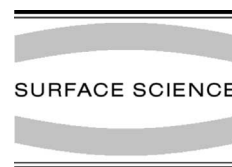




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Effect of the electronic subsystem excitation on the ionisation probability of atoms sputtered from metals by atomic and molecular projectiles

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Abstract

In the present work an effect of excitation of the metal electronic subsystem on the ionisation probability of atoms sputtered under fast ion bombardment has been studied. Atomic and molecular primary ions with the same velocity were used to produce different degrees of the electronic excitations. Information on the ionisation probability was obtained from the kinetic energy distributions of Nb⁺ and Ta⁺ ions sputtered from the respective clean Nb and Ta targets by Au_m⁻ projectiles ($1 \leq m \leq 3$) with the energy of $E_0 = 6$ keV per atom. It was found that, as compared with the atomic ion bombardment ($m = 1$), the molecular one ($m = 2, 3$) leads to the increase of the ionisation probability P_m^+ ($P_1^+ < P_2^+ < P_3^+$). Such an effect depends on the kinetic energy E of the secondary ions, increasing with decreasing E . It was shown that the bombardment of metals by the molecular projectiles produces non-additive sputtering of atomic ions, which is determined by the joint action of such two factors as non-additive sputtering of atoms and non-additive process of their charge state formation. The results obtained are discussed in the framework of the model where the charge state formation occurs in electron exchange between sputtered atoms and a local surface area excited by the impact of the projectile. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Secondary ion mass spectrometry; Ion emission; Ion bombardment; Ion–solid interactions; Sputtering; Niobium; Tantalum; Semi-empirical models and model calculations

1. Introduction

It is well known that the bombardment of metals by keV energy atomic ions results in emis-

sion of secondary particles (including polyatomic ones) in different charge states [1]. Ion fractions in the total flux of sputtered atoms depend on many factors, such as the electronic structure of a surface, species of particles, their velocities and escaping angle [2]. According to the existing theoretical models, the dominant process of ion formation is the interaction between the outgoing particle and the solid surface. The interaction is

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considered either as a time-depending perturbation [3] or as a certain electron exchange process [4–9]. In all these models [3–9] are assumed that the ionisation probability of sputtered atoms does not depend on the parameters of projectiles.

A majority of the secondary particles is formed as a result of several many-body collisions in the subsurface region of the solid. When leaving the surface they interact with a local surface area where both the electronic subsystem and the lattice structure are perturbed by a continuing cascade of collisions. Therefore, a theoretical description of the charge state formation processes is not easy, first of all, because of an uncertainty of electronic properties of a local surface area from which the emission of secondary atomic ions occurs. For the first time the attempts to explain the effect of the electronic subsystem excitation on the ionisation probability of sputtered atoms were undertaken by Šroubek [10,11]. However, the question “whether perturbation of the target electronic subsystem affects on the charge state formation of sputtered atoms” is still under discussion.

Excitation of the electronic subsystem under solid bombardment by keV-energy atomic ions plays a principal role in such phenomena as kinetic ion–electron emission [12], multiply charged ion emission [2] and emission of metastable excited neutral atoms [13]. The electronic subsystem is excited by energetic collisions with involvement of the projectile and fast recoil atoms, leading to the formation of vacancies in inner shells of target atoms [2,12]. For the case of transition metals, most of these excitations manifest themselves as the d-band holes [13]. In principle, such a non-equilibrium excitation of the electronic subsystem may affect the processes of the charge state formation of sputtered atoms. But this effect is only to be essential if the sputtered atoms leave the surface before the excitation is able to relax. In this context, it is important to know the relaxation time t_0 of the electronic excitations.

As a rough estimate for relaxation time of one-electron excitations in metals, the value $t_0 \sim 10^{-16}$ s, obtained from simple kinematics considerations, is usually used. Since $t_0 \ll \tau_0$ ($\tau_0 \sim 10^{-12}$ s is the time of collision cascade development) it seems that for metals the effect of the electronic sub-

system excitation on charge state formation of sputtered atoms is inessential owing to the fast relaxation of the excitation. However, collective effects of electron gas in metals (for instance, dynamical screening of electrons [14]) can weaken the electron–electron interactions, resulting in raising t_0 . This is justified by direct measurements demonstrating that the relaxation time of the electronic subsystem after its excitation in the gold sample by a femtosecond pulse of laser radiation has the value of $t_0 \sim 5 \times 10^{-13}$ s [15]. One could expect that for other metals t_0 will not be less. As measured by Sun et al. [15], $t_0 \sim \tau_0$ is in agreement with the values calculated within the different models, that take into consideration the dynamical screening of electrons in metals [16,17]. It should be noted that under the ion bombardment, t_0 will be not less because the electronic excitation is caused by a collision cascade rather than a single pulse. Indeed, in this case a bombarding ion and fast recoil atoms are able to generate the electron–hole pairs in inelastic collisions with electrons and target atoms until these collisions become energetically impossible. The relaxation time of d-band holes produced by the collision cascade was estimated by Wucher and Šroubek [13], according to which t_0 is 10^{-13} s.

On the basis of all this, it is quite natural to suppose that the electronic subsystem of a metal within the collision cascade will be in the non-equilibrium excited state while energetic collisions involving the projectile and the fast recoil atoms occur.

