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Effect of projectile parameters on charge state formation of sputtered atoms

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In the majority of the electron-exchange models, it is assumed that the charge state formation processes of atoms sputtered (scattered) from a solid do not depend on projectile parameters. This means that an electronic subsystem excitation produced by projectiles in the impact region does not affect on the ionization probability P^+ of ejected atoms. In the present work this basic assumption has been subjected to experimental examination. To study it the clean surface of a silicon sample was bombarded by the following atomic and molecular projectiles: Al^- ions with the energy of $E_0 = 9$ and 18 keV; Au^- ions with $E_0 = 18$ keV; Al_2^- ions with $E_0 = 4.5$ and 9 keV/atom. The kinetic energy distribution $f(E)$ of sputtered Si^+ ions were used to obtain information on P^+. It was found that the ionization probability P^+ depends on the projectile parameters increasing with the rise of energy E_0, mass M_0, and the number m of atoms in projectile. The results obtained are discussed in the framework of the simple model in which the charge state formation occurs in the electron exchange between the sputtered atom and a local surface area where the relaxation of the electronic subsystem excited by the projectile impact takes place.

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I. INTRODUCTION

It is well known that the bombardment of solids by keV energy atomic projectiles leads to sputtering of particles in different charge states.[1] The secondary atomic ion yield depends on species, the velocity ν, and the escaping angle θ of the ejected particles, and the electronic structure of the surface.[2] According to existing theoretical ideas, the ion formation process is the atom-surface interaction. Using a ''wide-band model,'' this interaction is considered either as a time-depended perturbation[3–5] or as an electron-exchange process between a valence level ε_a of the ejected atom and the delocalized states of the metal.[6–10] Usually an ionization probability P^+ in positive-ion emission is estimated by the expression obtained in a quantum-mechanical treatment (the zero-temperature limit) by Blandin, Nourtier, and None[4] and by Norskov and Lundqvist[5] and by Brako and Newns:[8]

$$P^+ = \frac{2}{\pi}\exp(-\pi C_1[I-\varphi]/\hbar\gamma\nu_z)\exp(-\pi C_2/\hbar\gamma\nu_z) \propto \exp(-\nu_0/\nu_z), \qquad (1)$$

where ν_0 is the ionization parameter; C_1 and C_2 are constants in a linear interpolation scheme, which accounts for the variation in the effective difference between the ionization potential I and the work function φ, as a sputtered atom moves outward from the surface; $1/\gamma$ is a characteristic decay length; $\nu_z = \nu\cos\theta$ is the normal component of the emission velocity; $\hbar$ is Plank's constant. For atoms sputtered from adsorbed layers on metallic surfaces (in this case the level ε_a intersects the Fermi level ε_F of a solid on the distance z ∼several Å from the surface), the experimental dependence of P^+ on the velocity ν_z, the angle θ and the work function φ has been explained well by electron-tunneling models[7,8] while the attempts to describe the ion emission from clean metal surfaces (when the level ε_a does not cross ε_F) have met no success, or only very limited success.[2]

In models,[3–10] it is assumed that the charge state formation processes do not depend on the projectile parameters [see Eq. (1)]. Strictly speaking, it does not correspond to the sputtering reality, because the atom ejection is a result of several many-body collisions in the subsurface region. When atoms leaving a solid, they interact with the local surface area where both the electronic subsystem and the lattice structure are perturbed by a continuing collision cascade.

The analytical description of the charge state formation when the structural and electronic properties of the sputtering region are changed in time is very complex and it still has not been made. The computer simulations of this task have been carried out by Šroubek *et al.*[11] and Garrison *et al.*[12] for a limited number of atoms in a substrate. In Ref. 11, for a cluster substrate consisting of five atoms, it was shown that the velocity dependence of P^+ is much smaller than the exponential dependence described by Eq. (1). Using larger number of atoms (up to 18), in Ref. 12 was found that the velocity dependence of P^+ ranges from a power law ν^n dependence where n is between 2 and 4 at small ν to an exponential dependence on $1/\nu_z$ when the interaction is stronger.

The affect of the electronic excitation on the charge state formation of sputtered atoms was considered analytically in Refs. 13–16. Invoking a combination of the wide-band structure and the collision effects, Nourtier, Jardin, and Quazza[13] proposed the model, in which the sputtered atom is pushed by another atom, itself interacting with the rest of the solid. It was shown that for the clean metal surface sputtering the ionization process due to the collision effect is similar to Landau-Zener mechanism (the interaction of atoms in the quasimolecule). This ionization process manifests itself, making the velocity dependence of P^+ ''less'' exponential and ''more'' power-law-like.

In the nonequilibrium thermodynamic model of Šroubek[14–16] it was assumed that the electrons in the collision cascade region are excited to the empty energy states ε above ε_F with a probability $\exp(-\varepsilon/k_B T_e)$. The excitation is described by "electronic temperature T_e" which is postulated to be constant during the cascade collision evolution (T_e is not the real thermodynamic temperature; it characterises the nonequilibrium energy distribution of electrons near the emission point). So, as compared with the models,[3–10] this approach considers the interaction of ejected atoms with the excited substrate. The ionization probability P^+ of sputtered atoms is expressed as

$$P^+ = \exp\left[\frac{\varepsilon_a(z_0)-\varepsilon_F}{k_B T_e}\right], \tag{2}$$

where

$$z_0 = \frac{1}{\gamma}\ln(2\Delta_0/\hbar\gamma\nu_z) \tag{3}$$

is the "freezing" distance[10] which means that for $z < z_0$ closer to the surface, the charge state is close to the equilibrium one and outside this region the electron exchange is being frozen out; Δ_0 is the half width of the ε_a level at $z=0$; and k_B is the Boltzmann constant. Equation (2) is formally equivalent to those developed by Overbosch *et al.*[10] and by Brako and Newns[8] (the high-temperature limit) to describe the ionization of the hyperthermal Na atoms scattered by the externally heated tungsten substrate. The velocity dependence of P^+ is introduced in Eq. (2) through the time variation of the atomic level $\varepsilon_a(z_0)$ at z_0 [see Eq. (3)]. In the assumption that $\varepsilon_a(z)$ varies linearly from $\varepsilon_a(0)$ to $\varepsilon_a(\infty)$ in distance Γ^{-1}, Eq. (2) leads to the power law velocity dependence of P^+:[14]

$$P^+ \propto \nu_z^{\Gamma|\varepsilon_a(0)-\varepsilon_a(\infty)|/\gamma k_B T_e} = \nu_z^n. \tag{4}$$

The combined model of the ion formation included both the nonadiabatic process [see Eq. (1)] and electronic excitation in the metal [see Eqs. (2), (4)] has been proposed in Refs. 17, 18.

