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NON-ADDITIVE SPUTTERING OF NIOBIUM AND TANTALUM AS LARGE NEUTRAL AND ION CLUSTERS*

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NON-ADDITIVE SPUTTERING OF NIOBIUM AND TANTALUM AS NEUTRAL AND CHARGED CLUSTERS

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Abstract.

An analysis of available literature data on both the positive ion emission from *Nb* and *Ta* bombarded by 6 *keV/atom* Au_m^- atomic and molecular ions (m=1, 2, 3) and positive ionization probabilities of Nb_n and Ta_n neutral clusters sputtered from the same metals by 5 *keV* Ar^+ ions have been conducted. Dependencies of cluster yields $Y_{n,m}$ (regardless of a charge state) on number of atoms n in a sputtered particle were found to follow a power law as $Y_{n,m} \sim n^{-\sigma_m}$ where σ_m decreased with an increase of m. A non-linear enhancement of yields for large Nb_n^+ and Ta_n^+ cluster ions (n>4) appeared to be due to a non-additive process of *sputtering* rather than because of a non-additive process of their *ionization*. A manifestation of the non-additive sputtering in kinetic energy distributions of secondary ions found to be different for atomic and cluster ions.

Keywords: Secondary ion emission, Atomic and molecular ion bombardment, Kinetic energy distribution, Non-additive sputtering, Niobium, Tantalum

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1. Introduction

It is well known that bombardment of solids by molecular projectiles leads to non-additive enhancement of sputtering [1,2]. This enhancement can be quantitatively characterized by an integral non-additivity factor $K_{m,m'}$ defined as

$$K_{m,m'} = m' Y_{n,m} / m Y_{n,m'} \qquad (1),$$

where the yields $Y_{n,m}$ and $Y_{n,m'}$ (n and m are numbers of atoms in the sputtered particle and the projectile, respectively) have to be measured for projectiles with equal velocities.

Even though the non-additive enhancement of total sputtering yield $Y_m = \sum_n Y_{n,m}$ was discovered more than twenty years ago [3,4], only during the last decade "molecular projectile - solid" interactions have been studied extensively, and many new experimental results have become available (see Refs.[1, 2] and references therein). Nevertheless, non-additive phenomena in sputtering are still poorly understood, and answers to many key questions have to be found. One of them is what are non-additivity factors $K_{m,m'}$ for neutral and for charged products of the sputtering process.

Recently, the first study of the emission of neutral clusters Ag_n (n=1-4) from the Ag target bombarded by 8 keV Ag_m^+ projectiles (m=1, 2, 3) has been carried out using laser post-ionization of sputtered neutral products [5]. Unfortunately, all the projectiles had the same energy E_o=8 *keV* so that results obtained for molecular projectiles could not be easily interpreted in the framework of the approach to non-additive sputtering described above. It is obvious that more efforts to study non-additivity of sputtering in the form of *neutral* atoms and clusters are needed to reveal basic trends of the phenomena.

For various sputtered *ions*, dependencies of the non-additive sputtering on projectile parameters have been studied and reported in a large number of publications [1, 2]. By now, a consensus have been reached that the observed non-linear effects originate from the "molecular projectile - solid" interaction, and the intensity of this process must depend not only on the projectile parameters but also on the sort of sputtered particles as well as on the electronic and structural properties of the region of solids modified by a molecular impact. In this context, studies of non-additive sputtering of a variety of secondary ions produced by various molecular projectiles under identical experimental conditions would be especially important.

In an effort to do so, experiments have been carried out in Refs. [6-8] for Nb_n^+ (n=1÷16) and Ta_n^+ (n=1÷13) ions sputtered from the *Ta* and *Nb* targets by Au_m^- projectiles (m=1÷3) with the energy E_0 =6 *keV/atom*. In these works, $K_{m,m'}$ factors were found to be different for various sputtered products, as follows. For atomic ions, the following values of $K_{m,m'}$ were determined: $K_{3,1}(Nb^+)$=7, $K_{2,1}(Nb^+)$=3, $K_{3,1}(Ta^+)$=3.5, $K_{2,1}(Ta^+)$=2.5. For cluster ions, $K_{m,m'}$ strongly increased with increase of the n and m values. For example, for Nb_9^+ and Ta_{10}^+ the following numbers were reported: $K_{3,1}(Nb_9^+)$=255; $K_{2,1}(Nb_9^+)$=44 and $K_{3,1}(Ta_{10}^+)$=723; $K_{2,1}(Ta_{10}^+)$=100. This dramatic increase in the non-additivity of cluster sputtering for larger values of *n* and *m* was called «the effect of anomalous high non-additivity of sputtering in the form of large cluster ions (n>4) under bombardment of metals by heavy molecular projectiles» [6-8].

