si_n^+ ions.

CONCLUSIONS

Investigation of the dependences of the emission and unimolecular fragmentation of sputtered silicon clusters on the oxygen pressure near a bombarded surface shows that the change in their yield can be explained by the sequential binding of neutral monomers to cluster ions. Studies of the decay processes for these clusters indicate that the probabilities of their unimolecular fragmentation and, consequently, the

excitation energy are independent of the sputtering conditions.

The results allow one to draw a conclusion concerning the possibility of the description of the Si_n^+ -cluster formation process under the ion bombardment of a surface within the mechanism of combinatorial synthesis [8]. This, in turn, suggests that the mechanism of cluster formation [8] is universal and does not depend on the specific type of clusters formed and the conditions of ion bombardment.

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