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Study of the Formation and Unimolecular Fragmentation of $Si_nO_m^+$ Clusters under Ion Bombardment

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Abstract—The dependences of the emission and fragmentation of $Si_nO_m^+$ clusters sputtered by Xe^+ ions from the surface of Si on the oxygen pressure near the bombarded surface are studied using secondary ion mass spectrometry. It is shown that the process of $Si_nO_m^+$ cluster formation under ion bombardment can be described within the framework of the mechanism of combinatorial synthesis by taking into account the mutual reversibility of the reactions of formation and unimolecular decay.

Keywords: secondary ion mass spectrometry, formation and decay of silicon-oxide clusters, oxygen pressure, combinatorial-synthesis mechanism

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INTRODUCTION

Among the objects in studies of cluster physics, silicon oxide is of special interest [1–3]. From the point of view of the synthesis of cluster structures with various dimensions and stoichiometries and the determination of their fundamental properties within the framework of a single experiment, secondary ion mass spectrometry (SIMS) has unique possibilities. The use of SIMS makes it possible to study the emission and fragmentation of sputtered cluster $Si_nO_m^{\pm}$, ions and determine the decay channels and dissociation rate [4–6] and energy [4, 6] constants. At the same time, the mechanism of silicon-oxide-cluster formation under ion bombardment remains unclarified [4–6].

To describe the process of $Si_nO_m^-$ cluster formation, the author of [7] proposed the mechanism of their combinatorial synthesis during the recombination (above the surface) of ions, atoms, and molecules independently sputtered in individual cascades. In accordance with [7], clusters form by the successive attachment of neutral products of Si, O, SiO, and SiO_2 (monomer) sputtering to active O^- and Si^- ions as a result of pair collisions in the case of their different combinations. In this case, the formed cluster ion acquires an internal energy that is sufficient for reverse decay. The regularities of the emission and fragmentation of homogeneous Si_n^+ clusters were described when oxygen was let to the bombarded surface [8] and a series of features of processes of unimolecular decay of metal-oxide clusters [9, 10] and of the energy spectra of sputtered $Si_nO_m^-$ clusters [11] was explained within the framework of this mechanism [7].

The aim of this paper is to study the influence of sputtering conditions on the processes of emission and fragmentation of homonuclear $Si_nO_m^+$ clusters and analyze the possibilities of describing the obtained regularities within the framework of the model [7].

EXPERIMENTAL EQUIPMENT AND INVESTIGATION PROCEDURE

The processes of the formation, emission, and fragmentation of sputtered $Si_nO_m^+$ clusters were studied using a secondary ion mass spectrometer [12] with double focusing of reverse geometry using a procedure analogous to that described in [4–11]. Primary 8.5-keV Xe^+-ions bombarded the Si targets under study at an angle of 45° during surface scanning into a grid with dimensions of 1.5 × 1.5 mm. The ion currents were 0.4–0.5 μA for a current density of $\approx 10^{-4}$ A cm^{-2}. To determine the variation in the cluster yields as a function of the oxygen pressure near the bombarded surface, we used a puffing system that made it possible to gradually vary the pressure in the chamber from 2×10^{-6} to 5×10^{-3} Pa. The ion intensities were measured with a resolution of $M/\Delta M \sim 300$. The relative measurement error for the secondary-ion yield after oxygen inlet into the target chamber was ±20–30% and was due to the accuracy of oxygen-pressure measurement.

The procedure for studying fragmentation was described in detail previously in [4–12] and was based on the fact that, in the device, there are regions in which the decay of secondary ions can be recorded directly within various time intervals. The first field-free region S_1 made it possible to record cluster fragmentation in the time range of 10^{-6}–10^{-5} s after emission; the clusters decayed in the second field-free region S_2 in the time range of 10^{-5}–10^{-4} s.