Until now, there are no direct experimental studies of an effect of non-equilibrium excitation of the metal electronic subsystem on the ionisation probability of sputtered atoms. Nevertheless, such studies are of both fundamental and applied interest; in principle, they can be carried out if characteristics of atomic ions sputtered for different degrees of electronic subsystem excitation are compared. In any experiment, there are several parameters allowing a change of the degree of electronic excitation. For example, one can vary the primary energy of a given atomic projectile or, one can change the species of the atomic projectile at a fixed primary energy. Another possibility is connected with the change of the number of atoms

in the projectile while keeping constant the projectile velocity.

In our opinion, the latter case is more attractive for such studies. Indeed, in comparison with the atomic bombardment, the molecular one, as a rule, results in a greater yield of sputtered particles per one atom of the projectile, in other words, in non-additive sputtering. In the 1970s it was found [18] that under bombardment of heavy metal targets (Ag, Au, Pt) by heavy atomic and molecular ions (As^+ , As_2^+ , Sb^+ , Sb_2^+ , Sb_3^+ , Bi^+ , Bi_2^+) with $E_0 = 10\text{--}250$ keV per atom the non-additive total yield Y_m of sputtered particles is observed. Here $Y_m = \sum_n Y_{n,m}$ is the average number of sputtered atoms, molecules and clusters in different charge states per one incident ion. Non-additive sputtering is usually described by the non-additive factor (or the enhancement factor) $K_{m,m'} = m'Y_{n,m}/mY_{n,m'}$, where $Y_{n,m}$ and $Y_{n,m'}$ are the yields of n -atomic particles, which are measured at the same projectile velocity and m and m' are the numbers of atoms in the projectiles. Using the definition of $K_{m,m'}$, the results of Ref. [18] mean that under the metal bombardment by m -atomic projectiles Y_m is more than by a factor of m higher as compared to the yield Y_1 under the bombardment by the atomic ions ($m' = 1$). According to the results of Refs. [18–21], for $E_0 > 10$ keV per atom the values of $K_{2,1} = Y_2/2Y_1$ do not exceed several units. For example, in Ref. [18] it is shown that under the bombardment of Au (an element characterised by a greater yield of sputtering [22]) with Bi^+ and Bi_2^+ ions $K_{2,1}$ is equal to 3.9 at 45 keV per atom and 2.5 at 30 keV per atom. There are no available measurements of $K_{2,1}$ for $E_0 < 10$ keV per atom. However, the extrapolation of these data to the range of lower E_0 values predicts even lower values of $K_{2,1}$.

Taking into account the features of molecular bombardment, different assumptions have been made to explain reasons for non-additive sputtering. The unique character of molecular bombardment resides with the fact that it ensures spatial localisation and time synchronisation of projectile atom collisions with the surface. The following factors might be responsible for increasing the sputtering yield in conditions of molecular ion bombardment.

- Practically simultaneous impact of the constituent atoms onto a small area of the surface ($\sim 10^{-16}$ cm²) increases the density of energy released in the subsurface region of the solid (hence, causing non-linear cascades [23]).
- Each subsequent atom of the molecular ion interacts over the time $\Delta t \leq 10^{-15}$ s with a local surface area excited by the impact with a front-runner atom. This means that the subsequent atom can be considered as a “probe” sampling the surface before the excitations of both the electronic subsystem and the lattice structure to relax. Such excitations can decrease the binding energy of atoms in the cascade region increasing the sputtered atom yield [18]. On the other hand, they can change the conditions of charge state formation leading to the raise of the atomic ion yield.

It has been found that neutral atoms dominate in the total yield Y_m of secondary particles [24–28]. Hence, determined in Refs. [18–21], non-additive yields Y_m are mainly defined by non-additive sputtering of neutral atoms. Atomic ions constitute a large fraction in the total flux of secondary charged particles. In the case of bombardment of Nb and Ta targets (Nb and Ta have lower yields of sputtering [22] than gold) by ions of Au_m^- ($1 \leq m \leq 3$) with $E_0 = 6$ keV per atom the following data are obtained: $K_{3,1}(\text{Nb}^+) = 7$; $K_{2,1}(\text{Nb}^+) = 3$; $K_{3,1}(\text{Ta}^+) = 3.5$; $K_{2,1}(\text{Ta}^+) = 2.5$, respectively [29–32]. It is important that these values of $K_{m,m'}$ obtained for atomic ions are comparable or even exceed the ones determined for the gold sputtering yield [18–21] at higher values of E_0 . Such an excess of $K_{m,m'}$ for atomic ions compared to those of neutral particles leads to the assumption that molecular bombardment not only leads to the increase of the sputtered atom yield but also changes the conditions of charge state formation resulting in an increase of the ionisation probability of sputtered atoms.

These reasons for the non-additive yields of atoms and atomic ions under molecular bombardment of metals need to be justified experimentally. Until now, there are no final replies to the following questions.

- Does the molecular bombardment effect the charge state formation process of sputtered atoms?
- What are the contributions of the processes of sputtering and charge state formation to non-additive yield of atomic ions?

In the present work a method to study the effect of electronic subsystem excitation in solids on the ionisation probability of sputtered atoms is proposed. It was used for the analysis of the kinetic energy distributions of Nb^+ and Ta^+ ions sputtered from Nb and Ta targets by atomic and molecular Au_m^- ions ($1 \leq m \leq 3$) with an energy of $E_0 = 6$ keV per atom. The results obtained highlight the important role of the metal electronic excitations in ion emission processes.

2. Experimental conditions, method and results

Important information on the features of the non-additive sputtering of solids can be obtained from the comparison of the kinetic energy distributions $f_{n,m}(E)$ of secondary ions. In our previous works [29–32] the energy distributions $f_{n,m}(E)$ of Nb_n^+ ($1 \leq n \leq 16$) and Ta_n^+ ($1 \leq n \leq 13$) ions sputtered from Nb and Ta targets by Au_m^- ($1 \leq m \leq 3$) projectiles with the energy $E_0 = 6$ keV per atom were measured under identical experimental conditions.

