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Nonadditive sputtering of silicon by keV energy molecular projectiles of heavy and light elements

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Abstract

In the present work a positive secondary ion emission from a silicon produced by Au_m^- projectiles (m = 1–3) with energies of E_0 = 9 and 18 keV and by Al_m^- projectiles (m = 1,2) with energies of E_0 = 6, 9, 12, and 18 keV have been studied. Anomalous high nonadditivity of sputtering as large cluster Si_n^+ ions (n > 4) under molecular Au_m^- ion bombardment has been found. As compared with heavy (Au_m^-) projectiles, the light (Al_m^-) projectiles are not effective for sputtering of large cluster ions. For molecular Al_m^- ion bombardment nonadditivity of sputtering of small cluster Si_n^+ ions (n ≤ 4) increases with decreasing of the energy E_0 from 9 to 6 keV/atom. This effect shows that the efficiency of nonadditive sputtering strongly depends on the penetration depth of molecular projectile and, hence, on the energy density deposited by molecular projectile into subsurface layers of the target from which the cluster ion emission occurs. (Int J Mass Spectrom 209 (2001) 141–152) © 2001 Elsevier Science B.V.

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1. Introduction

During the past years processes of solid sputtering by molecular projectiles have been studied actively [1,2]. Such studies are of both fundamental and applied interest. It is well known that the bombardment of heavy metals [3–5] as well as a silicon [6] by heavy molecular projectiles with energies of E_0 = 10–250 keV/atom leads to a nonlinear increase in the total sputtering yield Y_m. Here, $Y_m = \Sigma_n Y_{n,m}$ is the yield of all sputtered particles in both neutral and charged states (m and n are numbers of atoms in a molecular projectile and in a sputtered particle, respectively). It is a common practice to quantitatively describe this enhanced sputtering process using a nonadditivity factor $K_{m,1}$ (or an enhancement factor), which can be defined as:

$K_{m,1} = Y_m / mY_1$ for the total sputtering yield;
$K_{m,1} = Y_{n,m} / mY_{n,1}$ for the separate components of sputtering.

In this case, the yields Y_m, $Y_{n,m}$, Y_1, and $Y_{n,1}$ have to be measured for projectiles with the same velocities.

As was found in [3–6], the values of $K_{2,1} = Y_2/2Y_1$ does not exceed several units. For example, in [4] the Bi-Bi_2 nonadditivity factor $K_{2,1}$ for the total

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gold sputtering yield Y_m was found to be 2.5 at 30 keV/atom and 3.9 at 45 keV/atom.

To interpret these experimental observations [3–l6], it has often been assumed that nonlinear regimes of sputtering described by a shock wave model [7], a thermodynamical model [8], or a collision spike model [9], led to the nonadditivity of the process. However, theoretical models [7–9] are not capable of explaining all features of nonadditive sputtering. To clarify the reasons for nonadditive sputtering it is necessary to know the factors $K_{m,1}$ for separate components of sputtering, including neutral and charged clusters with n atoms.

In the past decade, a method of neutral particle detection based on laser post ionization of sputtering neutral products and time-of-flight mass spectrometry was developed. Using this method, the emission of neutral atom and cluster was studied in a series of experiments [10–14] where it has been found that neutral atoms dominate in the total yield of secondary particles. Hence, determined in [3–6], nonadditivity of yields Y_m is mainly defined by nonadditive sputtering of neutral atoms. However, in experiments [10–14], the atomic ions were used only as projectiles. Therefore, nonadditive sputtering in the form of neutral clusters still has to be studied.

Information on nonadditive sputtering of both atomic and cluster ions from different kinds of targets can been found in [15–26]. For keV energy range of polyatomic projectiles fundamental studies of secondary ion emission from organic, inorganic, and metal targets have been carried out by the groups of Delmore [15], Le Beyec and Schweikert [16], and Cooks [17]. They found that both nonadditivity of sputtering and the fragmentation of secondary ions depend strongly on the projectile parameters. The efficiency of nonadditive sputtering increase with the rise of the incident energy E_0, the mass M of projectile, and the number m of atoms in projectile [15–17] while the degree of fragmentation is proportional to the factor *m/v*, where *v* is the velocity of the primary ion [17]. For the very large energy range of projectiles (4 keV/atom $< E_0 <$ 10 MeV/atom), important results were obtained by Le Beyec's group [18–21]. They observed the strong nonadditive effects in emission of large clusters from inorganic and organic solids under bombardment by heavy polyatomic projectiles of MeV energy [18] as well as by ones of keV energy [19]. Recently, they found a general experimental trend, according to which both the maximum rate of ion emission [21] and the highest total sputtering yield Y_m [19] are observed at much lower velocity than the velocity of the maximum nuclear stopping power. For Au_4^+ projectiles, this velocity corresponds to the energy of 30 keV/atom. These results show clearly that the features of nonadditive sputtering and the well-known peculiarities of linear sputtering process produced by atomic ion bombardment are different.

It should be note that in [15–21], nonadditive sputtering was studied only for separate secondary atomic or polyatomic ions. Such an experimental approach limits the possibilities of measurements due to it does not permit to study the peculiarities of nonadditive sputtering for different secondary ions sputtered from the same target (for example, for small and large cluster ions of the same element) in identical sputtering conditions. However, nonadditive sputtering originates from the interaction between molecular projectiles and the subsurface region of solids and, therefore, the efficiency of such a process must depend not only on the parameters of projectiles but also on the species of sputtered particles.