RESULTS AND DISCUSSION

Our studies of the dependences of the cluster $Si_nO_m^+$ ion yields and the intensities of their unimolecular decay on the oxygen pressure in the bombardment chamber were conducted during the sputtering of silicon by Xe^+ ions and demonstrated that, at a maximum pressure of $P = 5 \times 10^{-3}$ Pa, the intense emission of homogeneous Si_n^+, and heterogeneous $Si_nO_m^+$ clusters with different numbers of Si and O atoms was observed. The distributions of the Si_n^+ and $Si_nO_m^+$ cluster yields at the given pressure correspond to that described previously [5]. For $Si_nO_m^+$, there were hardly any clusters that were distinguished explicitly by their relative intensities. Only SiO^+, Si_2O^+, and $Si_2O_2^+$ clusters depleted of oxygen have large yields comparable with or exceeding the Si_2^+, dimer yields.

One of the main concepts of the combinatorial-synthesis mechanism [7] is the mutual reversibility of reactions of sputtered-cluster formation and unimolecular decay. The experimentally observed reactions of unimolecular fragmentation with the formation of initial products are inverse reactions forming the cluster by means of combinatorial chemical reactions. Within the framework of the model [7], the process of cluster-ion evolution can be divided into two stages: at the first stage, clusters form with their simultaneous activation, and at the second stage, they decay. Thus, the unimolecular fragmentation of cluster ions is regarded as the second part of the bimolecular chemical reaction, and the cluster decay channels indicate which initial components form the given cluster ion.

To describe $Si_nO_m^+$ formation in the combinatorial-synthesis reactions, we extensively studied their previously partially investigated fragmentation channels along all possible stoichiometric directions [5, 6]. The obtained data showed that the positive silicon-oxide clusters have no characteristic decay channels. For the majority of $Si_nO_m^+$, the presence of several fragmentation channels is typical, which reflects the combinatorial character of the process of formation of these clusters [7]: $Si_nO_m^+$ clusters are synthesized in several parallel chain reactions occurring simultaneously. In this case, one of the decay directions is predominant in the majority of cases. For the majority of $Si_nO_m^+$ clusters, the channel with the ejection of SiO^+ is presented, which leads to a significant intensity of the given ion in the mass distribution. The probabilities of fragmentation with the formation of neutral SiO and SiO_2 increase with increasing cluster size. For the majority of $Si_nO_m^+$ clusters, we observed decays with the ejection of one or several neutral oxygen atoms. The abundance of decays with the formation of homonuclear Si^+ and Si_2^+ ions also having large intensities in the spectrum attract attention.

Since one of the main concepts of the combinatorial-synthesis mechanism [7] is the mutual reversibility of reactions of sputtered-cluster formation and unimolecular decay, we can describe the formation of different groups $XY^{\pm}$ within the framework of the model by comparing the dependences of the intensities of yields of cluster ions $XY^{\pm}$, their "initial" cluster ions $Y^{\pm}$, and fragment ions $Y_D^{\pm}$, formed in the field-free device zones S_1 and S_2 [7]. Let the main fragmentation channel of the following form be observed for the $Si_nO_m^+$ cluster

$$Si_nO_m^+ \xrightarrow{\tau} Si_{n-k}O_{m-l}^+ + Si_kO_l, \tag{1}$$

where τ is the lifetime of the $Si_nO_m^+$ cluster ion before decay, $k = 0$–n, $l = 0$–m. The change in the intensity of the $Si_nO_m^+$ cluster yield with increasing oxygen pressure must depend on the concentration of charged ($Si_{n-k}O_{m-l}^+$) and neutral (Si_kO_l) particles because of the reversibility of the formation and decay reactions. At the same time [13, 14], if the concentration of one of the two components is much larger in the formation reaction, then the concentration of the final product is proportional to that of particles with smaller concentration. It is known [15, 16] that, as a rule, the main fraction in the sputtered ion component consists of atomic ions, and among cluster ions, dimers and trimers constitute the main fraction. On the other hand, the probability of the ionization of sputtered atomic particles in the majority of cases is on the order of 10^{-3} [17]. Consequently, under our experimental conditions, Si, O, SiO and SiO_2 neutrals give the main yield of sputtered products, and the intensities of the $Si_nO_m^+$ cluster ions must be proportional to the yields of positively charged ($Si_{n-k}O_{m-l}^+$) and fragment ($Si_{n-k}O_{(m-l)D}^+$) ions, which are the main decay products for $Si_nO_m^+$.