The experimental SIMS instrument used for the measurements has been described in detail elsewhere [30,32]. Here we only discuss the experimental conditions and the cleaning procedures used for the preparation of the target surfaces. It is a well-known fact that the reaction of metals with electronegative elements (for example, oxygen) usually proceeds through chemisorption to the formation of surface oxides. This changes the electronic properties of metallic surfaces and can result in dramatic enhancement of positive secondary ion yields relative to those from clean metals [2]. That is why for a reliable comparison of secondary ion yields determined under the bombardment by the atomic and molecular projectiles, the clean conditions on the target surfaces are required. Niobium and tantalum were chosen as

targets owing to their high melting temperatures. The cleaning procedures included both the heating and the ion sputtering of the targets. These were cleaned by heating to high temperatures (2400 K for Nb and 2600 K for Ta) and by the subsequent Au^- ion bombardment for several hours. The yields of NbO^+ and TaO^+ molecules sputtered from Nb and Ta surfaces by the Au^- , Au_2^- and Au_3^- projectiles were controlled before and after the cleaning procedures. They were observed to drop by more than three orders of magnitude after the cleaning procedures applied. Since the probability of chemical reactions increases on hot solid surfaces, we believe that this drop in the NbO^+ and TaO^+ yield indicates a corresponding decrease in the oxygen concentration on the target surfaces. The target surfaces prepared in such a way were believed to be “clean surfaces”. During the measurements the temperatures of the Nb and Ta samples were maintained at 2100 and 2300 K, respectively, and the residual gas pressure did not exceed 1×10^{-5} Pa.

In such experimental conditions it was found that the shape of the distributions $f_{n,m}(E)$ is defined by the species of secondary ions used. For a given secondary ion the shape of curves $f_{n,m}(E)$ depends on the number m . It essentially differs for the atomic bombardment and the molecular one. In this work we analysed only the energy distributions $f_{1,m}(E)$ of atomic Nb^+ and Ta^+ ($n = 1$) ions. The analysis of the energy distributions $f_{n,m}(E)$ of n -atomic ions will be given in an other article.

The main point of the method proposed here is the study of an effect of non-equilibrium excitation of an electronic subsystem of metals on the ionisation probability of sputtered atoms. This is realised by a comparison of the energy distributions of atomic ions sputtered from clean metal surfaces by atomic and molecular projectiles.

In general, the kinetic energy distribution $f_{1,1}(E, \theta)$ of sputtered atomic ions is defined according to [1]:

$$f_{1,1}(E, \theta) = F_{1,1}(E, \theta)P^+(E, \theta), \quad (1)$$

where $F_{1,1}(E, \theta)$ is the energy distribution of sputtered atoms and $P^+(E, \theta)$ is the probability of their ionisation. For atoms, the expression $F_{1,1}(E, \theta)$

follows from the Sigmund cascade theory of sputtering [33] is usually used as:

$$F_{1,1}(E, \theta) = \frac{E}{(E + U_0)^3} \cos \theta, \quad (2)$$

where U_0 is the binding energy. The function $F_{1,1}(E, \theta)$ depends on the binding energy U_0 , the kinetic energy E , and the escape angle θ of sputtered atoms. It does not depend on the species and the energy E_0 of the projectile. According to conventional theoretical ideas [3–9], the ionisation probability of sputtered atoms is defined by tunnelling of an electron between the metal surface and the emitted particle. In the framework of the electron tunnelling theory [7], the ionisation probability of sputtered atoms is described by the exponential function:

$$P^+(E, \theta) \propto \exp(-v_0/v_z), \quad (3)$$

where v_0 is the parameter characterising the ionisation efficiency, $v_z = v \cos \theta$, where $v = \sqrt{2E/M}$ and M are the velocity and mass of the sputtered atom, respectively. The parameter v_0 depends on the ionisation potential I of the sputtered atoms and on the work function ϕ of the metal surface. In the interpretation we tentatively assume the validity of Eq. (3) also in our case.

As compared with atomic ion bombardment of metals, the molecular one results in the enrichment of the energy distribution by low energy atoms while the higher energy part of this distribution does not practically change [19]. In this connection, we assume that the distribution $F_{1,m}(E, \theta)$ for the molecular bombardment does not change over the energy range $E > 5$ eV as compared with that for the atomic bombardment (i.e. $F_{1,1}(E, \theta) = F_{1,2}(E, \theta) = F_{1,3}(E, \theta)$). Thus Eq. (1), after the substitution of experimental distributions $f_{1,m}(E, \theta)$ and the calculated ones $F_{1,m}(E, \theta)$, can provide information on the value of v_0 .

The energy distributions of Nb^+ and Ta^+ ions (Fig. 1a, b) sputtered from clean targets by Au_m^- ($m = 1-3$) projectiles with the energy $E_0 = 6$ keV per atom [29–32] were used as the distributions $f_{1,m}(E, \theta)$. For experiments in Refs. [29–32] $\theta = 0^\circ$. To calculate the distribution $F_{1,m}(E, \theta)$ according to Eq. (2) the value of $U_0 = 3$ eV was used.