A comparison of Eqs. (1) and (2) shows that each of the models predicts different velocity dependencies of P^+. According to Eq. (1), the dependence of P^+ on ν_z is strong and $\ln P^+$ is a linear function of $1/\nu_z$. On the contrary, Eq. (2) leads to the power law velocity dependence of P^+ which is a much weaker than the dependence $P^+(\nu_z)$ described by Eq. (1). As was shown in Ref. 10, for copper sputtering, Eq. (2) predicts a factor of 5 increase only in the secondary ion yield over an energy range from 4 to 40 eV.

One would think that the key parameter that will distinguish these two alternative conceptions is the velocity dependence of P^+. However, experimental examinations, in which, as a rule, the atomic ions with invariable parameters were used as projectiles, did not permit us to distinguish clearly which theories are the most promising for further refinement. There are experimental evidences in support of both the strong velocity dependence of P^+ (Refs. 19, 20) as well as the weak one.[21–23] This means that the effect of the electronic subsystem excitation on the ionization probability P^+ of sputtered atoms must be examined using some other experimental approaches. The direct way for this examination is the comparison of the kinetic energy distributions of neutral and ionized atoms sputtered from the same sample by different projectiles with various parameters in identical experimental conditions using the methods of laser post ionization of sputtering neutral atoms and time-of-flight mass spectrometry.[24,25] However, until now, such experiments have not been carried out and the question of "whether the electronic subsystem excitation affects the charge state formation of sputtered atoms" is still under discussion.

At the same time, it is well known that the electronic excitation in solids produced by keV- and sub-keV-energy atomic projectile and fast recoils plays an important role in phenomena such as kinetic ion-electron emission,[26] multiply charged ion emission,[2] and emission of the metastable excited neutral atoms.[27] In this case, the electronic excitations manifest themselves as the vacancies in the inner shell of the atom[2,26] or, for transition metals, as *d*-band holes.[27] The efficiency of these excitations strongly depends on the experimental parameters in a given "projectile-solid" system (for example, the incident energy E_0, incident angle, projectile species and kind of solids). In principal, the electronic excitation may affect also the charge state formation of sputtered atoms if they leave the surface before the excitation is able to relax.

In this context, it is important to know the relaxation time τ of the electronic excitation in solids. The experimental measurements[28] and theoretical calculations[29–31] show that for the metals the relaxation time is estimated as $\tau \approx 1\times 10^{-14} - 1\times 10^{-13}$ s. In Ref. 27 the relaxation time of *d*-band holes produced by the collision cascade was estimated as $\tau \sim 10^{-13}$ s. One could expect that for the semiconductors τ will not be less. It is important that the value $\tau \leqslant t_0$ ($t_0 \sim 10^{-12}$ s is the characteristic time of the cascade collision evolution[2]) and τ is commensurable with the time $t^* = z_0/\nu_z$ which the sputtered atom moves from the surface to the "freezing" distance z_0. So, the comparison of the τ, t_0 and t^* values shows clearly that the relaxation of the electronic excitation must be taken into account if this excitation affects really on the charge state formation of sputtered atoms.

Recently, the effect of the electronic excitation on the ionization probability P^+ of atoms sputtered from metals by the molecular projectiles was discovered experimentally.[32] This effect manifests itself as the enhancement of P^+ in going from the atomic projectiles to the molecular ones. However, up to now most studies of a secondary ion emission have been carried out when the atomic ions were used as projectiles. Therefore, it is interesting to study the effect of the atomic projectile parameters on P^+. Such a study may lead to a better understanding of the charge state formation process and, hence, to the further development of the charge state formation models.

The basic problem addressed in this work is a comparative study of the ionization probability P^+ of the Si^+ ions sputtered from the same clean silicon surface by both the atomic and molecular projectiles with different parameters.

The specific question is whether or not we observe a change of the velocity dependence of P^+ when the projectile parameters are changed. The results obtained highlight the important role of the electronic subsystem excitation in the charge state formation of sputtered atoms. These results are discussed in the framework of a simple model, in which the charge state formation is considered as the electron exchange between the sputtered atom and a local surface area where the relaxation of the electronic subsystem excited by the projectile impact takes place.

II. EXPERIMENTAL

The experimental SIMS instrument used in this work has been described earlier in detail.[33] To study the secondary ion emission under the atomic and molecular ion bombardment, a modified standard magnetic sector mass spectrometer was equipped with negative Al_m^- and Au_m^- cluster ion sources,[34] a primary ion column, a target assembly and a secondary ion optical system. The column included a mass separator and an ion optical system for primary ions. In the experiments, Al_m^- $(m=1,2)$ and Au^- projectiles with energies of 9, 18 keV are incident on the target at 45° to the target normal. The current density j of the projectiles had a typical value of $j \sim 10^{-6}\ A/\mathrm{cm}^2$. The detected secondary Si^+ ions are emitted at an angle of 0° with respect to the target normal.

Monocrystalline silicon was chosen as a target. The specific resistance ρ of this metal-like semiconductor sample is $\rho=7\ \Omega$ cm. To obtain a clean Si sample, it was heated for several hours up to a temperature of about 1400 K and it was then cleaned by the subsequent Al^- or Au^- ion bombardment. The yields of SiO^+ molecular ions sputtered from the Si surface by Al^- or Au^- projectiles were controlled before and after the cleaning procedure. The yields were observed to drop by more than two orders of magnitude after the cleaning procedure was applied. Since the probability of chemical reactions increases on a hot solid surface, we believe that this drop in the SiO^+ yield indicates a corresponding decrease in the oxygen concentration on the silicon surface. The target surface prepared in such a way was believed to be a "clean surface." During the measurements the temperature of the Si target was 1400 K and under working conditions the residual pressure did not exceed the value of 1×10^{-5} Pa. the kinetic energy distributions of the secondary Si^+ ions were studied by a variation of accelerating voltage U over the range ± 300 V relative to $U=2000$ V. In order to determine the energy resolution of the SIMS instrument, the kinetic energy distributions of alkaline metal ions (Na, K, and Cs) evaporated from the heated Si surface were measured in the absence of the primary ion beam. The measured full width at half maximum (FWHM) resolution was 5.5 eV. The transmission of the measuring instrument as a function of the secondary ion energy E was not determined because the comparison of the kinetic energy distributions of Si^+ ions sputtered from the same sample by various projectiles was the main aim of this work.