These results generated an intriguing question: *"What is enhanced under the molecular ion bombardment, the sputtering or the ionization of sputtered neutrals?"* For yields of Nb^+ and Ta^+ *atomic* ions, it has been demonstrated in Ref. [9] that the non-additivity was defined by the product $K_{m,m'} = K_{sput} \cdot K_{csf}$, where K_{sput} and K_{csf} were non-additive factors for the sputtering and the charge state formation, respectively. As for *cluster* ions, the nature of the non-additive enhancement of their emission under polyatomic ion bombardment it is not clear yet. Moreover, the observed non-additivity of sputtering might originate from different physical phenomena for atomic and cluster ions, and this might manifest itself in kinetic energy distributions of these sputtered particles.

In the present work, an all-round analysis of experimental results available for Nb and Ta was performed to extract more information on non-additive sputtering permitting new insights. The following two basic problems were considered:

- Formation of Nb_n and Ta_n clusters (regardless of a charge state) in the process of non-additive sputtering of niobium and tantalum.
- Manifestation of the sputtering non-additivity in kinetic energy spectra of sputtered ions.

2. Results and discussion

2.1. Non-additive sputtering of *Nb* and *Ta* as neutral and positively charged clusters

A comparison between yields of ionic and neutral sputtered clusters became possible after ionization probabilities η^+ for Nb_n (n=1 - 10) and Ta_n (n=3 - 9) neutrals sputtered from pure *Nb* and *Ta* targets by 5 keV Ar^+ ions have been reported in Ref. [10]. In this case, the value of η^+ was defined as:

$$\eta^+ = Y^+_{n,1} / Y_{n,1} \qquad (2)$$

where $Y_{n,1} = Y^0_{n,1} + Y^+_{n,1}$; $Y^0_{n,1}$ and $Y^+_{n,1}$ were the measured yields of neutral and positively charged *n*-atomic clusters, respectively. For sputtered *Nb* atoms, the value of $\eta^+ = 9.6 \cdot 10^{-5}$ was obtained. With the increase of the number of atoms *n* in the cluster, η^+ strongly increased and reached its saturation at $\eta^+ = 0.75$ for Ta_5 and $\eta^+ = 0.27$ for Nb_7. In contrast to sputtered atoms, these values demonstrate significance of the ionized fraction of the cluster emission, which can become its major component for $n \geq 4$.

Estimates of total yields $Y_{n,m}$ for both neutral and charged particles can be obtained from a comparison between results of Refs.[6-8] obtained for sputtered cluster *ions* and those of Ref.[10] obtained for sputtered neutral clusters if the following assumptions are made.

- The ionization probability η^+ of the Nb_n and Ta_n clusters is independent of the sort (atomic species) and the energy E_0 of atomic projectiles.
- Charge state formation processes are additive for sputtered clusters with $n > 4$.

Considering a possible increase in the ionization probability one should keep in mind that in Ref.[10] the values of η^+ measured for Ta_5 and Nb_7 clusters were of order of several tens percents, and that η^+ is limited by 100% by its definition (Eq.2). This means that the non-additive factors for the ionization of these clusters *cannot* exceed several times. A possible difference between values of η^+ for clusters sputtered by atomic and molecular ion bombardment cannot produce the anomalously high emission enhancement up to two to three orders of magnitude reported for cluster ions in Refs.[6-8]. This is why we stated values of η^+ to be about the same high for clusters sputtered by atomic and polyatomic primary ions. The estimated (total) yields $Y_{n,m}$ of sputtered cluster ions and neutral clusters as well as the experimental cluster ion yields $Y^{+}_{n,m}$ obtained in Refs. [6-8] are shown for Nb and Ta in Figs. 1a and 1b, respectively.