For Nb^+ and Ta^+ ions, the dependence of $\ln P^+ = \ln\{f_{1,m}(E, \theta)/F_{1,m}(E, \theta)\}$ on v_z^{-1} are plotted in Fig. 2a and b. One can see that the dependence is approximated satisfactorily by straight lines. This provides evidence that the charge state formation of Nb^+ and Ta^+ ions, both under the atomic bombardment and the molecular one, is described by Eq. (3). The slopes of the straight lines, according to Eq. (3), are equal to the corresponding values of v_0 and characterise the efficiency of the electron tunnelling process. In the case of Nb^+ ions the values of $v_0 \times 10^{-4}$ (s m⁻¹) are equal to 0.3796 ± 0.0137 , 0.3324 ± 0.0176 and 0.2918 ± 0.0123 for Au^- , Au_2^- and Au_3^- , respectively. For Ta^+ ions the values of $v_0 \times 10^{-4}$ (s m⁻¹) are equal to 0.5528 ± 0.0064 (Au^-), 0.4006 ± 0.0054 (Au_2^-) and 0.2956 ± 0.0071 (Au_3^-). Thus, these data demonstrate that under molecular ion bombardment the ionisation efficiency of sputtered atoms increases in comparison with the atomic one. This effect results in an increasing yield of secondary atomic ions, especially low energy ones.

This conclusion can be also obtained in another way. The energy distributions $f_{1,m}(E)$ of Nb^+ and Ta^+ ions (Fig. 1a, b) make it possible to establish a relation between non-additive sputtering and energy E of sputtered particles. The quantitative characteristic of this relation can be defined as the differential non-additive factor $k_{m,m'} = m'f_{n,m}(E)/mf_{n,m'}(E)$. Thus, $k_{m,m'}$ is equal to the ratio of yields of sputtered atomic ions with the given energy E per atom of the projectile. The factors $K_{m,m'}$ and $k_{m,m'}$ are connected with each other by the simple relation: $K_{m,m'} = 1/(E_{\max} - E_{\min}) \int_{E_{\min}}^{E_{\max}} k_{m,m'}(E) dE$ or using the mean-value theorem: $K_{m,m'} = k_{m,m'}(E^*)$ where $E_{\min} < E^* < E_{\max}$.

The functions $k_{3,1}(E)$ and $k_{2,1}(E)$ for Nb^+ and Ta^+ ions within the energy range of E ($1 < E < 25$ eV) are presented in Fig. 3a and b. As is seen from Fig. 3a, for Nb^+ ions the curve $k_{3,1}(E)$ has a maximum value of $k_{\max} = 10.5$ at $E = 1$ eV and then decreases monotonously with E , reaching the value $k_{\min} = 6$ at $E = 25$ eV. In this case the following inequality is valid $k_{\max} > K_{3,1} > k_{\min}$, where the non-additive factor $K_{3,1} = 7$ is measured for the Nb^+ ion flux over the energy range $0 < E < 300$ eV [32].

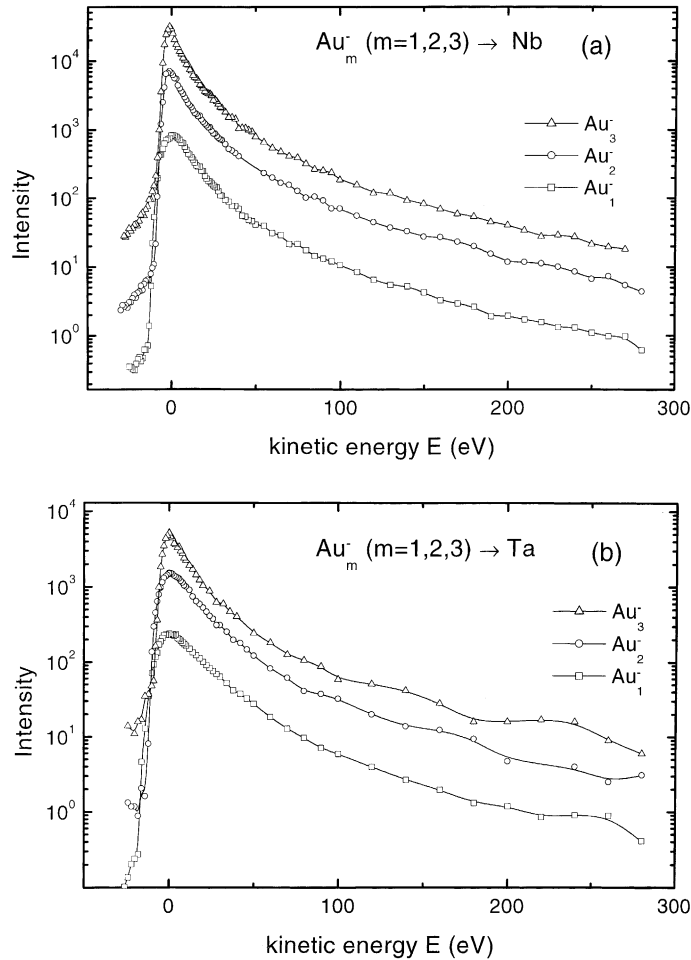


Fig. 1. Kinetic energy distributions of atomic (a) Nb^+ and (b) Ta^+ ions sputtered from niobium and tantalum targets by atomic and molecular Au_m^- projectiles ($1 \leq m \leq 3$) with the primary energy of 6 keV per atom. For the convenience of a curve shape comparison all energy distributions are displaced arbitrarily to each other along the ordinate axis. For all distributions the levels of background are the same and ones are equal 1–3 count/s.