III. RESULTS

The kinetic energy distributions $f_1(E,\theta)$ are very characteristic for the secondary ion emission. The attempts to extract from functions $f_1(E,\theta)$ various data about the respective element concentrations in the subsurface layers of solids,[23] the binding energies of sputtered atoms,[35] and the charge state formation mechanism of atoms sputtered from different samples[19–23] are well known. Information related to the effect of the electronic subsystem excitation produced by projectiles in solids on the ionization probability P^+ of sputtered atoms can be obtained from distributions $f_1(E,\theta)$ also. In our previous work[32] such an approach was applied for the analysis of energy distributions $f_m(E,\theta)$ of Nb^+ and Ta^+ ions sputtered from niobium and tantalum targets, respectively, by atomic and molecular projectiles of Au_m^- $(m=1-3)$ with an energy of 6 keV/atom. Briefly this method can be described as follows. As a general practice,[1] the energy distribution $f_1(E,\theta)$ for atomic ions is defined according to

$$f_1(E,\theta)=F_1(E,\theta)P^+(E,\theta). \tag{5}$$

Here $F_1(E,\theta)$ is the energy distribution of the neutral atoms sputtered from the solid by the atomic projectiles and $P^+(E,\theta)$ is the ionization probability. For the incident energy $E_0\sim$several keV, $F_1(E,\theta)$ is described well by Sigmund's isotropic cascade sputtering theory[36]

$$F_1(E,\theta)\propto\frac{E}{(E+U_0)^3}\cos\theta. \tag{6}$$

The function $F_1(E,\theta)$ depends on the surface binding energy U_0, the kinetic energy E, and the escape angle θ of the emitted atoms and it does not depend on species, the incident energy E_0, and the angle of projectiles. So, Eq. (5), after the substitution of experimental distributions $f_1(E,\theta)$ and calculated $F_1(E,\theta)$, can provide information on the velocity dependence of P^+.

A special case is the bombardment of a sample by molecular projectiles. In comparison with the atomic bombardment, the molecular bombardment, as a rule, results in a greater yield of sputtered particles per atom of the projectile, in other words, in nonadditive sputtering.[37] Nonadditive sputtering is described by the nonadditive factor $K_{2,1}=Y_{n,2}/2Y_{n,1}$, where $Y_{n,2}$ and $Y_{n,1}$ are the yields of n-atomic particles (in our case $n=1$) sputtered by the molecular and atomic projectiles, respectively, with the same projectile velocity. It is well known that, as compared with atomic ion bombardment of metals, the molecular bombardment results in the enrichment of the energy distribution $F_2(E,\theta)$ by the low-energy atoms while the higher energy part of this distribution does not practically change.[38] In this connection, we assume that the same result will be also valid for silicon sputtering. In other words, the distribution $F_2(E,\theta)$ for the molecular bombardment does not change over the energy range $E>3$ eV as compared with that for the atomic bombardment $[F_1(E,\theta)=F_2(E,\theta)]$. In the interpretation we tentatively assume the validity of Eq. (5) also in the case related to the molecular ion bombardment.

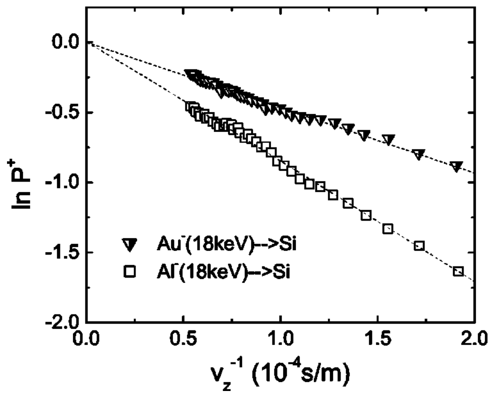

FIG. 1. The natural logarithm of the ionization probability P^+ vs v_z^{-1} for atomic Si^+ ions sputtered from the silicon target by the Al^- and Au^- projectiles with the energy of $E_0=18$ keV.

The energy distributions of Si^+ ions sputtered from a clean silicon surface by Al^- and Al_2^- projectiles with the energies of $E_0=9$ and 18 keV as well as by Au^- projectiles with an energy of $E_0=18$ keV were used as the distributions $f_1(E,\theta)$ and $f_2(E,\theta)$. For our experiments the emission angle $\theta=0$. To calculate the distribution $F_1(E,\theta)$ according to Eq. (6) the value of $U_0=3$ eV was used.

The various forms of the velocity dependence of $\ln P^+ = \ln\{f_1(E,\theta)/F_1(E,\theta)\}$ were examined. The results obtained are plotted in Figs. 1, 2, 3, and 4. These data were grouped in following pairs: Fig. 1, $\mathrm{Al}^-(18\ \mathrm{keV})$ and $\mathrm{Au}^-(18\ \mathrm{keV})$; Fig. 2, $\mathrm{Al}^-(9\ \mathrm{keV})$ and $\mathrm{Al}_2^-(18\ \mathrm{keV})$; Fig. 3, $\mathrm{Al}^-(9\ \mathrm{keV})$ and $\mathrm{Al}^-(18\ \mathrm{keV})$; and Fig. 4, $\mathrm{Al}_2^-(9\ \mathrm{keV})$ and $\mathrm{Al}_2^-(18\ \mathrm{keV})$. Within the studied velocity range $[5.2-14.4\times10^5$ cm/s$]$ the dependencies $\ln P^+$ on $1/\nu_z$ are approximated satisfactorily by the straight lines. This evidences that the charge state formation of the Si^+ atoms sputtered by both the atomic and molecular projectiles is described by the exponential function of P^+ on $1/\nu_z$. The slopes of straight lines are equal to the values of ν_0 and characterize the efficiency of the electron exchange process: the smaller ν_0 is the higher P^+ becomes. For convenience of the comparison, these results were plotted in the arbitrary units and the values of $\ln P^+$ at the larger velocities $(\nu_z\to\infty)$ were set equal to 1. The values of $\nu_0\times10^4(\mathrm{m\,s}^{-1})$ are equal to 0.466 ± 0.003 for $\mathrm{Au}^-(18\ \mathrm{keV})$, 0.784 ± 0.004 for $\mathrm{Al}_2^-(18\ \mathrm{keV})$, 0.827 ± 0.004 for $\mathrm{Al}^-(18\ \mathrm{keV})$, 0.910 ± 0.006 for $\mathrm{Al}_2^-(9\ \mathrm{keV})$, and 0.984 ± 0.004 for $\mathrm{Al}^-(9\ \mathrm{keV})$, respectively. From these data it can be extracted the following features.