The dependences of the yields of SiO^+, SiO_2^+, and SiO_3^+ clusters and also of O^+, O_2^+, and Si^+ ions, which are the beginning of the chain of combinatorial-synthesis reactions of $Si_nO_m^+$, clusters in accordance with [7], on the oxygen pressure near the sputtered surface are given in Fig. 1. As can be seen from the graphs, an increase in the intensity with increasing O_2 pressure is

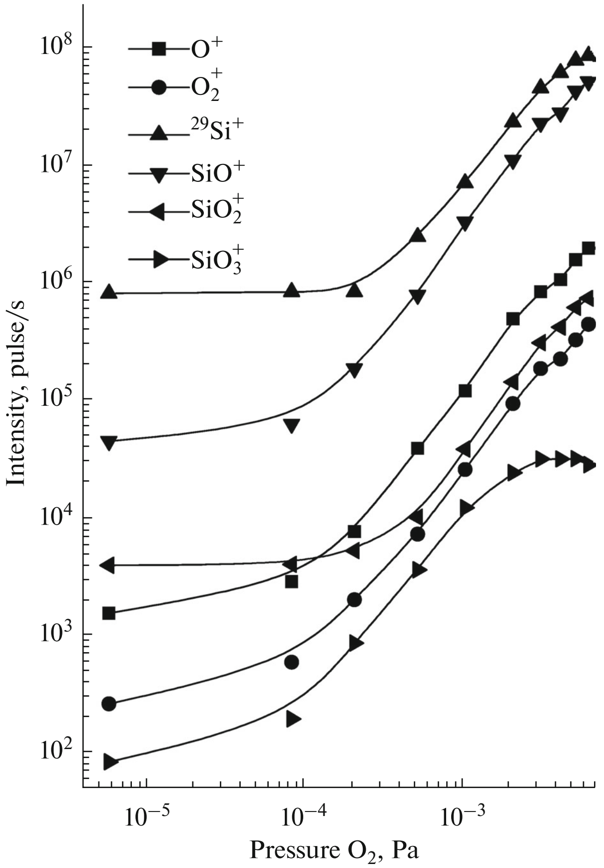

Fig. 1. Dependence of the O^+, O_2^+, Si^+, SiO^+, SiO_2^+, and SiO_3^+ ion yields on the O_2 pressure.

characteristic for all these groups of ions except SiO_3^+. For the SiO_3^+ cluster, a weakly expressed maximum of the yield lying in the oxygen pressure range of $P = (2–4) \times 10^{-3}$ Pa is observed. The proportionality of the SiO^+ and SiO_2^+ intensities to the yield of atomic Si^+ can serve as experimental confirmation of the presence of the effective channel of SiO^+ and SiO_2^+ formation by the subsequent attachment of a neutral oxygen atom to the Si^+ ion in accordance with [7].

Obviously, the chains of successive reactions of $Si_nO_m^+$ synthesis must begin with the formation of small particles, namely, homonuclear Si_2^+ and heteronuclear SiO^+ dimers and, then, Si_3^+, SiO_2^+ and Si_2O^+ trimers. In this case, there must be the correspondence between the oxygen-pressure dependences of the yields of small clusters and fragment ions constituting them. At the same time, it was mentioned in [8] that direct correspondence between the emission of small clusters and the intensities of their fragments need not be experimentally observed. Indeed, in accordance with [7], cluster ions form in the excited state. Dimers and trimers have no vibrational degrees of freedom required for the accumulation of excess energy on them, and the decay of the majority of them occurs during time intervals that are comparable with the periods of atomic oscillations. Only a part of the charged dimers and trimers with excitation energies insufficient for decay initiate subsequent reactions of $Si_nO_m^+$ synthesis along different parallel channels or reach the detector in the form of “stable” ions. This leads to differences between the experimentally observed dependences of the intensities of “stable” dimers and trimers, on the one hand, and of their fragments, on the other hand. In addition, in accordance with published data, the energies of SiO and SiO_2 dissociation into atoms are rather high and are 8.26 and 13.2 eV, respectively [3]. This makes it possible to suggest that, under our conditions during sputtering, the emission of SiO dimers and SiO_2 trimers as a whole can also occur in accordance with the mechanism of direct emission [18, 19] with their positive ionization.