In this context, it is interesting to study the nonadditive sputtering of a wide variety of secondary ions using molecular projectiles with low energy ($E_0 <$ 10 keV/atom). Detailed studies of nonadditive sputtering of various Ta_n^+ (n = 1–13), Nb_n^+ (n = 1–16), and Si_n^+ (n = 1–17) ions under bombardment of Ta, Nb, and Si targets by atomic and molecular Au_m^- ions (m = 1–3) with the energy of E_0 = 6 and 9 keV/atom were carried out in [22–26,28–30]. The results of these works show that the main peculiarities of nonadditive sputtering are determined by both the parameters of projectiles and the species of sputtered particles. Let us represent the some of them.

- There are two different mechanisms of cluster ion emission for small (n ≤ 4) and large (n > 4) clusters.

- The efficiency of fragmentation of sputtered ions increases with the rise of cluster size and the number m of atoms in projectile.
- Sputtering of all the mass spectra components is nonadditive.
- The nonadditivity factors $K_{m,1}$ are different for different ion components in the sputtered flux. The value of $K_{m,1}$ increases strongly with the cluster size and for given n increases with the rise of m.

It was found that for atomic ions the nonadditivity factors $K_{m,1}$ are slightly greater than 1, while for cluster ions, $K_{m,1}$ increases sharply with the rise of the cluster size. For $n > 5$ the values $K_{m,1}$ reach 100–700. This dramatic increase of the nonadditivity of the cluster ion emission for increasing n and m values has been called "the effect of anomalously high nonadditivity of sputtering in the form of large cluster ions under bombardment of metals and semiconductors by molecular projectiles" [23–26].

Possible origins of a large neutral cluster ($n > 4$) emission were considered in [27], where a theoretical model capable of describing peculiarities of the process was proposed. In this model the binding energy between atoms in the impact region of sputtered metals is used as fitting parameter. A comparison of experimental data [14] (mass spectra of the Al_n, Ag_n, Nb_n, and Ta_n neutral clusters sputtered from the Al, Ag, Nb, and Ta targets by atomic Ar^+ projectiles with the energy of 5 keV) with the calculated ones [27] shows a satisfactory agreement if well-known tabled values of the binding energy are used. It is important that the experimental results obtained in [23–25] for Nb_n^+ and Ta_n^+ cluster ions can be directly compared with calculations of the model [27] because, as it was shown in [28], the anomalous high nonadditivity of sputtering in the form of large Nb_n^+ and Ta_n^+ cluster ions ($n > 4$) under molecular ion bombardment originates from nonadditive sputtering rather than processes associated with the charge state formation of sputtered particles. In the case of the molecular ion bombardment, such a comparison gives a good agreement when the smaller values of the binding energy are used [27]. This postulated feature of the molecular ion bombardment was confirmed experimentally. Indeed, in [29] an analysis of kinetic energy distributions of Nb^+ and Ta^+ ions sputtered from Nb and Ta targets by monomer, dimer, and trimer Au_m^- projectiles shown the decrease of the binding energy in going from the monomer projectiles to the dimer and trimer ones. Thus, the results [23–29] highlight the important role of the binding energy decrease, induced by the heavy molecular bombardment in nonadditive sputtering formation. The possible reason for the decrease of the binding energy can be connected with the electronic subsystem excitation in metals produced by molecular projectile bombardment [30].

The mentioned above results [18–26,28–30] have been obtained under the bombardment of various targets by heavy molecular projectiles. Until now, there are no systematic studies of nonadditive sputtering of solids by light molecular projectiles. For heavy and light molecular projectiles there are strong differences in the solid penetration as well as in the energy loss of primary ions. That is why it is interesting to compare the characteristics of nonadditive sputtering under bombardment of the same target by atomic and molecular projectiles of light and heavy elements in identical experimental conditions.

In this work, for the first time, the relative yields $Y_{n,m}$, mass spectra $Y_m(n)$, and nonadditivity factors $K_{m,1}$ of the secondary atomic and cluster Si_n^+ ion emission from a silicon produced by heavy [Au_m^- ($m = 1$–3)] projectiles with energies of $E_0 = 9$ and 18 keV and by light [Al_m^-($m = 1,2$) and Si_m^- ($m = 1-3$)] projectiles with energies of $E_0 = 6$, 9, 12, and 18 keV have been measured. The comparison and discussion of the results obtained, as well as the analysis of the experimental conditions, leading to the more effective generation of sputtered atomic and cluster ions are presented.

2. Experimental

Two experimental setups were used to study a secondary ion emission. The first home made experimental secondary ion mass spectrometry (SIMS) instrument used was described earlier in detail [23,25]. To study the cluster ion emission under atomic and molecular ion bombardment, a modified standard magnet mass spectrometer was equipped with negative Al_m^- and Au_m^- cluster ion sources [31], a primary ion column, a target assembly, and a secondary ion optical system. The column included a mass separator and an optical system for primary ions. In the present experiments, the Al_m^- (m = 1,2) and Au_m^- (m = 1–3) ions bombarded the target at an incidence angle of 45°. The incident energy E_0 of primary ions was 6, 9, 12, and 18 keV. The current density, j, of projectiles had a typical value of j $\sim 10^{-6}$ A/cm^2.

Monocrystalline silicon was chosen as a target because silicon is the basic material for the semiconductor technology. The specific resistance, ρ, of this metallike semiconductor sample was $\rho = 7$ Ωcm. The cleaning procedures included both the heating and the ion sputtering of the target. To get a clean Si sample, it was heated up to a temperature of about 1400 K and it was then cleaned by the Au^- or Al^- ion bombardment during several hours. The yields of SiO^+ ions sputtered from the Si surface by Au^- or Al^- projectiles were controlled before and after the cleaning procedures. They were observed to drop by more than two orders of magnitude after the cleaning procedures applied. Since the probability of chemical reactions increases on hot solid surface, we believe that this drop in the SiO^+ yield indicates a corresponding decrease in the oxygen concentration on the target surface. The Si surface prepared in such a way was believed to be "clean surface". During the measurement, the temperature of the Si target was maintained at 1400 K also and the residual pressure did not exceed the value of 1×10^{-5} Pa. The mass spectra Y(n) of secondary ions were measured by magnetic scanning. To make a comparison between the relative yields of secondary ions, their intensities were normalized according to the ratio of the corresponding primary ion currents.