The dependence $k_{m,m'}(E)$ is also sensitive to the number of atoms in the projectile. The change of m from $m = 2$ to $m = 3$ (at $m' = 1$) results in increasing $k_{m,m'}$ ($k_{3,1} > k_{2,1}$) and the difference between k_{\max} and k_{\min} . Indeed, for Nb^+ ions the values of k_{\max} ($k_{\max} = 8$ and $k_{\max} = 10.5$) exceed those of $K_{2,1} = 3$ and $K_{3,1} = 7$, respectively. For Ta^+ ions the values of k_{\max} ($k_{\max} = 3.3$ and $k_{\max} = 6.7$) also exceed those of $K_{2,1} = 2.5$ and $K_{3,1} = 3.5$. Thus, as compared with the atomic bombardment, the molecular one results in increasing the yield of slow Nb^+ and Ta^+ ions. The

higher the number m is the higher the yield becomes.

As established by numerous studies, under bombardment of metals by keV atomic projectiles [2], the yield of sputtered atomic ions is a factor of 10^3 – 10^5 less than that of neutral atoms. The difference in the yields of neutral atoms and atomic ions is connected with the process of charged state formation. As mentioned above, the ionisation probability of sputtered atoms is defined by the tunnelling of an electron between the metal surface and the emitted particle. In accordance with Ref.

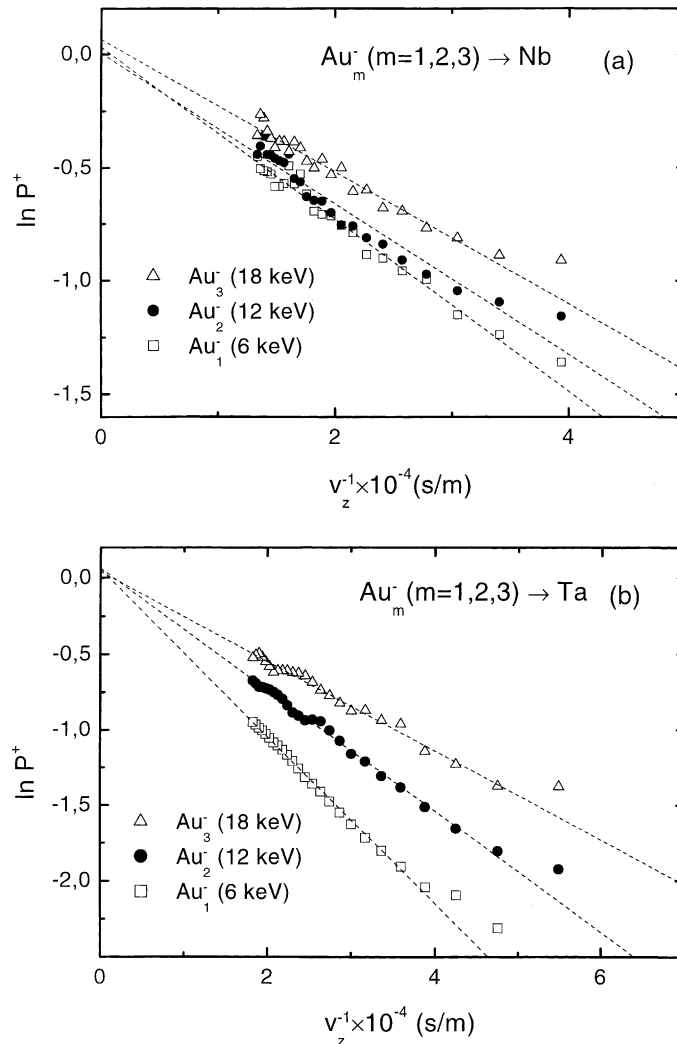


Fig. 2. Ionisation probability logarithm vs v_z^{-1} for atomic (a) Nb⁺ and (b) Ta⁺ ions sputtered from niobium and tantalum targets by atomic and molecular Au_m⁻ projectiles ($1 \leq m \leq 3$) with the energy of 6 keV per atom.

[2], the ionisation probability essentially decreases with the decrease of energy E . However, in our case the functions $k_{2,1}(E)$ and $k_{3,1}(E)$ for Nb⁺ and Ta⁺ ions demonstrate an opposite tendency: the ratio of yields of atomic ions increases, when E decreases. Moreover, this tendency becomes more pronounced with the rise of m .

Thus, the molecular ion bombardment creates on the metal surface conditions favouring the increase of the ionisation probability of sputtered atoms, especially of atoms with low E .

3. Discussion

Based on the results of the analysis, the physical reasons for the increase in the ionisation probability of atomic particles can be defined. Indeed, according to Eq. (3), $P^+(E, \theta)$ depends on the characteristics of sputtered atoms (the ionisation potential I , the velocity v and the escape angle θ) as well as on the electronic properties of the surface (the work function ϕ). For the given species of secondary atomic ions each of the dependence