The variation in the intensities of the $Si_nO_m^+$ cluster ion yields as a function of the oxygen pressure is shown in Fig. 2. The obtained data demonstrate that the $Si_2O_3^+$ and $Si_2O_4^+$ cluster yields increase with increasing pressure, while the yield maxima are observed for Si_2O^+ and $Si_2O_2^+$ at high pressures. The indicated differences can be explained by the combinatorial mechanism of $Si_2O_m^+$ cluster formation. Indeed, for $Si_2O_m^+$, the presence of several reactions of their formation with comparable probabilities, which are reverse to the channels of their decay, is characteristic. The probability of the attachment of an oxygen atom to the growing cluster increases as the O_2 pressure near the surface increases. This leads to the fact that, at large pressures, the yields of Si_2O^+ and $Si_2O_2^+$ depleted of oxygen (as such as the homogeneous Si_2^+) decrease, while the $Si_2O_3^+$ and $Si_2O_4^+$ yields continue to increase.

Figure 3 shows the dependences of the intensities of the $Si_2O_3^+$ cluster emission and fragmentation on the oxygen pressure; the decay channel

$$Si_2O_3^+ \xrightarrow{t} SiO^+ + SiO_2. \tag{2a}$$

is the main one for them. Consequently, $Si_2O_3^+$ forms mainly in the reverse reaction:

$$SiO^+ + SiO \xrightarrow{k} Si_2O_2^+, \tag{2b}$$

Indeed, the data shown in Fig. 3 confirm this conclusion: the $Si_2O_3^+$ cluster intensities are proportional to both “stable” SiO^+ ions and fragment dimers formed during decay (Fig. 2a) in both field-free zones. As for the proportionality of the $Si_2O_3^+$ yields to the intensi-

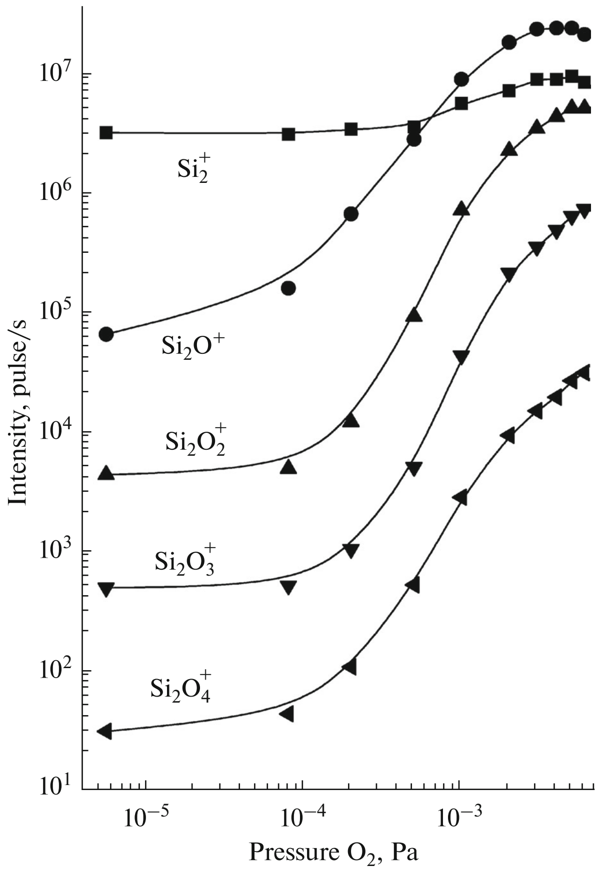

Fig. 2. Dependence of the Si_2O^+, $Si_2O_2^+$, $Si_2O_3^+$, and $Si_2O_4^+$ion yields on the O_2 pressure.