The second experimental set up was a standard Cameca IMS 4f instrument. The cesium sputter ion source developed in the framework of NATO SfP Project 97.1929 [32] was mounted directly on a Cameca IMS 4f instrument in the place of the standard duoplasmatron source without any additional ion-optical system. The Si_m^- primary ion flux is generated during bombardment of a silicon target by Cs^+ ions with the energy of 7.5 keV (the Cs^+ ion current was 60 μA). The primary accelerating voltage was −7.5 kV. The mass spectrum of the primary ion beam from the sputter ion source using the silicon target consists of the Si_m^- ion (m = 1–6) peaks. Typical primary Si_m^- ion currents (as measured with the primary Faraday Cup of the instrument) were 5.6, 2.8, and 0.48 nA for Si^-, Si_2^-, Si_3^- and 85, 28, and 6.3 pA for Si_4^-, Si_5^-, and Si_6^- ions. The secondary accelerating voltage applied to a silicon target was +4.5 kV. So, the impact energy E_0 of primary Si_m^- projectiles was 12 keV. The primary silicon atomic and cluster beams focused on the sample surface to a spot size of a 60μm. The raster-scanned area was in the range (150 μm)^2. In these experiments, a silicon target had the room temperature.

3. Results and discussion

The results obtained are represented in following consequence. Firstly, the comparative study of secondary ion emission from a silicon target produced by atomic and molecular projectiles of heavy (Au) and light (Al) elements are discussed in Sec. 3.1. Secondly, analysis of sputtering conditions that allows obtaining larger yields of secondary ions is given in Sec. 3.2. Finally, the peculiarities of the secondary ion emission from silicon produced by atomic, dimer, and trimer Si_m^- projectiles are presented in Sec. 3.3.

3.1. The comparative study of secondary ion emission from silicon produced by Au_m^-(m = 1–3) and Al_m^-(m = 1,2) projectiles

The normalized mass spectra Y(n) of secondary Si_n^+ ions sputtered from the silicon target by Au_m^- (m = 1– 3) projectiles with energy E_0 = 9 and 18 keV and by Al_m^- (m = 1,2) projectiles with energy E_0 = 6, 9, 12, and 18 keV in the identical experimental conditions are presented in Figs. 1(a) and 1(b), respectively.