One of the most important results obtained under the bombardment of metals by atomic projectiles (m=1) is a power law dependence of neutral cluster yields $Y^{0}_{n,1} \sim n^{-\sigma_1}$ on the number of atoms in the cluster n, where σ_1 is defined by sputtering conditions for a given "projectile–target" combination. This empirical dependence was first experimentally found in Refs [11, 12] and later qualitatively proven in Ref.[13] using molecular dynamics simulations of cluster emission in sputtering. It is interesting to examine how good the dependencies $Y_{n,m}(n)$ we obtained here obey this power law. One can see from Figs.1a and 1b that all the (total) dependencies $Y_{n,m}(n)$ calculated for the Nb_n ($n \geq 2$) and Ta_n ($n \geq 4$) clusters can be approximated by the power law function much better than the dependencies $Y^{+}_{n,m}(n)$ obtained for cluster ions only. The values of σ_m decreased with the increase of m, as follows. For sputtering of *Nb*: σ_1=9.27±0.45 (for Au^- primary ions), σ_2=7.58±0.37 (for Au_2^-) and σ_3=6.88±0.32 (for Au_3^-). For sputtering of *Ta*: σ_1=8.10±0.23 (for Au^-), σ_2=5.31±0.15 (for Au_2^-), and σ_3=4.16±0.19 (for Au_3^-). Thus, changing an atomic projectile for polyatomic ones lowers σ_m, which corresponds to an increase in the cluster emission intensity under molecular ion bombardment.

These results permit extracting information on $K_{m,m'}$ enhancement factors. In fact, under to the two assumptions mentioned above, the dependence $K_{m,m'}(n)$ for the yields $Y_{n,m}$ of clusters regardless of their charge state, should be very similar to that obtained for the yields $Y_{n,m}^{+}$ of cluster ions in Ref.[8]. Dependencies $K_{m,m'}(n)$ are shown in Figs. 2a and 2b. One can see, the values of $K_{m,m'}$ increased strongly with increase of the number of atoms n in the sputtered cluster, and, for a given n, they increased with the increase of the number of atoms m in the projectile.

Thus, the (total) yields $Y_{n,m}$ of clusters as well as the yields $Y_{n,m}^{+}$ of cluster ions emitted under the polyatomic ion bombardment appear to be *non-additive*. This allows us to derive a conclusion that the anomalously high non-additivity of sputtering of *Nb* and *Ta* in form of large cluster ions (n>4) observed in Refs.[6-8] under molecular ion bombardment originates from a non-additivity of the sputtering process, rather than from a non-additivity of a charge state formation process.

2.2 A manifestation of the sputtering non-additivity in kinetic energy spectra of sputtered ions

In this Section, we demonstrate how kinetic energies E of sputtered ions measured in Refs.[6-8] correlate with the non-additivity of the sputtering process. The energy distributions $f_{n,m}(E)$ of the Nb_n^+ (n=1-16) and Ta_n^+ (n=1-13) ions sputtered from pure *Ta* and *Nb* targets by 6 *keV/atom* Au_m^- primary ions (m=1, 2, 3) were measured in our previous works [6-8]. To reveal a correlation between the non-additive sputtering and the observed kinetic energy E of the sputtered ion, let us introduce a differential non-additivity factor $k_{m,m'}$, defined as:

$$k_{m,m'} = m' f_{n,m}(E) / m f_{n,m'}(E) \tag{3}$$

where $f_{n,m}(E)$ and $f_{n,m'}(E)$ are kinetic energy distributions of n-atomic ions sputtered by the ion bombardment with m- and m'-atomic projectiles, respectively. In our case, m=2, 3 and m'=1. The relationship between the integral factor $K_{m,m'}$ and the differential factor $k_{m,m'}$ can be expressed by an equation: $K_{m,m'} = \frac{1}{(E_{\max} - E_{\min})} \int_{E_{\min}}^{E_{\max}} k_{m,m'}(E)dE$ or using the Mean Value Theorem: $K_{m,m'} = k_{m,m'}(E^*)$ where $E_{min} < E^* < E_{max}$. Figs. 3 and 4 present dependencies $k_{3,1}(E)$ calculated for the range of 1 $eV<E<25$ eV the Nb_n^+ (n=1-5,7) and Ta_n^+ (n=1-4,6-8) ions, respectively. As seen from Figures 3 and 4, the $k_{3,1}(E)$ dependencies change their behaviour when the number n is changing, and significant differences between atomic ions (Figs 3a and 4a) and cluster ions (Figs. 3b and 4b) can be noticed.