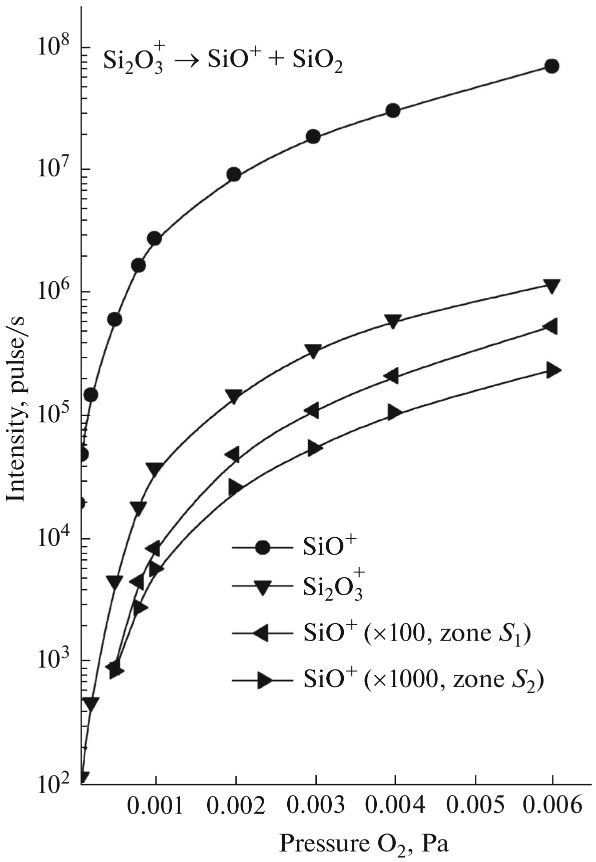

Fig. 3. Dependence of the SiO^+ and $Si_2O_3^+$ yields and the intensities of SiO^+ fragment ions on the O_2 pressure.

ties of SiO^+ ions formed during decay, it is due to the appearance of additional vibrational degrees of freedom of $Si_2O_3^+$, unlike small clusters, as a result of which their fragmentation occurs much later.

Figure 4 shows the dependences of the $Si_2O_3^+$ and $Si_2O_2^+$ ion yields and the intensities of $Si_2O_2^+$ fragment ions on the O_2 pressure for the $Si_2O_3^+$ decay channel:

$$Si_2O_3^+ \xrightarrow{t} Si_2O_2^+ + O. \tag{3a}$$

As can be seen from the figure, within the limits of experimental accuracy, the intensities of all these ions are also proportional to each other, which demonstrates the presence of the second channel of $Si_2O_3^+$ cluster formation of the form

$$Si_2O_2^+ + O \xrightarrow{k} Si_2O_3^+. \tag{3b}$$

The dependences of the $Si_3O_m^+$ cluster yields on the oxygen pressure are shown in Fig. 5. For $Si_3O_2^+$ and $Si_3O_3^+$ clusters, yield maxima are observed at different pressures; in this case, the maximum positions are shifted toward higher pressures as the number of oxygen atoms in the cluster increases. For the $Si_3O_4^+$ cluster, the intensity maximum located at higher pressures is expressed weakly, and, for the $Si_3O_5^+$ cluster, a continuous increase in the yield is characteristic as the oxygen pressure near the sputtered surface increases. Such a peculiarity of the $Si_3O_m^+$ yields is easily explained within the framework of the combinatorial-synthesis mechanism: as the number of oxygen atoms increases in the cluster-formation region, the probabilities of their capture to chains of successive combinatorial-synthesis reactions increase.