As can be seen from Fig. 1(a), under Au^-, Au_2^-,

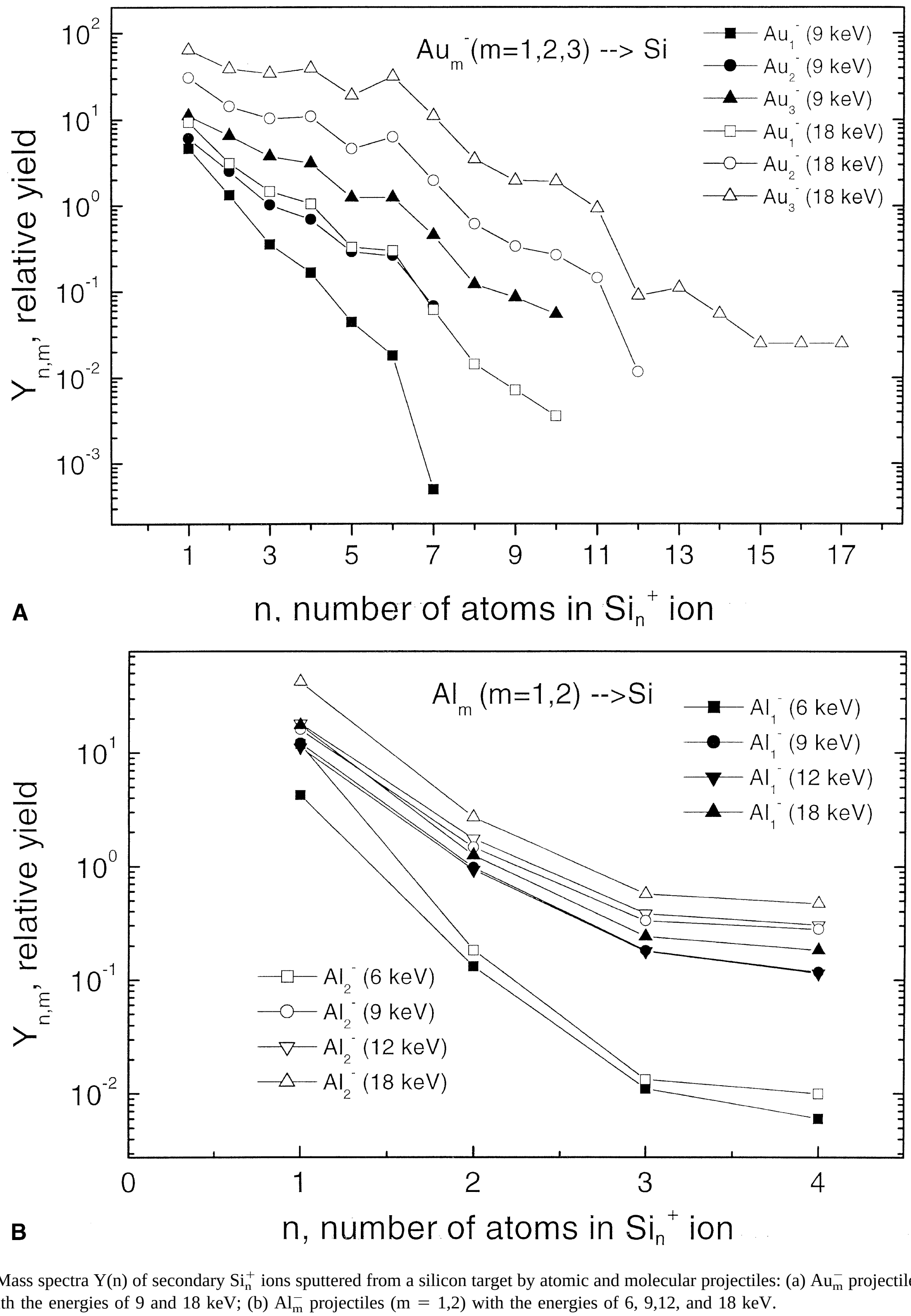


Fig. 1. Mass spectra Y(n) of secondary Si_n^+ ions sputtered from a silicon target by atomic and molecular projectiles: (a) Au_m^- projectiles (m = 1–3) with the energies of 9 and 18 keV; (b) Al_m^- projectiles (m = 1,2) with the energies of 6, 9,12, and 18 keV.

and Au_3^- ion bombardment, mass spectra show peaks that correspond to the sputtered Si_n^+ ions with n up to n = 17. The efficiency of the large cluster sputtering increases strongly with the rise of both the incident energy E_0 and the number m of atoms in the projectile.

It is interesting that under Al^- and Al_2^- ion bombardment [Fig. 1(b)], mass spectra show peaks that correspond only to the Si_n^+ ions with $n \leq 4$. Thus, the bombardment of silicon by light atomic Al^- and molecular Al_2^- projectiles does not lead to sputtering of large cluster ions ($n > 4$).

By using these data, one can estimate the ratios between the yields of atomic and large cluster ions. For the range of $4 \leq n \leq 10$, these ratios $Y_{1,m}\Sigma_{n=4}^{10}Y_{n,m}$(18 keV) have the following values: 5.4 and 0.59 for Au^- and Au_3^- projectiles and 100 and 84 for Al^- and Al_2^- projectiles, respectively. Therefore, in changing from atomic Au^- ion bombardment to molecular Au_3^- bombardment, an essential increase in the contribution of large clusters to the total yields of charged particles is observed. On the contrary, Al^- and Al_2^- projectiles are considerably less effective for cluster ion generation. In connection with this, further comparison of results obtained under bombardment of silicon by heavy and light projectiles will be made for secondary ions with $n \leq 4$.

The bombardment by molecular ions can result in nonadditive effects that manifest themselves as a nonlinear dependence of the emission yields on the number m. As mentioned previously, the nonadditive effect is described by the nonadditivity factor $K_{m,1}$. The different forms of dependence of $K_{m,1}$ on cluster size are shown in Figs. 2(a) and 2(b). In the case of Au_m^- bombardment with the energy of $E_0 = 9$ keV/atom for atomic Si^+ ions, $K_{2,1}$ is 2.5 [see Fig. 2(a)]. This value of $K_{2,1}$ is consistent with the well-known data obtained for total sputtered yield Y_m [3–6] or (see Sec. 1) for the yield of sputtered neutral atoms. For cluster ion emission, a dramatic increase of $K_{2,1}$ with the rise of cluster size was determined. For example, for Si_4^+ and Si_6^+ cluster ions, the values of $K_{2,1}$ are equal to $K_{2,1} = 40$ and $K_{2,1} = 200$, respectively. Thus, these results demonstrate the effect of the anomalous high nonadditivity of Si_n^+ cluster ion sputtering under bombardment of silicon by molecular Au_m^- projectiles with the energy of $E_0 = 9$ keV/atom. The effect increases with cluster size.

In the case of Al_m^- bombardment with the same energy per atom in projectile, for atomic Si^+ ions the value $K_{2,1}$ is 1.7 [see Fig. 2(b)], while, as compared to the Au_m^- ion bombardment, for cluster ion emission, we have much smaller values of $K_{2,1}$. For instance, for Si_4^+ cluster ions the value of $K_{2,1}$ is only 2.

Thus, a comparison of results obtained for Si_n^+ ions sputtered from silicon by Au_m^- and Al_m^- projectiles with the energy of $E_0 = 9$ keV/atom shows that under the Au_m^- bombardment the nonadditive effect in cluster ion emission is much higher than that under the Al_m^- bombardment.

The essential difference in the nonadditive effect may be connected with the peculiarities of an interaction of heavy and light projectiles with a silicon lattice. Indeed, for heavy atomic projectiles, the collision cross-section with Si atoms is great and the projectile energy E_0 is basically deposited within several subsurface layers of a lattice. This corresponds to optimal conditions of a large cluster generation, which are justified by the results of molecular dynamics simulations of cluster emission in sputtering [33,34]. Bombardment by heavy molecular projectiles leads to the formation of an "impact" region near the target surface. It is important that constituent atoms of projectile move together in the target matter because there is the strong difference in masses of Au and Si atoms ($M_{Au} \gg M_{Si}$). Such a correlated movement of constituent atoms of Au_m^- projectile leads to the essential increase of the energy density deposited into the impact region. One can modify properties of this region and stimulate the origin of anomalous high nonadditivity of sputtering of large cluster ions. Possible variants of a modification of lattice properties under the molecular bombardment are discussed in Sec. 1.

