Average Decay Rate Constants and Excitation Energies for Metal Clusters Sputtered by SF_5^+ and Inert Gas Ions

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Abstract—Results from a comparative SIMS study of the fragmentation of metal clusters sputtered with atomic Xe^+ and molecular SF_5^+ ions are presented. It is shown that the average decay rate constants and, hence, the excitation energies of clusters of the same stoichiometry do not depend on the type of bombarding ions.

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INTRODUCTION

In studies of the processes of ion interaction with a surface, effects related to sputtering by molecular and cluster beams are of special interest [1–6]. Despite the high fundamental and practical meaning of such investigations, the nonlinear and collective processes that occur when a solid body is bombarded with polyatomic ions are still in the investigation stage, and the nature of the processes responsible for cluster emission enhancement under the action of a molecular beam is still not clear. To date, no experimental data have been published on the fragmentation of metastable clusters sputtered by polyatomic ions, although the decay of emitted particles [7–13] supply important information on both the fundamental properties of the clusters themselves and on the mechanism of their formation, and are important for understanding the nature of solid-body surface sputtering under the impact of molecular and the cluster ions.

We used secondary ion mass-spectrometry (SIMS) to perform a comparative study of the monomolecular decay of Cu_n^+, Ag_n^+, Au_n^+, Nb_n^+, and Ta_n^+ clusters sputtered upon bombardment by atomic Xe^+ ions and molecular SF_5^+ ions of approximately equal mass [14]. We selected these objects because both the main channels of these clusters' decay [8, 15–17] and the processes of cluster emission upon the sputtering of Nb, Ta, and Ag ions with ions of Xe^+ and SF_5^+ [4, 18] were investigated earlier.

EXPERIMENTAL

We performed our experimental comparative study of metal cluster fragmentation upon bombardment by beams of molecular and inert gas ions using a double-focusing secondary ion mass-spectrometer with reverse geometry [7]. The figure shows its schematic diagram. Measurements were performed at a pressure inside the bombardment chamber of $\approx 5 \times 10^{-8}$ Torr. The primary ions were generated by our own electron hit ion source (*1*) with an axially symmetric magnetic field that allowed us to obtain beams of SF_5^+ molecular ions and their fragments. The primary ion currents were ~1.2 μA for SF_5^+ and ~0.7 μA for Xe^+ at a current density of $\approx 3-5 \times 10^{-3}$ A/cm². The primary ion energy was 8.5 keV.

We performed all experiments at room temperature. In surface bombardment with the molecular ion beams, we began our measurements 15–20 min after the start of sputtering, corresponding to the establishing of stationary conditions for the emission of all types of secondary ions. The sputtered secondary ions were accelerated to energies $eU_0 = 3$ keV, focused by immersion lens (*8*), and entered input slit (*10*) of mass-analyzer (*11*), a stigmatic magnetic prism, in the dynamic balance regime [7]. Electrostatic analyzer (*12*), a three-electrode electrostatic mirror, was located behind the magnetic prism. Ions with the selected mass were registered by secondary-electron multiplier (*15*) and ion counter (*16*).