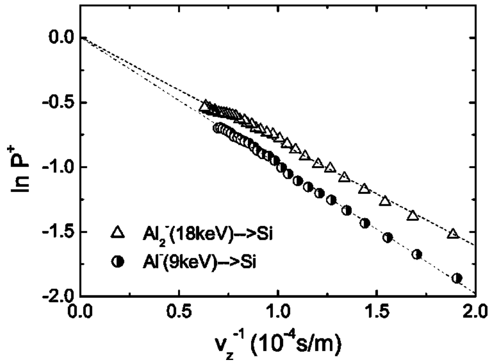

FIG. 2. The natural logarithm of the ionization probability P^+ vs v_z^{-1} for atomic Si^+ ions sputtered from the silicon target by the Al^- and Al_2^- projectiles with the same energy of $E_0=9$ keV/atom.

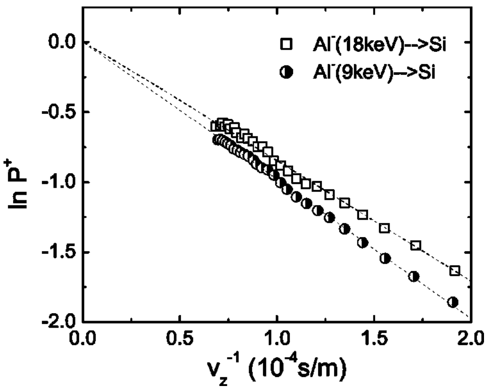

FIG. 3. The natural logarithm of the ionization probability P^+ vs v_z^{-1} for atomic Si^+ ions sputtered from the silicon target by the Al^- projectiles with the energies of $E_0=9$ and 18 keV.

The comparison of results presented in Figs. 1–4 shows the difference in the values of ν_0 when the parameters of projectiles are changed.

For the Al^- and Au^- projectiles with the energy of $E_0=18$ keV, the ionization probability P^+ enhances with the increase of the projectile mass M (see Fig. 1). The ratio of the ν_0 values is equal to $\nu_0(\mathrm{Al}^-\ 18\ \mathrm{keV}):\nu_0(\mathrm{Au}^-\ 18\ \mathrm{keV})=1.77$.

For the same velocity of Al^- and Al_2^- projectiles, the value of P^+ increases in going from the atomic bombardment to the molecular bombardment (see Fig. 2). The ratio of ν_0 is equal to $\nu_0(\mathrm{Al}^-\ 9\ \mathrm{keV}):\nu_0(\mathrm{Au}_2^-\ 18\ \mathrm{keV})=1.25$.

For the Al^- projectiles with energies of $E_0=9$ and 18 keV, P^+ increases with the rise of E_0 (see Fig. 3). In this case the ratio of ν_0 is less: $\nu_0(\mathrm{Al}^-\ 9\ \mathrm{keV}):\nu_0(\mathrm{Al}^-\ 18\ \mathrm{keV})=1.19$.

The bombardment of silicon by the molecular projectiles with energies of $E_0=4.5$ and 9 keV/atom leads to the change of ν_0 (see Fig. 4): $\nu_0(\mathrm{Al}_2^-\ 9\ \mathrm{keV}):\nu_0(\mathrm{Al}_2^-\ 18\ \mathrm{keV})\approx1.16$.

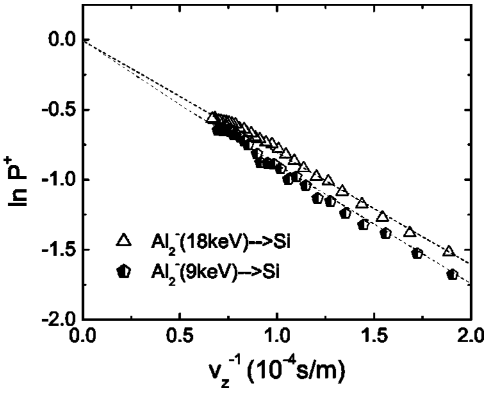

FIG. 4. The natural logarithm of the ionization probability P^+ vs v_z^{-1} for atomic Si^+ ions sputtered from the silicon target by the Al_2^- projectiles with the energy of $E_0=4.5$ and 9 keV/atom.

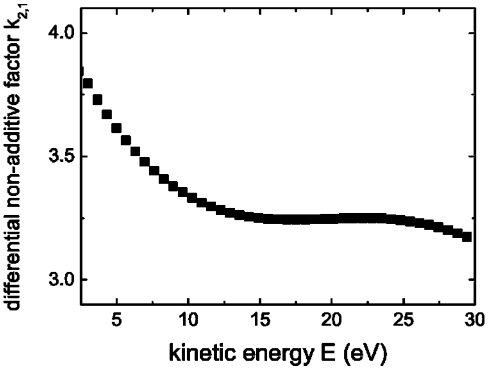

FIG. 5. Differential nonadditive factor $k_{2,1}$ vs the kinetic energy E of sputtered Si^+ ions. The dependence $k_{2,1}(E)$ was calculated using the kinetic energy distributions of sputtered Si^+ ions measured under the bombardment of the silicon target by atomic Al^- and molecular Al_2^- projectiles with the energy of 9 keV/atom.

The results presented in Figs. 1–4 show clearly that the ionization probability P^+ enhances when the mass, energy, and number of atoms in the projectiles increase. This enhancement depends also on the velocity ν_z of sputtered Si^+ ions: for smaller velocities ν_z the ratio of P^+ becomes higher.

For the molecular ion bombardment the latter conclusion can be also obtained in another way. The knowledge of the energy distributions $f_1(E,\theta)$ and $f_2(E,\theta)$ of Si^+ ions makes it possible to establish a relation between non-additive sputtering and the energy E of sputtered particles. The quantitative characteristic of this relation can be defined as the differential nonadditive factor[25] $k_{2,1}=f_2(E,)/2\,f_1(E,)$ which is equal to the ratio of the yields of sputtered Si^+ ions with a given energy E per atom of the projectile. The nonadditive factor $K_{2,1}$ and the differential nonadditive factor $k_{2,1}$ are connected with each other by the simple relation $K_{2,1} = 1/(E_{\max}-E_{\min})\int_{E_{\min}}^{E_{\max}} k_{1,2}(E)dE$. Data about of $K_{2,1}$ can be found in Ref. 40 where the study of nonadditive sputtering under the bombardment of silicon by the molecular projectiles of the heavy and light elements has been carried out.

The dependence $k_{2,1}(E)$ within the energy range of E $(3 < E < 30\text{ eV})$ is presented in Fig. 5. The curve $k_{2,1}(E)$ has a maximum value of $k_{\max}=3.8$ at $E=3$ eV and then decreases monotonously with E, reaching the value $k_{\min}=3.1$ at $E=30$ eV. This result shows that the molecular Al_2^- ion bombardment of the clean silicon surface leads to the increase in the ionization probability P^+ of sputtered atoms, especially of atoms with the low energy of E. The same conclusion was made in Ref. 32 from an analysis of energy distributions of Nb^+ and Ta^+ ions sputtered from niobium and tantalum targets by atomic and molecular Au_m^- projectiles $(m=1-3)$ with an energy of 6 keV/atom.