For Nb^+ atomic ions, $k_{3,1}(E)$ decreased from k_{max}=10.5 observed at E=1 eV to k_{min} =6 at E=25 eV. For the corresponding integral non-additivity factor $K_{3,1}$=7 [8] (see also Fig.2a) an inequality $k_{max} > K_{3,1} > k_{min}$ is valid. For the Nb_2^+ ions, values of $k_{3,1}(E)$ slightly decreased with the increase of E, and the difference between their maximum and minimum values became insignificant: k_{max} = 8 and k_{min} =6. At the same time, the dependencies $k_{3,1}(E)$ determined for Nb_n^+ cluster ions ($n \geq 3$) show an opposite tendency. For example, values of $k_{3,1}(E)$ increase for Nb_3^+ ions with the increase of E from k_{min} =14 at E=1 eV to k_{max} = 20 at E=25 eV. In this case, the inequality $k_{max} > K_{3,1} > k_{min}$ is valid for $K_{3,1}$=16 [8]. Further, for Nb_4^+, Nb_5^+ and Nb_7^+ ions, the behaviour of $k_{3,1}(E)$ is similar to that for Nb_3^+ ions but values of $k_{3,1}(E)$ strongly increase with the increase of both E and n, as do the differences between values of k_{min} and k_{max}. For example, for the Nb_7^+ ions, k_{min} =100 at E=1 eV and k_{max} =375 at E=25 eV. Similar trends can be seen in Fig.4 for Ta_n^+ ions.

The dependencies $k_{m,m'}(E)$ were also sensitive to the number of atoms m in the projectile (see Figs. 3a and 4a). A comparison between $k_{2,1}(E)$ and $k_{3,1}(E)$ dependencies reveals that a change in the value of m from m=2 to m=3 (for m'=1) results in the higher values of $k_{m,m'}$ ($k_{3,1} > k_{2,1}$) that increase sharper with E making the difference between the k_{max} and k_{min} values greater.

The obtained $k_{3,1}(E)$ dependencies can be approximated by simple analytical functions. For Nb_n^+ (n=2-5,7) and Ta_n^+ (n=2-4,6-8) ions, the $k_{3,1}(E)$ dependencies are approximated by the functions $k_{3,1}(E) \sim exp(\alpha_n E)$ where a factor α_n increases with the increase of n (see Figs.3b and 4b). It is interesting to notice that *only* for atomic ions Nb^+ and Ta^+, $k_{3,1}(E)$ converted into dependencies $k_{3,1}(v^{-1})$ obey the exponential dependence on the inverse velocity v^{-1} the atoms (see Fig. 5a, b in Ref. [9]).

3. Conclusion.

To summarize, we demonstrated for larger Nb_n and Ta_n clusters (n>4) that the molecular ion bombardment does not significantly change the efficiency of their ionisation. Thus, it cannot cause the non-additive enhancement of the yields of the corresponding Nb_n^+ and Ta_n^+ cluster ions observed in experiments. Rather, the non-additivity of the sputtering process plays the major role in this case. This non-additivity manifests itself in kinetic energy spectra of sputtered particles and can be characterized by the differential non-additivity factors $k_{m,m'}$ who behave differently for atomic ions and for cluster ions. A behaviour change for $k_{m,m'}(E)$ dependencies is observed for a transitional range of 2<n<4 where a competition between two different processes of sputtered ion formation apparently starts [6]. For atomic sputtered ions, it remains unclear if any process becomes predominant: both non-additive sputtering and non-additive ion formation seem equally probable. New experiments are needed to derive any conclusion about this complex phenomenon.