A certain distribution over excitation energies $\delta N / \delta E_{ex} = f(E_{ex})$ was observed for the sputtered clusters [8]; they therefore decayed over the whole distance from the target to the detector. Our technique of fragmentation investigation [7–13] was based on there being zones in the device where the direct registration of the secondary ion decay is possible within different time ranges. In the first field-free zone S_1 (i.e., in the space between the immersion objective and the magnetic analyzer), clusters decay within the range of 10^{-7} to 10^{-5} s after emission (see figure). In the second field-free zone S_2 (i.e., in the space between the mass-
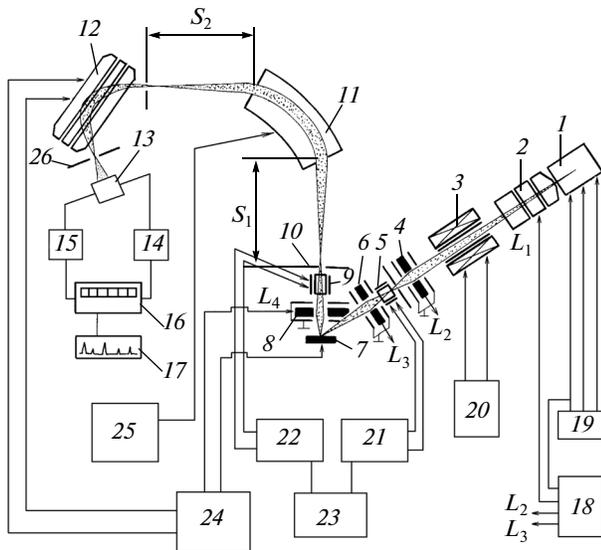
Scheme of the secondary ion mass analyzer: (*1*) ion source; (*2, 4, 6*) lenses for focusing the primary beam (L_1, L_2, L_3, respectively); (*3*) Wien filter; (*5*) system for primary beam scanning of a sample's surface; (*7*) sample; (*8*) lens for focusing the secondary beam (L_4); (*9*) secondary beam deflection system; (*10, 26*) diaphragms; (*11*) magnetic analyzer; (*12*) energy analyzer; (*13*) DCA–SEA switch; (*14*) DC amplifier (DCA); (*15*) secondary electron amplifier (SEA); (*16*) pulse counter; (*17*) recorder; (*18*) high voltage and lens supply unit; (*19*) ion source power supply; (*20*) Wien filter power supply; (*21*) control unit for primary beam scanning; (*22*) control unit for secondary beam scanning; (*23*) unit for coordinating (*21*) and (*22*); (*24*) target and energy analyzer power supply; (*25*) magnet control unit. S_1 and S_2 are the field-free zones of the mass analyzer.

analyzer field and the input energy analyzer), cluster fragmentation occurs within the range of 10^{-5} to 10^{-3} s.

If we take the decay reaction in the second field-free zone S_2 in the form

$$M_n^\pm \rightarrow m^\pm + m_0, \qquad (1)$$
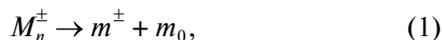
where $M_n^\pm$ is the parent ion mass and $m^\pm$ and m_0 are the masses of the charged and neutral fragments, respectively, the kinetic energy of the charged fragments formed in the S_2 zone will be

$$E_{fr} = \frac{m^\pm}{M_n^\pm} e U_0, \qquad (2)$$

where U_0 is the acceleration voltage applied to the sample.

We can register ion fragments formed as a result of reaction (1) in the first field-free zone S_1 by tuning the mass analyzer to gate ions with an apparent mass of M^* [7]:

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

while also tuning the energy analyzer to energy E_{fr} determined by expression (2).

RESULTS AND DISCUSSION

Our technique of estimating the average value of rate constant k of sputtered cluster unimolecular fragmentation [9, 10, 12] is based on comparing the number of decays to times of flight Δt_1 and Δt_2 through field-free mass spectrometer zones S_1 and S_2, assuming that the number of metastable clusters able to fragment during those times, ΔN_1 and ΔN_2, is proportional to the initial quantity of the ions at the entrances to those zones, N_1 and N_2.

The decay law is

$$N = N_0 \exp(-k\Delta t), \qquad (4)$$

where k is the decay rate constant, N is the number of metastable ions that do not decay after passage of time Δt, and N_0 is the initial number of metastable ions. For each of the mass spectrometer field-free zones S_1 and S_2 [9, 10, 12], we have

$$\Delta N_1 = N_0 \exp(-kt_1)[1 - \exp(-k\Delta t_1)],$$
$$\Delta N_2 = N_0 \exp(-kt_2)[1 - \exp(-k\Delta t_2)], \qquad (5)$$

where t_1 and t_2 are the times of reaching the respective zones, determined by the device's geometry; and Δt_1 and Δt_2 are the times of flight through these zones. After determining ΔN_1 for the first field-free zone and ΔN_2 for the second, we obtain from their ratio average constant k of the decay rate using the equation

$$\Delta N_1^+ / \Delta N_2^+ = \exp k(t_2 - t_1)$$
$$\times [1 - \exp(-k\Delta t_1)]/[1 - \exp(-k\Delta t_2)]. \qquad (6)$$

Table 1 presents average decay constants k and respective average lifetimes $\tau \equiv 1/k$ for the most intense decay channels of certain metal cluster ions, calculated according to formulas (4)–(6).

Our results show that the numerical values of the decay rate constants and the lifetimes of clusters of different metals sputtered with molecular ions SF_5^+ and atomic ions Xe^+ coincide within the accuracy of the experimental technique. This indicates that the internal energies of the vibrational excitation of these clusters are, in our case, independent of the number of atoms in the primary bombarding ions.