Oxygen-pressure dependences of yields that are analogous to those shown in Figs. 1–5 are also observed for $Si_4O_m^+$ and $Si_5O_m^+$ clusters. For all these clusters, the increase in the intensities with yield maxima at a pressure of $P > 10^{-3}$ Pa is typical as the O_2 pressure increases. The formation of $Si_4O_m^+$ and $Si_5O_m^+$ cluster ions and the indicated peculiarities of the intensities of their yields can also be described within the framework of the combinatorial-synthesis mechanism. At the same time, however, because of the small

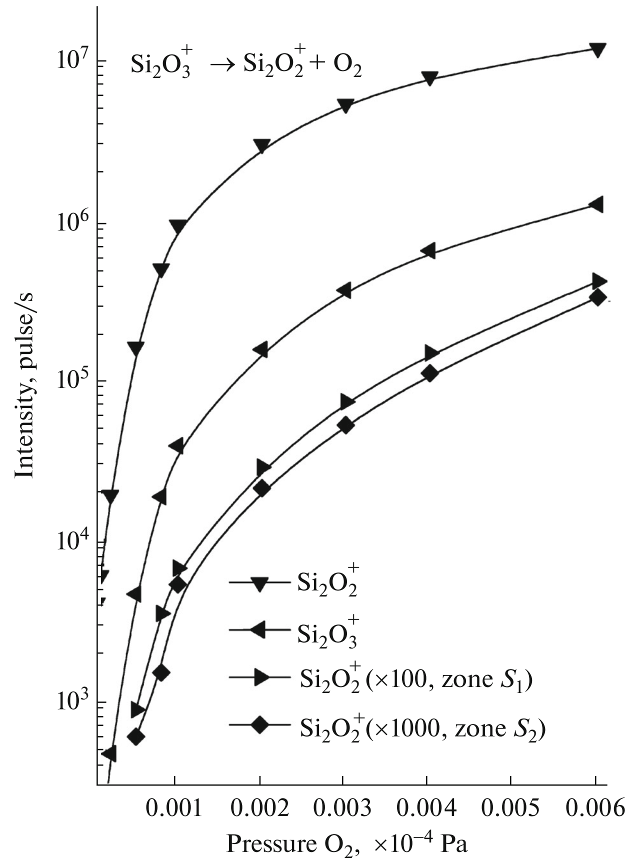

Fig. 4. Dependence of the $Si_2O_2^+$ and $Si_2O_3^+$ yields and the intensities of $Si_2O_2^+$ fragment ions on the O_2 pressure.

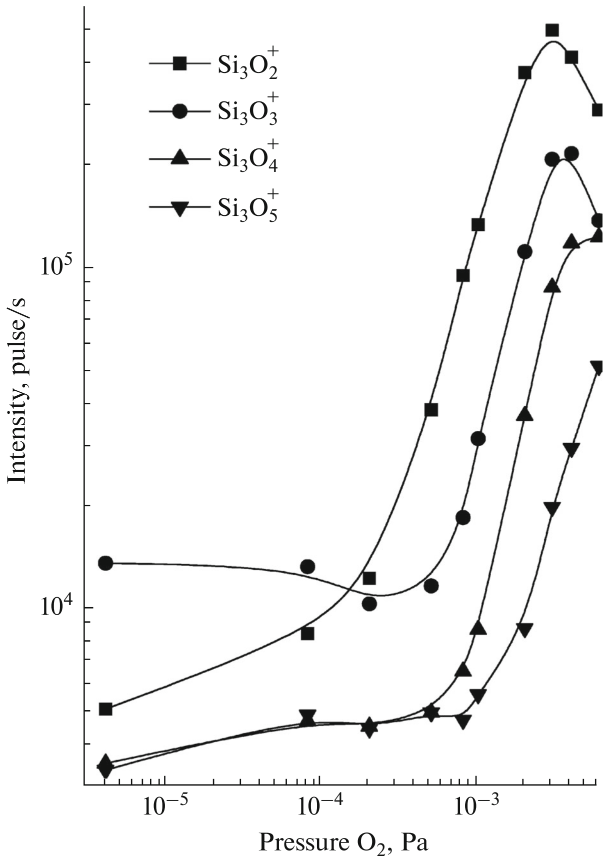

Fig. 5. Dependence of the $Si_3O_2^+$, $Si_3O_3^+$, $Si_3O_4^+$, and $Si_3O_5^+$ cluster yields on the O_2 pressure.