Thus, the experimental results of the present work demonstrate that the basic assumption of electron-exchange models[3–10] related to the independence of the charge state formation process of sputtered atoms on the projectile parameters does not correspond to the reality when the clean solid surface is sputtered. The ionization probability P^+ depends on the projectile parameters increasing with the rise of the mass and the energy of atomic projectiles as well as in going from the atomic projectiles to the molecular ones. For the studied velocity range, the increase in P^+ manifests itself for both the small and large velocities of sputtered atoms, being more pronounced for the small velocity interval. The degree of the alteration of P^+ depends on the individual features of the interaction in a given "projectile-solid" system. The velocity dependence of P^+ is approximated by the exponential function on $1/\nu_z$.

IV. MODEL AND DISCUSSION

According to Eq. (1), the ionization probability P^+ depends on the characteristics of the ejected atoms (the ionization potential I, the velocity ν_z, and the escape angle θ) and on electronic structure of the solid surface (the work function φ). For sputtered Si^+ ions, each of dependencies $\ln P^+$ on $1/\nu_z$ (see Figs. 1–4) corresponds to the same values of I and θ and the same range of ν_z. Hence, the change in P^+ must be connected with the alteration of the electronic properties of a local surface area from which the Si^+ ion emission occurs. The electronic properties of the local surface area should be considered rather than the work function because φ is an integral characteristic of the macroscopic surface area and it does not characterize the microscopic nature of the charge state formation process. The change of electronic properties is caused by the electronic subsystem excitation resulting from the ion bombardment of a solid.

The electronic excitations within the collision cascade region can be a result of two mechanisms. In the first mechanism, the inelastic collisions between fast moving and immovable Si atoms produce the vacancies in inner shell(s) of Si atoms. The vacancy decay leads to the electron emission or/and the generation of electron-hole pairs in the valence and conduction bands.[2] In the second mechanism, the projectile and the fast moving target recoil atoms interact with the valence band electrons, transferring some part of their kinetic energy into the electronic subsystem. As a result electron-hole pairs are created in the valence and conduction band also.[27] The appearance of nonoccupied levels below the Fermi level ε_F opens an additional channel for the electron exchange. It may result in an increase of P^+ due to the electron tunnelling from the sputtered atoms to the nonoccupied levels if these atoms leave the surface before nonoccupied levels are able to relax. The contribution of an additional channel of the electron exchange in the secondary ion emission from the adsorbed layers on metallic surfaces is small but it may become significant when the clean solid surfaces are sputtered.[13]

Let us consider the simple model in which the charge state formation occurs in the electron exchange between the sputtered atom and a local surface area where the relaxation of the electronic subsystem excited by projectile impact takes place. Following Šroubek,[14–16] the electronic excitation in the substrate will be described also in terms of the electronic temperature T_e. However, we will suppose that T_e is not constant during the collision cascade evolution and T_e relaxes to the equilibrium temperature T. To express the ionization probability P^+, we make the following assumptions.

When the clean solid surface is sputtered, the electron-hole pairs generated by projectile and fast recoil atoms into several subsurface layers of a solid play the main role in the interaction between the ejected atoms and the surface. The holes created into a bulk far away from the surface do not participate in this interaction. It is assumed also that the electron-hole pairs are generated into subsurface layers during the initial stage of the collision cascade.

When the electron-hole generation into the subsurface layers is stopped (this moment is determined as $t=0$), the excited state of the electronic subsystem corresponds to the stationary nonequilibrium electron energy distribution f_e at the electronic temperature T_e. Later on the collisions between electrons as well as the direct electron-hole recombination lead to the relaxation of the excitation so that f_e aspires to the equilibrium electron distribution f_F (f_F is the Fermi function) at the temperature $T \geqslant 0$.

The simplest assumption related to the relaxation process is that the restoration velocity of the equilibrium is proportional to the deviation $(f_t - f_F)$ of function f_t from the equilibrium

$$\frac{\partial f_1}{\partial t} = -(f_t - f_F)\frac{1}{\tau}, \tag{7}$$

where f_t is the nonequilibrium electron energy distribution at the moment t and τ ($\tau > 0$) is the relaxation time. In Eq. (7) the sign "$-$" shows that the excited electronic subsystem aspires to the equilibrium. As $f_F \approx 1$ at $T \geqslant 0$ and $\varepsilon < \mu$, the solution of Eq. (7) can be expressed as

$$1 - f_t = (1 - f_e)\exp\left(-\frac{t}{\tau}\right), \tag{8}$$

where $(1-f_t)$ and $(1-f_e)$ are the nonequilibrium hole energy distributions at the moment t and $t=0$, respectively. The kind of functions f_t and f_e is unknown. Therefore, as a rough approximation, f_t and f_e will be represented by the Fermi functions at the temperatures T_t and T_e, respectively. Then, Eq. (8) is rewritten as

$$\exp\left(\frac{\varepsilon - \varepsilon_F}{k_B T_t}\right) = \exp\left(\frac{\varepsilon - \varepsilon_F}{k_B T_e}\right)\exp\left(-\frac{t}{\tau}\right). \tag{9}$$

Here we taken into account that $\varepsilon < \varepsilon_F$ and $\varepsilon_F - \varepsilon > k_B T_e$. Equation (9) gives the relation between temperatures T_t and T_e:

$$\frac{1}{T_t} = \frac{1}{T_e} + \frac{t k_B}{\tau(\varepsilon_F - \varepsilon)}. \tag{10}$$

According to Ref. 14–16, for a given "projectile-solid" system and a constant value of T_e, the ionization probability P^+ [see Eqs. (2) and (3)] depends only on the atomic level energy ε_a at the "freezing" distance z_0. However, if the relaxation of the electronic excitation exists and the relaxation time $\tau < t_0$, the electronic temperature T_t of a local surface area from which the secondary ion emission occurs is decreased quickly in time [see Eq. (10)]. In this case, P^+ must depend both on the time $t^* = z_0/\nu_z = (1/\nu_z\gamma)\ln(2\Delta_0/\hbar\gamma\nu_z)$ that the sputtered atom moves from the surface ($z=0$) to the distance z_0 and the emission time t_s. The emission time t_s ($0 < t_s < t_0$) is defined as the time a sputtered atom starts from the surface. So, the moment, when the charge state is formed mainly is $t = t_s + t^*$. In other words, the sputtered atoms have both the velocity distribution and the frequency distribution of the emission times and, when these atoms achieve the distance z_0, they "match" the different temperature T_t of the local surface area. For the given value of t_s, the quick atoms "match" higher temperatures T_t while the slow atoms "match" lower values of T_t. This feature must be reflected in the final expression for P^+. In connection with it, let us express Eq. (2) as

$$P^+ = \exp\left(\frac{\varepsilon_a(z_0) - \varepsilon_F}{k_B T_t}\right). \tag{11}$$