Numerical estimates of cluster excitation energies E_{excit} are possible using the Rice–Ramsperger–Kassel (RRK) theory [19] with allowance for the obtained values of the decay rate constants:

$$E_{excit} = E_d(n)/[1 - (k_n/\nu_0)^{1/s-1}], \qquad (7)$$

where $\nu_0 \approx 10^{13}$ s^{-1} is the frequency factor; E_d is the energy of dissociation; n is the number of particles in a cluster; and $s = 3n - 6$ is the number of harmonic oscillators in it. The energies of dissociation for sputtered clusters Nb_n^+ and Ta_n^+ were determined in [8]. Table 2 presents the results from estimating the average

Table 1. Decay rate constants k and average lifetimes τ of metal clusters sputtered by SF_5^+ and Xe^+ ions

Ion		Decay	SF_5^+		Xe^+		Δk, %
			k, 10^3 s^{-1}	τ, 10^{-6} s	k, 10^3 s^{-1}	τ, 10^{-6} s	
Ag_n^+	Ag_5^+	$Ag_3^+ + Ag_2$	78.1	12.8	86.6	11.6	10.85
	Ag_7^+	$Ag_5^+ + Ag_2$	70.5	14.2	61.0	16.4	13.52
Au_n^+	Au_5^+	$Au_3^+ + Au_2$	67.8	14.8	59.8	16.7	11.69
	Au_6^+	$Au_5^+ + Au$	54.1	18.5	54.0	18.5	0.13
	Au_7^+	$Au_5^+ + Au_2$	60.1	16.67	55.0	18.2	8.46
	Au_8^+	$Au_7^+ + Au$	56.3	17.8	47.3	21.2	16.00
Cu_n^+	Cu_4^+	$Cu_3^+ + Cu$	98.8	10.1	100.6	9.9	1.79
	Cu_6^+	$Cu_5^+ + Cu$	93.4	10.7	96.3	10.4	3.00
Nb_n^+	Nb_5^+	$Nb_4^+ + Nb$	190.2	5.3	187.2	5.3	1.57
	Nb_8^+	$Nb_7^+ + Nb$	124.7	8.0	126.6	7.9	1.53
	Nb_9^+	$Nb_8^+ + Nb$	119.1	8.4	118.5	8.4	0.47
	Nb_{10}^+	$Nb_9^+ + Nb$	116.7	8.6	123.0	8.1	5.44
Ta_n^+	Ta_5^+	$Ta_4^+ + Ta$	193.9	5.1	201.1	5.0	3.72
	Ta_6^+	$Ta_5^+ + Ta$	166.4	6.0	172.8	5.8	3.83
	Ta_7^+	$Ta_6^+ + Ta$	181.9	5.5	161.2	6.2	11.37

Table 2. Average energies of excitation for sputtered Nb_n^+ and Ta_n^+ clusters

Ion	Decay	E_d, eV [8]	E_{excit}, eV	E_{excit}/atom, eV
Nb_5^+	$Nb_4^+ + Nb$	5.69	5.76	1.15
Nb_8^+	$Nb_7^+ + Nb$	5.84	6.31	0.79
Nb_9^+	$Nb_8^+ + Nb$	5.87	6.54	0.73
Nb_{10}^+	$Nb_9^+ + Nb$	6.88	7.93	0.79
Ta_5^+	$Ta_4^+ + Ta$	7.02	7.10	1.42
Ta_6^+	$Ta_5^+ + Ta$	5.52	5.68	0.95
Ta_7^+	$Ta_6^+ + Ta$	8.34	8.78	1.25

energies of excitation for the number of Nb_n^+ and Ta_n^+ clusters that fragmenting in the above time ranges. Within the accuracy of the experiment, these energies are independent of the number of particles in a primary ion.

CONCLUSIONS

Our investigations show that the fragmentation of metal clusters in the time range of 10^{-7} to 10^{-3} s after emission does not depend on the nature of the bombarding ions. We may conclude the number of atoms in a primary ion has no effect on the fragmentation processes or on the energies of excitation of the sputtered cluster particles, at least within the investigated energy range and at relatively low masses of the bombarding polyatomic particles. Our experiments confirm the findings of [20, 21] and are evidence that the nature of the processes behind the release of energy from the

primary ions is not reflected directly in vibrational excitement or in sputtered cluster fragmentation.

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