decay intensities of these clusters, the dependences of their fragment ions on the oxygen pressure cannot be measured correctly and exactly in the entire range of experimental conditions. On the other hand, $Si_4O_m^+$ and $Si_5O_m^+$ formation in accordance with the mechanism in [7] can be described based on an analysis of the distributions of the intensities of these clusters compared with the intensities of "stable" ions that form during $Si_4O_m^+$ and $Si_5O_m^+$ decay and, correspondingly, determine the formation of these clusters. As a characteristic example, we can choose the oxygen-pressure dependences of the Si_3O^+ and Si_4O^+ cluster yields. The main channel for Si_4O^+ is the decay

Channels and probabilities P of the fragmentation of $Si_3O_2^+$ and $Si_4O_3^+$ clusters sputtered from the surface of Si by Xe^+ ions upon the introduction of O_2

Ion	Decay channel	Charged fragment	Neutral fragment	Zone S_2, P	Zone S_1, P
$Si_3O_2^+$	$Si^+ + Si_2O_2$	Si^+	Si_2O_2	1.8×10^{-2}	2.1×10^{-3}
	$SiO^+ + Si_2O$	SiO^+	Si_2O	6.4×10^{-1}	1.6×10^{-1}
	$Si_2O_2^+ + Si$	$Si_2O_2^+$	Si	1.7×10^{-2}	3.8×10^{-3}
$Si_4O_3^+$	$SiO^+ + Si_3O_2$	SiO^+	Si_3O_2	1.9×10^{-3}	2.6×10^{-2}
	$Si_2O^+ + Si_2O_2$	Si_2O^+	Si_2O_2	3.5×10^{-2}	2.0×10^{-1}
	$Si_2O_2^+ + Si_2O$	$Si_2O_2^+$	Si_2O	3.8×10^{-3}	22×10^{-2}
	$Si_3O_2^+ + SiO$	$Si_3O_2^+$	SiO	7.0×10^{-1}	5.3
	$Si_3O_3^+ + Si$	$Si_3O_3^+$	Si	1.4×10^{-2}	4.0×10^{-2}

$$Si_4O^+ \xrightarrow{\tau} Si_3O^+ + Si. \qquad (4a)$$

Correspondingly, in accordance with [7], the main reaction for the Si_4O^+ formation is the reaction that is reverse to (4a)

$$Si_3O^+ + Si \xrightarrow{k} Si_4O^+. \qquad (4b)$$

The obtained data confirm this conclusion completely: the Si_4O^+ cluster intensities in the entire range of oxygen pressures are proportional to the yields of the initial Si_3O^+ clusters.

It is necessary to note that the number of possible channels of cluster formation increases as its size increases. So, for example, the presence of five fragmentation channels is characteristic for the $Si_4O_3^+$ cluster (see Table). In accordance with this there exist five possible channels of $Si_4O_3^+$ cluster formation; they have different probabilities; in this case, the following channel is the main one:

$$Si_3O_2^+ + SiO \xrightarrow{k} Si_4O_3^+. \qquad (5)$$

In turn, there exist three channels of $Si_3O_2^+$ cluster formation (see Table). Similar chains of combinatorial reactions can be written for all sputtered $Si_nO_m^+$ clusters.

CONCLUSIONS

Our studies of the regularities of $Si_nO_m^+$ cluster emission and fragmentation during sputtering of the surface of Si by Xe ions as the oxygen pressure was varied near the bombarded surface make it possible to conclude that $Si_nO_m^+$ formation under these conditions can be described successively by the statistical combinatorial-synthesis mechanism [7]. This mechanism was used previously to describe the processes of $Si_nO_m^-$ [7] and Si_n^+ cluster emission and fragmentation [8], the peculiarities of metal-oxide cluster decay [9, 10] and the energy spectra of sputtered $Si_nO_m^-$ clusters [11]. In turn, this indicates that the combinatorial mechanism has a general character, and its applicability is independent of the type of bombarding ions and the nature of formed clusters.

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