The bombardment of silicon by light atomic projectiles with the same energy E_0 is characterized by the small value of the collision cross section. The light projectiles penetrate deeper into a lattice and their energy E_0 is deposited, in general, far away from the target surface. In this case, as compared to heavy atomic ion bombardment, the yield of cluster sputtering decreases. Bombardment by light molecular pro-

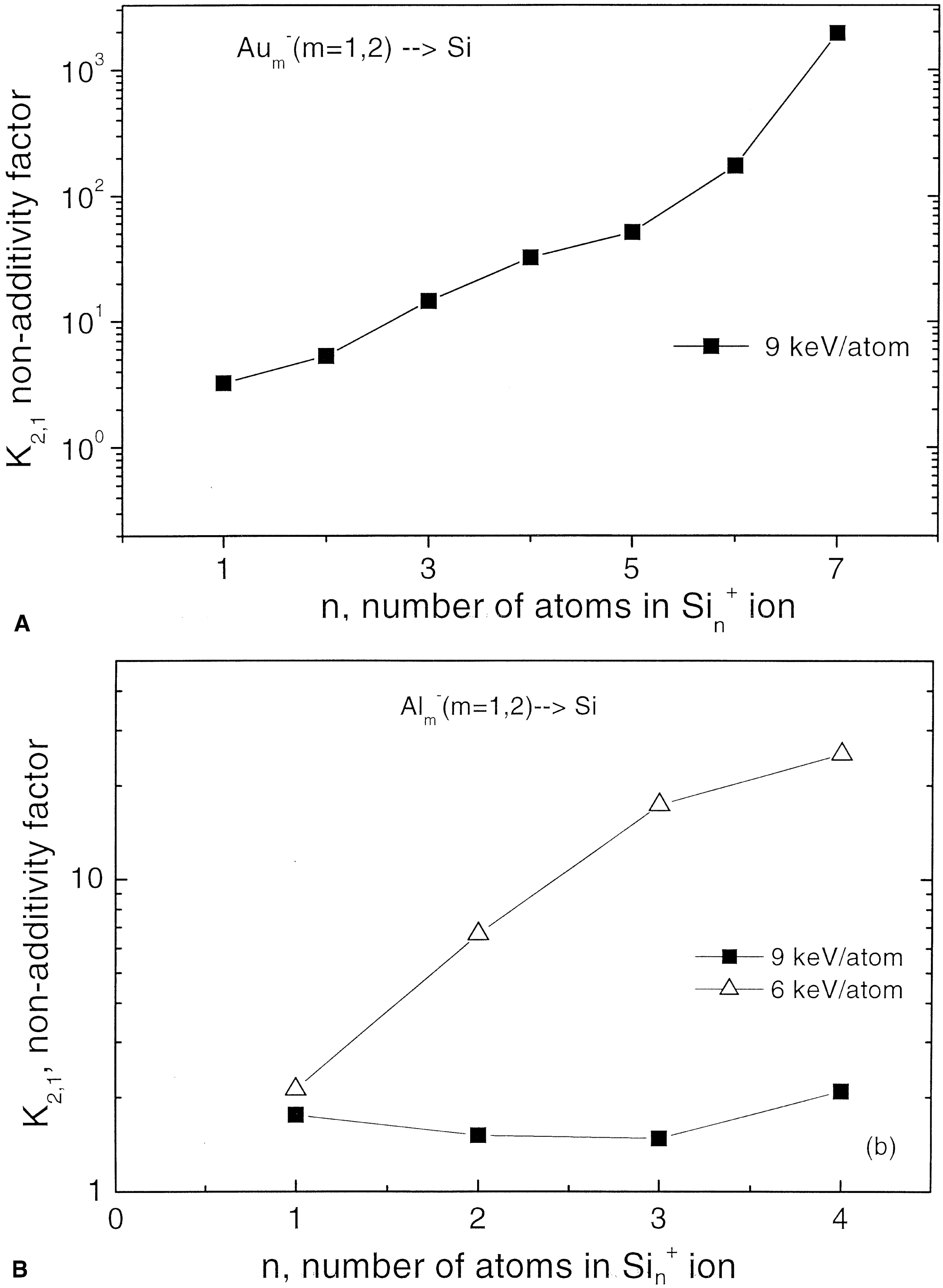


Fig. 2. Dependence of the nonadditive factor $K_{2,1}$ on the number n of atoms in the Si_n^+ ions sputtered from a silicon target by (a) Au_m^- projectiles with the energy of 9 keV/atom and (b) Al_m^- projectiles with the energies of 6 and 9 keV/atom.