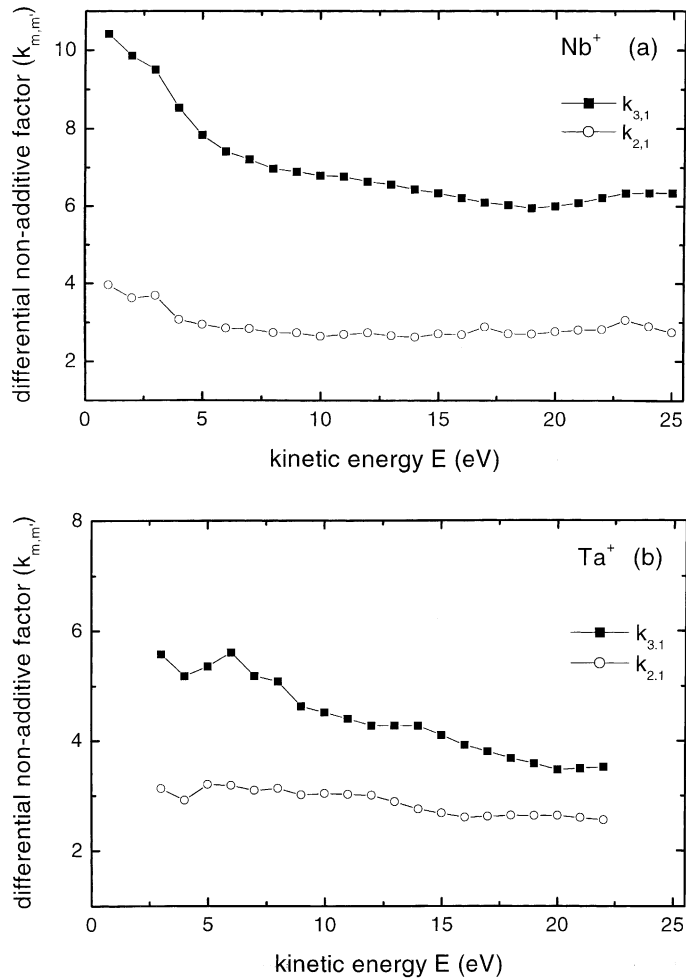


Fig. 3. Differential non-additive factors $k_{3,1}$ and $k_{2,1}$ vs the kinetic energy E of sputtered (a) Nb^+ and (b) Ta^+ ions.

$\ln P^+$ on v_z^{-1} (Fig. 2a, b) corresponds to the same values of I , v and θ . Therefore, the reasons for the increase in the ionisation efficiency for the molecular bombardment, as compared to the atomic one, are to be connected with the change of the electronic properties of a local surface area from which the emission of atomic ions occurs. In our opinion, the change of electronic properties of a local surface area should be considered rather than the change of the work function because φ is an integral characteristic of the macroscopic surface and this does not characterise the local nature of the processes of charge state formation. The change of electronic properties of the local surface

area is caused by the electronic subsystem excitation resulting from the ion bombardment of the metal.

Non-equilibrium electronic excitation within the collision cascade can be a result of two different mechanisms. In one of them the projectile ion as well as all fast moving target recoil atoms interact with the conduction band electrons, transferring part of their kinetic energy into the electronic subsystem of the solid. As a result electron-hole pairs form in the conduction band [13,34]. The other mechanism is inelastic collisions between moving target atoms leading to the formation of vacancies in inner shell(s) of the target atoms. The

decay of such vacancies results in electron emission or/and generation of electron–hole pairs in the conduction band [2]. The appearance of non-occupied levels below the Fermi level opens an additional channel for the electron exchange. This results in increasing the ionisation probability owing to tunnelling electrons from the sputtered atoms into these levels.

Following Šroubek [10,11], it is convenient to characterise the electronic subsystem excitation by some “effective electron temperature T_{eff} ”. It is necessary to stress that T_{eff} is not the real thermodynamic temperature of the metal target. A parameter T_{eff} characterises the shift of the electron energy distribution in the conduction band of the metal from its equilibrium state. The value of T_{eff} depends sensitively on the substrate parameter γ , which characterises the change of the width Δ of the atomic level with the distance from the surface z [2]: $\Delta = \Delta_0 \exp(-2\gamma z)$ where Δ_0 is the width of the atomic level on the surface ($z = 0$). According to Refs. [10,11] the final charged state of atoms sputtered from the clean metal surface, in the high temperature limit, becomes:

$$P^+ = \exp \left[-\frac{\varepsilon_{\text{F}} - \varepsilon_{\text{a}}(z_0)}{k_{\text{B}} T_{\text{eff}}} \right], \quad (4)$$

where ε_{F} is the Fermi energy, $\varepsilon_{\text{a}}(z_0)$ is the energy of the atomic level at the freezing point z_0 [8] and k_{B} is the Boltzmann constant, the energies being counted from the vacuum level. We remind, that for $z < z_0$, closer to the surface, the charge state is nearly the equilibrium one. Outside this region the electron exchange is considered being frozen out. Let us further define z_0 as the distance that the sputtered atom with the normal velocity v_z reaches within the relaxation time. Then $z_0 = v_z t_0$. In the case of emission from clean metals, the dependence of the atomic energy level ε_{a} on z can be well approximated for larger z by the image charge energy [10]:

$$\varepsilon_{\text{a}}(z) = \varepsilon_{\text{a}}(\infty) + e^2/4z, \quad (5)$$

where $\varepsilon_{\text{a}}(\infty) = -I$ is the energy of the atomic level at infinity and e is the electron charge. Then, inserting Eq. (5) in Eq. (4), for the dependence of P^+ on v_z we obtain the equation:

$$P^+ \propto \exp \left[-\frac{e^2}{4v_z t_0 k_{\text{B}} T_{\text{eff}}} \right] \quad (6)$$

which coincides with Eq. (3) if $v_0 = e^2/4t_0 k_{\text{B}} T_{\text{eff}}$.

Using Eq. (6) the values of T_{eff} can be derived from the experimental data (Fig. 2a, b). Putting $t_0 \approx 5 \times 10^{-13}$ s as in Ref. [15], one obtains 2200, 2500 and 2850 K for Nb sputtering at $m = 1, 2,$ and 3, respectively. For the Ta sputtering the values of T_{eff} become 1500, 2050 and 2800 K at $m = 1, 2, 3,$ respectively.