The dependence $\varepsilon_a(z)$ may be approximated roughly by different ways. One of them is a linear function of ε_a on z that is valid when $\Delta\exp(-\gamma/\Gamma) < \hbar\gamma\nu_z < \Delta$.[14] Inserting Eq. (10) and a linear approximation of $\varepsilon_a(z)$ in Eq. (11) and taking into account that $\varepsilon_a(0) \cong \varepsilon_F = -\varphi$ (for sputtering of a clean solid surface) and $\varepsilon_a(\infty) = -I$ (these energies being counted from the vacuum level), the velocity dependence of P^+ can be expressed as

$$\begin{aligned} P^+ &= \exp\left(\frac{\varepsilon_a(z_0) - \varepsilon_F}{k_B T_e} - \frac{t}{\tau}\right) \\ &= \exp\left(\frac{\varepsilon_a(0) - \varepsilon_F}{k_B T_e}\right)\exp\left(\frac{[\varepsilon_a(\infty) - \varepsilon_a(0)]\Gamma z_0}{k_B T_e} - \frac{t_s + t^*}{\tau}\right) \\ &\cong \exp\left\{-\left[\frac{(I-\varphi)\Gamma z_0}{k_B T_e} + \left(t_s + \frac{z_0}{\nu_z}\right)\frac{1}{\tau}\right]\right\}. \end{aligned} \tag{12}$$

The competition between two terms in an exponent of Eq. (12) determines the kind of the velocity dependence of P^+. When $(t_s + z_0/\nu_z)1/\tau \ll (I-\varphi)\Gamma z_0/k_B T_e$, P^+ is described by the power law function on ν_z and it coincides with the result obtained by Šroubek[14] [see Eq. (4)]. This inequality is valid in the following two cases:

(i) The relaxation time τ is large ($\tau \gg t_0$) that corresponds to the absence of the relaxation process in a substrate.

(ii) The velocity ν_z of the sputtered atom is large and the emission time t_s is small. This corresponds to the moment of the charge state formation when the electronic excitation is far away from its complete relaxation.

The inequality $(t_s + z_0/\nu_z)(1/\tau) \gg (I-\varphi)\Gamma z_0/k_B T_e$ leads to $P^+ \approx 0$. It corresponds to "instant relaxation" ($\tau \approx 0$) of the electronic excitation when the model[14–16] is inapplicable.

For $(t_s + z_0/\nu_z)(1/\tau) \approx (I-\varphi)\Gamma z_0/k_B T_e$ the charge state of sputtered atom is formed when the electronic excitation has decreased by the relaxation process. In this case, the velocity dependence of P^+ can be expressed by the exponential function on $1/\nu_z$. To do it, Eq. (12) must be averaged on all values of the emission time t_s. As a result of the t_s averaging, we will obtain the ionization probability $P^+(\overline{T_t})$ where $\overline{T_t}$ is the average temperature under which the charge state of atoms sputtered with the given velocity ν_z is formed.

The frequency distribution G of emission times t_s for all sputtered atoms was calculated using molecular dynamics simulations for 5 keV Ar^+ bombardment of a Cu surface.[39] This distribution is approximated well by the function $G(t_s)=(\overline{t_s})^{-2}\exp(-t_s/\overline{t_s})t_s$, where $\overline{t_s}$ is the most probable emission time. The dependence of $G(t_s)$ on ν_z is introduced through the time $\overline{t_s}(\nu_z)$. Taking into account the dependence of $G(t_s)$, Eq. (12) can be rewritten as

$$\begin{aligned} P^+(\overline{T_t}) &= \overline{t_s}^{-2}\exp\left[-\left(\frac{(I-\varphi)\Gamma z_0}{k_B T_e}+\frac{z_0}{\nu_z\tau}\right)\right] \\ &\quad\times\int_0^\infty \exp(-t_s/\tau)\exp(-t_s/\overline{t_s})t_s dt_s \\ &= (\tau/\tau+\overline{t_s})^2\exp\left[-\left(\frac{(I-\varphi)\Gamma z_0}{k_B T_e}+\frac{z_0}{\nu_z\tau}\right)\right] \\ &= (\tau/\tau+\overline{t_s})^2\exp\left[-\left(\frac{(I-\varphi)\Gamma z_0}{k_B T^*}\right)\right] \\ &= (\tau/\tau+\overline{t_s})^2\exp\left(-\frac{\nu_0(\nu_z,T^*)}{\nu_z}\right). \end{aligned} \tag{13}$$

Here T^* is the temperature at the time $t=t^*$ and $\nu_0(\nu_z,T^*)$ is the function of T^* and ν_z:

$$\nu_0(\nu_z,T^*)=\frac{(I-\varphi)\Gamma z_0\nu_z}{k_B T^*}. \tag{14}$$

Thus, Eq. (12) describes the velocity dependence of P^+. The consideration of the relaxation process at the large values of τ and ν_z leads to the power law dependence of P^+ on ν_z while the decrease of τ and ν_z makes the velocity dependence of P^+ "less" power-law-like and "more" exponential. Equation (13) shows that the t_s averaging procedure leads to the ionization probability $P^+(\overline{T_t})$ which is equal to $P^+(T^*)$ diminished by a factor $(\tau/\tau+\overline{t_s})^2$.

Within the studied velocity range the experimental velocity dependencies of P^+ are approximated by exponential functions $[P^+\propto\exp(-\nu_0/\nu_z)]$ where ν_0 is a constant depended on the projectile parameters (see Figs. 1–4). Supposing $\nu_0(\nu_z,T^*)=\nu_0$ and combining Eqs. (3), (11), and (13), we obtain the relation between the average temperature $\overline{T_t}$ and ν_z:

$$\overline{T_t}=\frac{(I-\varphi)\Gamma\ln(2\Delta_0/\hbar\gamma\nu_z)}{k_B\gamma\left(2\ln\left(1+\frac{\overline{t_s}}{\tau}\right)+\frac{\nu_0}{\nu_z}\right)}. \tag{15}$$

Equation (15) does not allow us to estimate the temperature $\overline{T_t}$ due to an uncertainty in the value of Γ [Γ is the characteristic distance where $\varepsilon_a(\Gamma)=-I$].