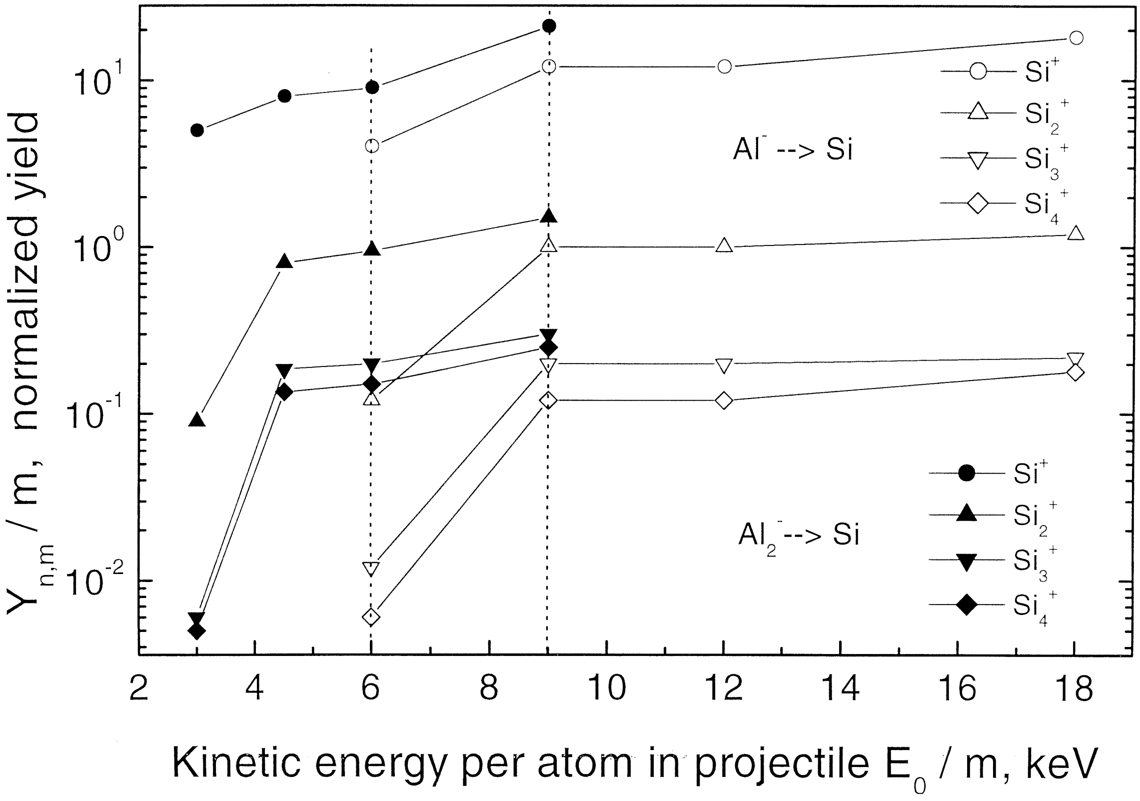


Fig. 3. Dependence of the normalized yield $Y_{n,m}/m$ of sputtered Si_n^+ ions on the kinetic energy E_0/m per one atom in Al_m^- projectiles.

jectiles may lead also to the formation of a region with modified properties. However, as compared to heavy molecular ion bombardment, the energy density deposited by constituent atoms of light molecular projectile is smaller because these atoms are scattered effectively and do not move together in the target matter ($M_{Al} \approx M_{Si}$). Moreover, such a region is located deep below the surface. These factors must decrease the energy density deposited by Al_m^- projectile into subsurface layers of the target and, therefore, the efficiency of nonadditive sputtering. Thus, in the framework of such a consideration, the nonadditivity of sputtering must depend on the energy density deposited by molecular projectile into several subsurface layers of the target from which the secondary cluster ion emission occurs. The energy density is proportional to a product E_0L^{-1}, where L is the penetration depth of projectile (L^{-1} decreases in a complicated way with the rise of the incident energy E_0). In this context, for any given combination "molecular projectile-target" exists the optimal value of the incident energy E_0 (keV/atom) which leads to maximum of $K_{m,1}$.

Such an explanation was confirmed by the results that were obtained under the bombardment of silicon by Al^- and Al_2^- projectiles with the energy of $E_0 = 6$ keV/atom. As shown in Fig. 2(b), the decrease in energy from $E_0 = 9$ to 6 keV/atom leads to a small increase in the nonadditive factor $K_{2,1}$ for atomic Si^+ ions and to a dramatic one for cluster Si_n^+ ions. Indeed, for Si^+ and Si_4^+ ions the values of $K_{2,1}$ are equal to $K_{2,1} = 2.1$ and $K_{2,1} = 25$, respectively.

The reasons for the increase in the factor $K_{2,1}$ with the decrease in E_0 can be illustrated by results in Fig. 3 where the dependence of secondary Si_n^+ ion yields $Y_{n,m}/m$ on energy E_0/m are presented. Here $Y_{n,m}/m$ and E_0/m are the yield and the energy, respectively, reduced to one atom in projectile. Indeed, for Al^-

(m = 1) monomer bombardment, the yields $Y_{n,1}$ of all Si_n^+ ions (n = 1–4) sharply increase with the rise of energy E_0 from 6 to 9 keV, and then with the further rise of E_0 from 9 to 18 keV they remain unchanged or slightly increase. For Al_2^- (m = 2) dimer bombardment, the sharp increase in $Y_{n,m}/m$ is observed within the range of smaller values of E_0/m (3–4.5 keV/atom), and then for the further increase in E_0/m from 4.5 to 9 keV/atom the change in $Y_{n,m}/m$ is small. Thus, the essential decrease in the nonadditivity factor $K_{2,1}$ with the rise E_0/m is connected with the difference in the energy ranges where the sharp increase in $Y_{n,m}/m$ is observed under monomer and dimer bombardment. According to data in Fig. 3, the larger difference in $Y_{n,m}/m$ is observed for $E_0/m = 6$ keV/atom.

It is important to note that with the rise of E_0, the increase in yields of all secondary Si_n^+ ions is observed under both atomic and molecular bombardment. In other words, yields of secondary ions depend on the incident energy E_0 deposited by projectiles into the target. Alongside with this, the decrease in the nonadditivity factors $K_{2,1}$ with the rise of E_0/m indicates that the efficiency of nonadditive sputtering depends not only on the incident energy E_0 but also on the penetration depth of projectiles. The decrease of the penetration depth allows the energy deposited by molecular projectile to be concentrated in the region near the target surface where the change of lattice properties can stimulate the enhancement of nonadditive sputtering of atomic and cluster ions. This conclusion is justified by the comparison of the yields of secondary ions sputtered by atomic and molecular projectiles with the same energy E_0. Indeed, in this case, energies deposited in the target matter by atomic and molecular projectiles are equal while the yields of secondary ions sputtered under molecular bombardment essentially exceed the corresponding yields measured under atomic bombardment.

3.2. Analysis of sputtering conditions leading to the larger yields of secondary ions

As mentioned above, silicon is the basic material for the semiconductor technology. That is why the search of experimental conditions leading to the larger yields of secondary ions from silicon is considered of practical interest. From this point of view it is interesting to compare the relative yields of secondary Si_n^+ ions not only for the same energy E_0 per atom in projectile, but also for different used values of E_0.