For the Nb and Ta sputtering the functions $T_{\text{eff}}(m)$ are presented in Fig. 4. These data show the following features:

- For the atomic bombarding ($m = 1$) the ratio $T_{\text{eff}}(\text{Nb})/T_{\text{eff}}(\text{Ta})$ approximates 1.5.
- T_{eff} increases approximately linearly with the rise of m .
- The slopes of $T_{\text{eff}}(m)$ are different for the Nb and Ta sputtering (0.46 and 0.68, respectively), being less than unit.

The degree of the electronic subsystem excitation, and, as a consequence, T_{eff} is connected with inelastic energy losses of projectiles and fast recoil atoms moving inside the cascade region. The inelastic energy losses are proportional to the velocity w of the moving particle, and T_{eff} can be estimated from the formula obtained by Lörinčik et al. [34]:

$$k_{\text{B}} T_{\text{eff}} = \frac{2\gamma \hbar w}{\pi}, \quad (7)$$

where \hbar is Plank’s constant. Taking into account that for the atomic projectile bombardment ($m = 1$) $T_{\text{eff}}(\text{Nb}) > T_{\text{eff}}(\text{Ta})$, we must assume that the main contribution to the electronic excitation result from fast target recoils. The average energy transferred by a gold atom to the recoil is $\bar{E} = 2\mu/(\mu + 1)^2 E_0$, where μ is the mass ratio. The average velocities w of recoils in the Nb and Ta substrates are 7.3×10^4 and 5.6×10^4 m s⁻¹, respectively. Using these values and $\gamma = 10^{10}$ m⁻¹ [34] for the both substrates (assuming the electronic properties of Nb and Ta to be identical) we find estimates for T_{eff} to be equal 2800 K for Ta

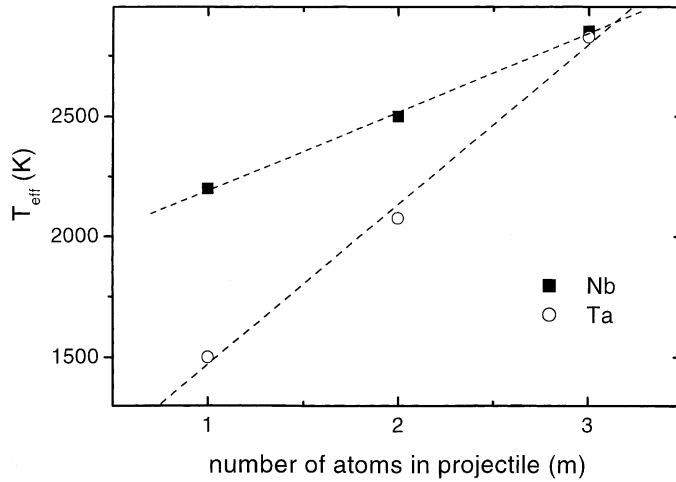


Fig. 4. Dependence of the effective temperature T_{eff} on the number atoms in Au_m^- projectiles for (■) Nb and (○) Ta sputtering.

sputtering, and 3600 K for the Nb. The temperature ratio for $T_{\text{eff}}(\text{Nb})/T_{\text{eff}}(\text{Ta}) = 1.3$, i.e. is close to the experimental value 1.47.

The rise of T_{eff} with increasing m can be easily understood, because the more atoms constitute the projectile the more fast recoils, exciting the electronic subsystem, they produce. This effect is “inverse” non-additive because the slopes of the $T_{\text{eff}}(m)$ functions are less than unity. This means that the electronic excitation produced by the impact of the molecular projectile is less the sum of the excitations induced by the independent constituents. It is clear that $T_{\text{eff}}(m)$ must depend in a complicated way on trajectories of m constituents of the projectile. However, a simple qualitative explanation of the inverse non-additive effect is possible in terms of a “clearing the way” effect [35–39]. Indeed, a frontrunner atom of the molecular projectile kicks the target atoms away from the trajectories of the subsequent projectile(s). As a result, the backrunner atoms collide with the target ones at larger collision parameters. Therefore, an amount of the energy transferred by the backrunner(s) to recoil atoms becomes less, and as a consequence, their velocities will be less than the velocities of recoils produced by the frontrunner. The longer time the molecular constituents move together in the target matter the more pronounced should be the inverse non-additive effect in the electronic subsystem excitation. The last must be

realised for the bombardment of light targets by heavy projectiles. On the contrary, the less the mass of a projectile constituents is with respect to the mass of the target atoms, the faster the molecule disintegrates on its path, the less pronounced the “clearing the way” effect should be.

Eq. (6) also allows one to describe the behaviour of the differential non-additive factor $k_{m,m'}$ with variation of energy E of the secondary ions and the change of the number m of atoms in the projectile. Indeed, according to the definition of $k_{m,m'}$ using Eqs. (1) and (6) one can write:

$$k_{m,m'} = \exp \left[\frac{e^2}{4t_0 k_B T_{\text{eff}}} \frac{(b_{m,m'} - 1)}{b_{m,m'}} \frac{1}{v_z} \right], \quad (8)$$

where $b_{m,m'} = T_{\text{eff}}(m)/T_{\text{eff}}(m')$, and $b_{m,m'} \geq 1$. Thus, within the approach considered here, $k_{m,m'}$ needs to increase with the raise of both $b_{m,m'}$ and v_z^{-1} . The dependence of $\ln k_{m,m'}$ on $b_{m,m'}$ and v_z^{-1} obtained from the data in Fig. 3 are plotted in Fig. 5. It is seen that the experimental dependences are satisfactorily described by linear functions. These results distinctly show that in going from the atomic bombardment to the molecular one an effective increase of the ionisation probability is observed. In the case of the molecular bombardment the increase of the ionisation probability manifests itself for both low energy sputtered atoms ($E < 5$ eV)