The quantitative estimation of $\overline{T_t}$ is possible using the other approximation of $\varepsilon_a(z)$. For clean metal-like silicon sputtering, $\varepsilon_a(z)$ can be well approximated for larger z by the image charge energy[14]

$$\varepsilon_a(z)=\varepsilon_a(\infty)+e^2/4z, \tag{16}$$

where e is the electron charge. The studied velocity range of the Si^+ ions corresponds to the "freezing" distance range of $(3.03–3.85)\times10^{-8}$ cm. These values of z_0 are commensurable with the atomic distance and it gives a basis for the use of Eq. (16). Inserting Eqs. (3), (10), and (16) in Eq. (11) and averaging on all values of t_s, we obtain again the exponential dependence of P^+ on $1/\nu_z$:

$$\begin{aligned} P^+(\overline{T_t}) &= \left(\frac{\tau}{\tau+\overline{t_s}}\right)^2\exp\left[-\left(\frac{I-\varphi-\frac{e^2}{4z_0}}{k_B T_e}+\frac{z_0}{\nu_z\tau}\right)\right] \\ &= \left(\frac{\tau}{\tau+\overline{t_s}}\right)^2\exp\left[-\left(\frac{I-\varphi-\frac{e^2}{4z_0}}{k_B T^*}\right)\right] \\ &= \left(\frac{\tau}{\tau+\overline{t_s}}\right)^2\exp\left(-\frac{\nu_0(\nu_z,T^*)}{\nu_z}\right), \end{aligned} \tag{17}$$

where $\nu_0(\nu_z,T^*)$ is the function of ν_z and T^*:

$$\nu_0(\nu_z,T^*)=\frac{\left(I-\varphi-\frac{e^2}{4z_0}\right)\nu_z}{k_B T^*}. \tag{18}$$

Supposing $\nu_0(\nu_z,T^*)=\nu_0$ and combining Eqs. (11) and (17), as it was made earlier, we obtain the relation between $\overline{T_t}$ and ν_z in the other form:

$$\overline{T_t}=\frac{I-\varphi-\frac{e^2\gamma}{4\ln(2\Delta_0/\hbar\gamma\nu_z)}}{k_B\left[2\ln\left(1+\frac{\overline{t_s}}{\tau}\right)+\frac{\nu_0}{\nu_z}\right]}. \tag{19}$$

Using Eq. (19), the dependencies of the temperature $\overline{T_t}$ on ν_z has been calculated for all studied "projectile-solid" systems. The velocity dependence of $\overline{t_s}$ in the form of $\overline{t_s}(\nu_z)=\overline{t_*}(\nu_{\max}/\nu_z)^{1/2}$ was introduced in Eq. (19). Here $\overline{t_*}$ is the most probable emission time for $\nu_z=\nu_{\max}=1.4\times10^6$ cm/s and ν_z is the velocity within the studied velocity range. This dependence was determined from the comparison of the temperatures T_e calculated for various magnitudes of ν_z. The typical values of the γ,[2] Δ_0,[2] $\overline{t_s}$,[39] and τ (Refs. 28–31) parameters ($\gamma=1.25\times10^8\ \mathrm{cm}^{-1}$; $2\Delta_0=5$ eV; $\overline{t_*}\sim2.5\times10^{-13}$ s; and $\tau=5\times10^{-14}$ s) were used. The dependencies of the temperature $\overline{T_t}$ on ν_z show in Fig. 6. One can see the following features.

The temperature $\overline{T_t}$ increases with the rise of ν_z. At $\nu_z=5.2\times10^5$ cm/s the typical values of $\overline{T_t}$ are near 4000–4800 K while at $\nu_z=1.4\times10^6$ cm/s these ones are near 5400–6000 K.

Along of all studied "projectile-solid" systems, for the given value of ν_z the more large $\overline{T_t}$ is observed when the

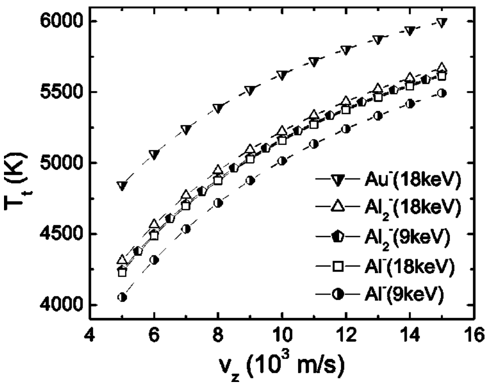

FIG. 6. The calculated dependencies of the average temperature $\overline{T_t}$ on the velocity v_z of sputtered Si^+ ions for various "projectile-solid" systems.

Au^- ions with the energy of $E_0 = 18$ keV are used as projectiles. These results can be explained in the framework of the proposed model.

The resonant transfer of an electron from the sputtered atom to a solid is possible if the energy level of the vacancy in the valence band coincides with the atomic level ε_a. For the studied velocity range, $\varepsilon_a(z_0)$ is located below ε_F $[\varepsilon_F - \varepsilon_a(z_0) = 2-2.6\ \mathrm{eV}]$. In this case, in accordance with Eq. (19), the charge state formation process can take place at the high value of $\overline{T_t}$ only. On the contrary, if $\varepsilon_a(z_0) \approx \varepsilon_F$ (it corresponds to sputtering of atoms from adsorbed layers on metallic surfaces), the ionization process is possible at $T \approx 0$ K.

The efficiency of the charge state formation process depends on both the electron-hole generation produced by the ion bombardment into the subsurface layers of a substrate, the relaxation of this excitation as well as the kinematics characteristics of atoms moved outward of the surface. In our experiment, the various projectiles bombarded the same silicon sample and the sputtered Si^+ ions have been detected with the same kinematics characteristics. So, assuming that the relaxation time τ depends only on the electronic properties of the substrate and it does not depend on projectile parameters, we must conclude that the Au^- projectiles produce the much strong electronic excitation. This excitation, and, as a consequence, T_e are determined by the inelastic energy losses of projectiles and fast recoils moving inside the collision cascade region. According to the mechanism,[2] the more effective formation of vacancies in inner shell(s) of the target atoms is produced due to the symmetrical Si-Si or Al-Si atom collisions. In the mechanisms,[26,27,42] the main factor responsible for the generation of the electron-hole pairs is the velocity of moving particle. However, the Au^--Si collisions are not symmetrical and, for a given energy E_0, the Au^- projectiles have the less velocity as compared with the velocity of both the Al^- projectiles and the Si recoils. Hence, the Au^- projectiles are not effective for the direct generation of the electronic excitation. In this context, the difference in the electronic excitation produced by heavy (Au^-) and light (Al^- and Al_2^-) projectiles may be connected with the peculiarities of a projectile penetration into a silicon lattice.[40,41] Due to the great cross section of the Au^--Si collisions the projectile energy E_0 is basically transferred to the Si atoms within several subsurface layers leading to the effective electronic excitation and the more strong effect of this excitation on P^+. In opposite, the cross section of the Al^--Si collisions is small and the Al^- projectiles penetrate deeper into a lattice so that their energy E_0 is deposited, in general, far away from the surface. In this case, as compared to the Au^- ion bombardment, the effect of the electronic excitation on P^+ is decreased. Bombardment by the Al_{2-} molecular projectiles may lead to the formation of the "impact" region with the modified property[40,41] where the energy density deposited by constituent atoms of the molecular projectiles is higher as compared with the atomic Al^- projectile. However, the effect of nonadditive interaction on the electronic excitation within several subsurface layers will be small. The constituent atoms of the light molecular projectile are scattered effectively and do not move together in the substrate ($M_{\mathrm{Al}} \approx M_{\mathrm{Si}}$) as compared to the atoms of heavy molecular projectile ($M_{\mathrm{Au}} \gg M_{\mathrm{Si}}$). Moreover, an excited region is not located near the surface. These factors must decrease the energy density deposited by Al_2^- projectiles into subsurface layers of the silicon target and, therefore, the efficiency of the electronic excitation. Thus, the electronic subsystem excitation and, hence, the ionization probability P^+ of sputtered atoms must depend on the energy density deposited by the projectile within several subsurface layers of the substrate.