From the analysis of mass spectra presented in Figs. 1(a) and 1(b), one can detect the following main peculiarities:

- The ratios of secondary ion yields from silicon depend on both the projectile parameters and the species of sputtered particles. They strongly increase with the rise of the incident energy E_0, the mass of constituent atom in projectile, the number m of atoms in projectile as well as the number n of atoms in sputtered particle. For Au_3^-(18 keV) and Au^-(9 keV) projectiles the ratios of yields for Si^+, Si_4^+, and Si_6^+ ions are: $Y_{1,3}$(18 keV):$Y_{1,1}$(9 keV) = 13.7:1, $Y_{4,3}$(18 keV):$Y_{4,1}$(9 keV) = 235:1, and $Y_{6,3}$(18 keV):$Y_{6,1}$(9 keV) = 1750:1 respectively. Under Al_m^- bombardment, these ratios for Si^+ and Si_4^+ ions are much less: $Y_{1,2}$(18 keV) : $Y_{1,1}$(9 keV) = 3.5 : 1 and $Y_{4,2}$(18 keV) : $Y_{4,1}$(9 keV) = 4.1 : 1
- For Au_m^- projectiles with the given energy of E_0 = 18 keV, the ratios of ion yields increase sharply with the rise of n. For Si^+, Si_4^+, Si_6^+, and Si_{10}^+ ions these ratios reach the following values: $Y_{1,3}$: $Y_{1,1}$ = 6.8 : 1, $Y_{4,3}$: $Y_{4,1}$ = 37 : 1, $Y_{6,3}$: $Y_{6,1}$ = 105 : 1, and $Y_{10,3}$: $Y_{10,1}$ = 536 : 1. For Al_m^- projectiles with the same energy, the ratios of ion yields increase only slightly with the rise of n. For Si^+ and Si_4^+ ions these ratios are: $Y_{1,2}$: $Y_{1,1}$ = 2.3 : 1 and $Y_{4,2}$: $Y_{4,1}$ = 2.7 : 1.
- For given projectile energy E_0, the ion yields increase with the rise of m. For Au_m^- projectiles with energies of E_0 = 9 and 18 keV, the ratios of the Si_4^+ ion yields are: $Y_{4,3}$: $Y_{4,2}$: $Y_{4,1}$ = 19 : 4 : 1 and $Y_{4,3}$: $Y_{4,2}$: $Y_{4,1}$ = 37 : 10 : 1, respectively. For Al_m^- projectiles with the energies of E_0 = 9 and 18 keV, the corresponding ratios of Si_4^+ ion yields are only: $Y_{4,2}$: $Y_{4,1}$ = 2.25 : 1 and $Y_{4,2}$: $Y_{4,1}$ = 2.77 : 1.

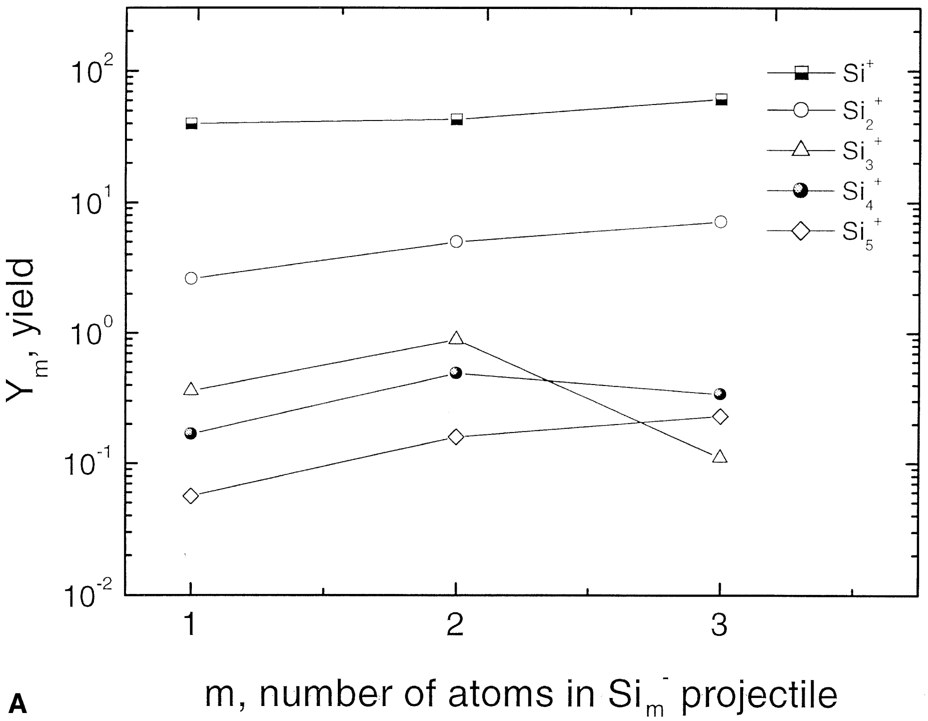
The analysis of sputtering conditions leading to the increase of the secondary ion emission from a silicon under bombardment by heavy and light atomic and molecular projectiles can be used for a prediction of main sputtering features for the other combination "projectile target". As an example, one can illustrate the features of secondary ion emission from a silicon produce by Si_m^- projectiles ($m = 1-3$) with the energy of $E_0 = 12$ keV.