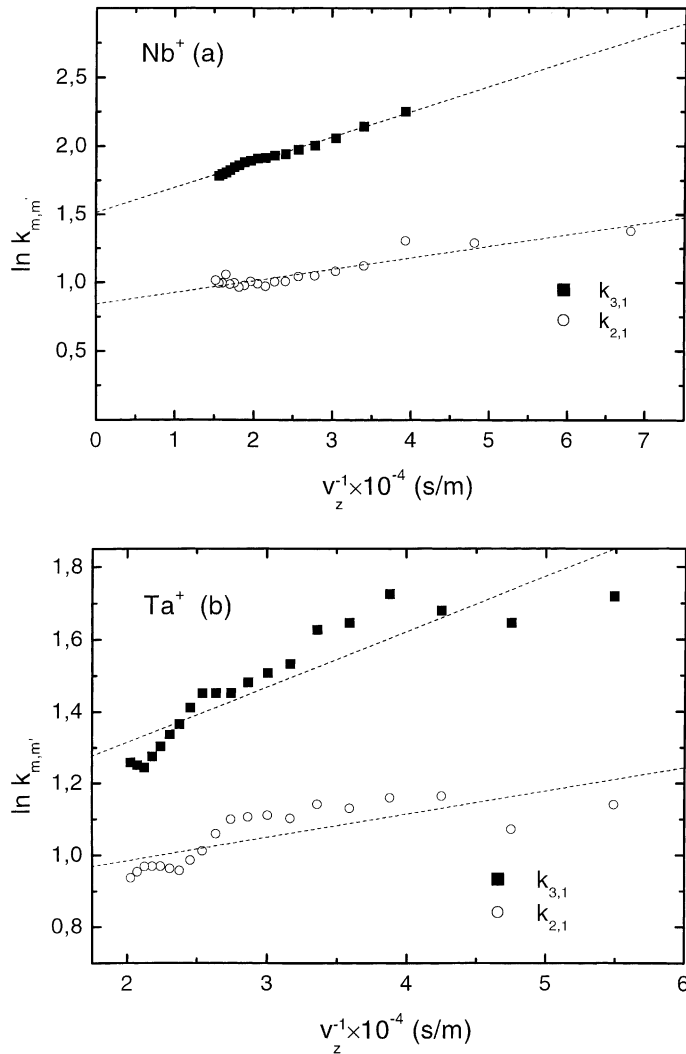


Fig. 5. Differential non-additive factors $k_{3,1}$ and $k_{2,1}$ vs v_z^{-1} for the sputtered (a) Nb^+ and (b) Ta^+ ions.

and high energy ones, being more pronounced for the lower energy interval. We should admit that the interpretation of these data in terms of the effective electronic temperature is not the only way to treat the increase of the yield of low energy ions sputtered under the molecular bombardment. The determination of a contribution of this effect demands a special study by either direct measurements of the kinetic energy distribution of sputtered neutral atoms or a proper molecular dynamics simulation. Those are out of the scope of the present work.

Taking into account the results obtained one can conclude that the bombardment of metals (Nb and Ta) by the gold atomic and molecular projectiles produces the electronic subsystem excitation which can be described by the effective temperature. Under the molecular ion bombardment the excitation process is inverse non-additive. On the contrary, the charge state formation of sputtered atoms (which demonstrates the exponential dependence of the ionisation probability on the effective temperature) displays itself as the non-additive process. Thus, non-additive sputtering of

atomic ions is defined by the joint action of such two factors as the non-additive sputtering of atoms and the non-additive process of their charge state formation. In this case, the non-additive factor $K_{m,m'}$ can be represented as a product: $K_{m,m'} = K_{\text{sput}} K_{\text{csf}}$ where K_{sput} is the non-additive sputtering factor and K_{csf} is the non-additive charge state formation factor.

4. Concluding remarks

The comparative study of the kinetic energy distributions of Nb⁺ and Ta⁺ ions sputtered from the respective clean Nb and Ta surfaces by Au_m⁻ ($1 \leq m \leq 3$) projectiles with the initial energy of $E_0 = 6$ keV per atom have been carried out. The main result obtained is experimental demonstration of the effect of the electronic subsystem excitation in the metals on the ionisation probability of sputtered atoms. It is found that, as compared with the atomic ion bombardment, the molecular one leads to the increase of the ionisation probability. It has been shown that this increase is connected with the change of the degree of the electronic subsystem excitation. Such excitation produced by both atomic and molecular ion bombardment results from inelastic collisions of the projectile and the fast recoil atoms in the substrate. As a result of these collisions the electron–hole pairs appear in the conduction band in the subsurface metal region from which the secondary ion emission occurs. The increase of a number of non-occupied levels below the Fermi level in going from the atomic ion bombardment to the molecular one leads to the increase in the ionisation probability owing to tunnelling electrons from the sputtered atoms into these levels.

Thus, one can conclude that the electronic excitation defining by the bombardment conditions affects the ionisation probability of sputtered atoms.

In our opinion, the future experimental and theoretical studies of the effect of the electronic subsystem excitation on the ionisation probability of sputtered atoms will allow to get a better knowledge of the features of secondary ion emis-

sion. The results obtained are an applied interest also. Indeed, they indicate the way of increase of the SIMS analysis sensitivity because the use of molecular ions as projectiles and the selection of the optimum sputtering condition result to the increase of the ion yield.

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