As it can see from Figs. 1–4, when the projectile parameters are changed, the alteration in P^+ is more pronounced for the atoms sputtered with the small velocity. With the increase of v_z, the "freezing" distance z_0 and the time $t^* = z_0/v_z$ are decreased and the atomic level $\varepsilon(z_0)$ moves to Fermi level ε_F. In this case the relaxation of the electronic excitation does not decrease essentially the hole number in the energy range near ε_F and the effect of the relaxation process on P^+ is not large. On the contrary, the decrease of v_z leads to the increase of both the distance z_0 and the time t^* and the level $\varepsilon(z_0)$ moves away from ε_F. The effect of the relaxation process on P^+ is become large because the hole number in the energy range far away from ε_F are decreased strongly. Using Eq. (17), the dependence of $\ln(P_1^+/P_2^+)$ on v_z can be expressed as

$$\ln \frac{P_1^+}{P_2^+} = \frac{v_{02} - v_{01}}{v_z}, \tag{20}$$

where v_{02} and v_{01} are the ionization parameters related to the different "projectile-solid" systems. Thus, within the approach considered here, the value of $\ln(P_1^+/P_2^+)$ is increased with the decrease of v_z. The dependence of $\ln(P_1^+/P_2^+)$ on v_z^{-1} obtained from the data in Fig. 5 is plotted in Fig. 7. It is seen that the experimental dependence is satisfactorily described by the linear function.

V. CONCLUDING REMARKS

In the present work the assumption used in the majority of the electron-exchange models and related to the indepen-

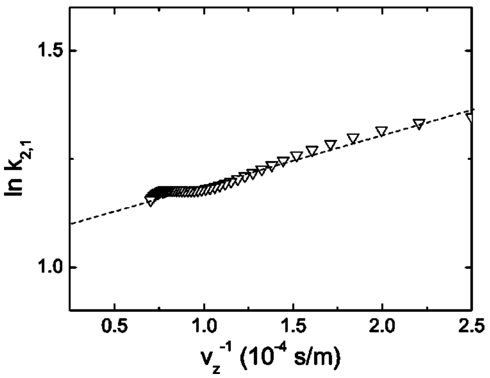

FIG. 7. Differential nonadditive factor $k_{2,1}$ natural logarithm vs v_z^{-1} for sputtered Si$^+$ ions.

dence of the charge state formation process of sputtered atoms on projectile parameters has been subjected to experimental examination. To study it the clean silicon surface has been bombarded by the atomic $(\mathrm{Al}^-, \mathrm{Au}^-)$ and molecular (Al_2^-) projectiles with different incident energies. The kinetic energy distribution $f(E)$ of the secondary Si$^+$ ions were measured to obtain information on the ionization probability P^+ of sputtered atoms. The main result obtained is the experimental demonstration of the effect of projectile parameters on P^+. It was found that, for a studied velocity range, P^+ is increased with the rise of the mass and the energy of projectiles as well as with the number of atoms in projectile. The increase in P^+ with the change of the projectile parameters manifests itself for both small and large velocities of sputtered atoms, being more pronounced for smaller velocities. The degree of the alteration of P^+ depends on the individual features of the interaction in a given ‘‘projectile-solid’’ system. As compared with the Al$^-$ (9 keV), Al$^-$ (18 keV), Al_2^- (9 keV), and Al_2^- (18 keV) ion bombardment, the Au$^-$ (18 keV) ion bombardment leads to larger values of P^+. Thus, these results evidence that the assumption related to the independence of the charge state formation process of sputtered atoms on the projectile parameters does not correspond to the clean silicon surface sputtering. It has been found that for all studied ‘‘projectile-solid’’ systems the velocity dependence of P^+ is approximated by the exponential function on the inverse velocity $1/\nu_z$. An analysis of results shown that the change in P^+ is connected with the electronic subsystem excitation produced by projectiles in several subsurface layers of a solid. As a result of this excitation the electron-hole pairs appear in the valence and conduction bands in the subsurface silicon region. The appearance of nonoccupied levels below Fermi level ε_F opens an additional channel for the electron exchange. It may result in an increase of P^+ due to the resonant transfer of electrons from sputtered atoms into nonoccupied levels if these atoms leave the surface before nonoccupied levels are able to relax.

A simple model was proposed in which the charge state formation occurs in the electron exchange between the sputtered atom and a local surface area where the relaxation of the electronic subsystem excited by the projectile impact takes place. In spite of the rough approximation of nonequilibrium energy distributions f_e and f_t, this model permit to explain the main results of the present work. It describes different kind of the velocity dependence of P^+ predicting the exponential dependence of P^+ on $1/\nu_z$ at the small values of the relaxation time τ and/or the velocity ν_z of sputtered atoms. The increase of τ and/or ν_z make the velocity dependence of P^+ ‘‘less’’ exponential and ‘‘more’’ power-law-like.

Future studies of the effect of the relaxed electronic subsystem excitation on the ionization probability of sputtered atoms will allow to obtain a better understanding of the charge state formation process and, hence, to the further development of charge state formation models. It is important that the results obtained are useful from an applied point of view. They indicate the way for the improvement of the SIMS analysis sensitivity due to the selection of both the ‘‘projectile-solid’’ system and the correspondent projectile parameters lead to the increase of the secondary atomic ion yield.

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