3.3. *Secondary ion emission from silicon produced by Si_m^- projectiles ($m = 1$–3)*

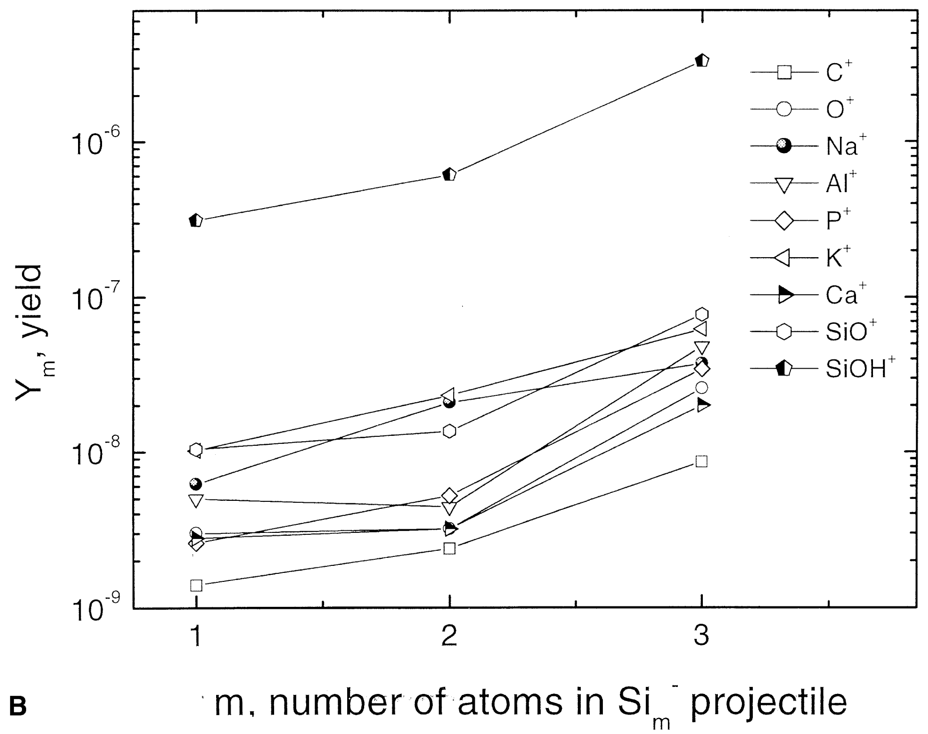
A second experimental set up (Cameca IMS 4f instrument) was used for a study of the relative yields and the mass spectra of positive secondary ions sputtered from a silicon by Si^-, Si_2^-, and Si_3^- projectiles with the energy of $E_0 = 12$ keV. All mass spectra obtained consist of peaks corresponding to the principal components of the target matter [atomic and cluster Si_n^+ ions ($n = 1-5$)], the impurities present in the sample (C^+, O^+, Na^+, Al^+, P^+, K^+, and Ca^+ ions) and the complex molecules (SiO^+ and $SiOH^+$ ions). A comparison of these data shows the following general trends [see Figs. 4(a) and 4(b)]. Secondary ion yields normalized according to the ratio of the corresponding primary ion currents are increased, as a rule, in going from the atomic ion bombardment to the dimer and trimer bombardment. Yields of impurity and complex molecular ions increase up to a factor of 5–12 while yields of atomic and cluster Si_n^+ ions increase up to a factor of 1.5–3 only have been observed when silicon is bombarded with Si_3^- instead of Si^-. The difference in yield enhancements of these ions may be connected with a fact that impurity atoms and complex molecules, as compared with Si atoms, have a smaller binding energy on the silicon surface. Thus, results obtained correspond approximately to the previously mentioned conclusions (see Sec. 3.2). They confirm the trend according to that sputtering of light targets by both atomic and molecular projectiles of light elements does not lead to the effective emission of large cluster ions. Results related to the more effective increase in yields of impurity and complex molecular ions, as compared to the atomic and cluster Si_n^+ ions, can be useful for practical applications, for example, for SIMS elemental analysis. Indeed, for given incident energy E_0, the use of molecular ions as projectiles instead of single atomic ions would be much more effective for analytical measurements of low-level impurities on Si surface.

4. Concluding remarks

Comparative studies of secondary ion emission from silicon produced by atomic and molecular projectiles of heavy and light elements have been carried out. The results obtained demonstrate the strong nonadditive effect in cluster Si_n^+ ion sputtering ($n = 1$–17) under the bombardment by heavy molecular (Au_m^-) projectiles with energy of 9 keV/atom. This effect manifests itself in the mass spectra as a dramatic increase in the relative yield of large cluster ions with the rise of cluster size and the number of atoms in projectile. As compared with the heavy molecular Au_m^- ions, the bombardment of silicon by light molecular (Al_2^-) projectiles with the same energy of 9 keV/atom does not lead both to sputtering of large cluster ions ($n > 4$) and to the strong nonadditive effect in sputtering of small cluster ions ($n \leq 4$). Thus, the Al_m^- projectiles ($m = 1,2$) are not effective for large cluster ion emission. It is shown that the decrease in the energy of Al_m^- projectiles from 9 to 6 keV/atom leads to the strong increase in the efficiency of nonadditive sputtering of small cluster ions. This indicates that the efficiency of nonadditive sputtering depends not only on the incident energy E_0 deposited by molecular projectile but also on the penetration depth of the projectile. The decrease in the penetration depth leads to the increase of the energy density deposited by molecular projectile into subsurface layers of the target from which the cluster ion emission occurs. Analysis of results obtained shows that the yield of a given sputtered ions increases with the rise of the incident energy E_0, the mass of constituent atom of projectile as well as the number m of atoms in projectile.



A



B

Fig. 4. Dependence of the normalized yields of different sputtered ions on the number m of atoms in the Si_m^- projectiles (m = 1–3): (a) Si_n^+ ions (n = 1–5); (b) C^+, O^+, Na^+, Al^+, P^+, K^+, Ca^+, SiO^+, and $SiOH^+$ ions. The impact energies for all projectiles used are equal to 12 keV.

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