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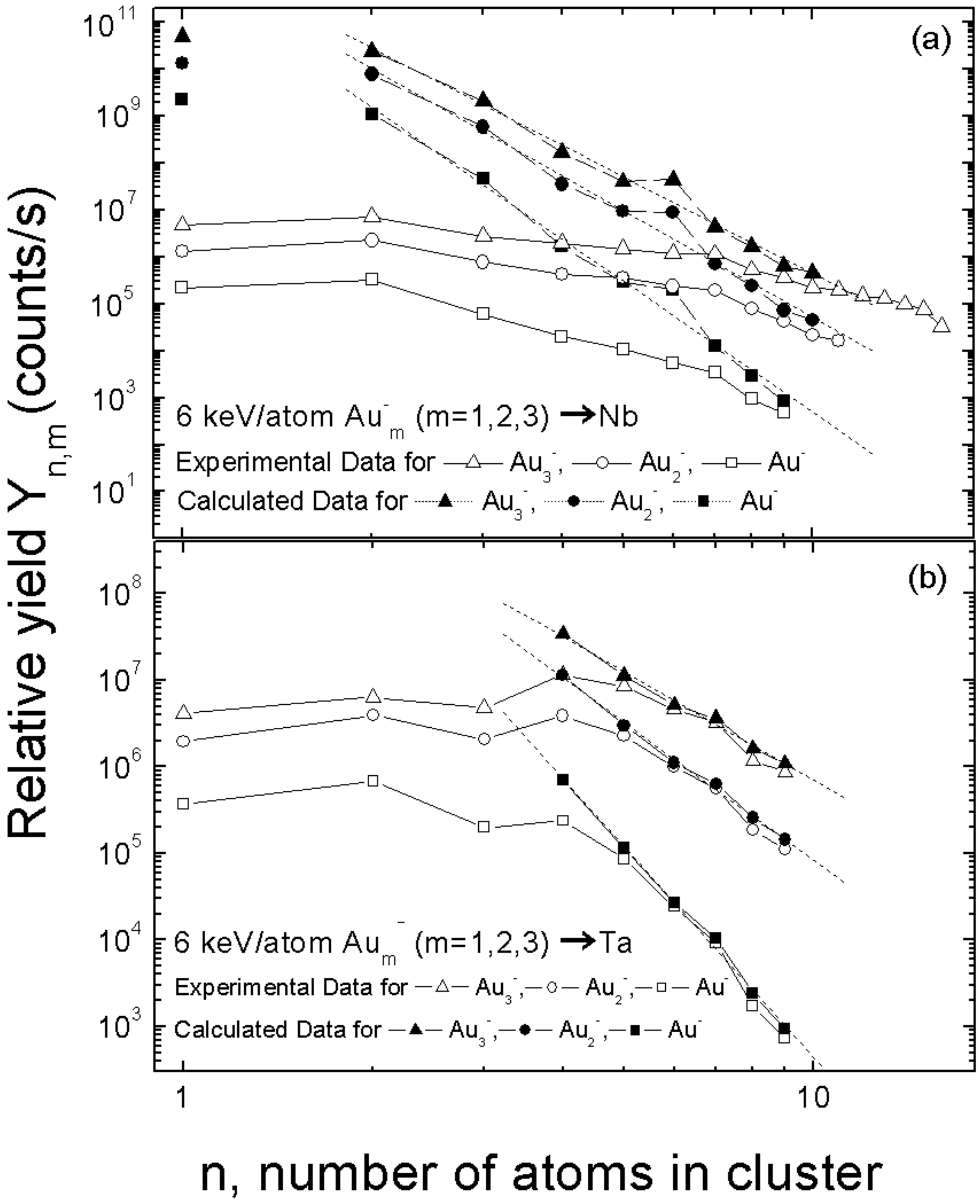

Figure 1.
Yields measured for cluster ions in Refs.[6-8] under bombardment of Nb (a) and Ta (b) targets by 6 keV/atom Au_m^- primary ions (open symbols) and the corresponding *total* yields of sputtered clusters (solid symbols) calculated from these experimental data using ionisation probabilities of the clusters determined in Ref.[10]. Dashed lines show fitting the latter dependencies by a power law function.

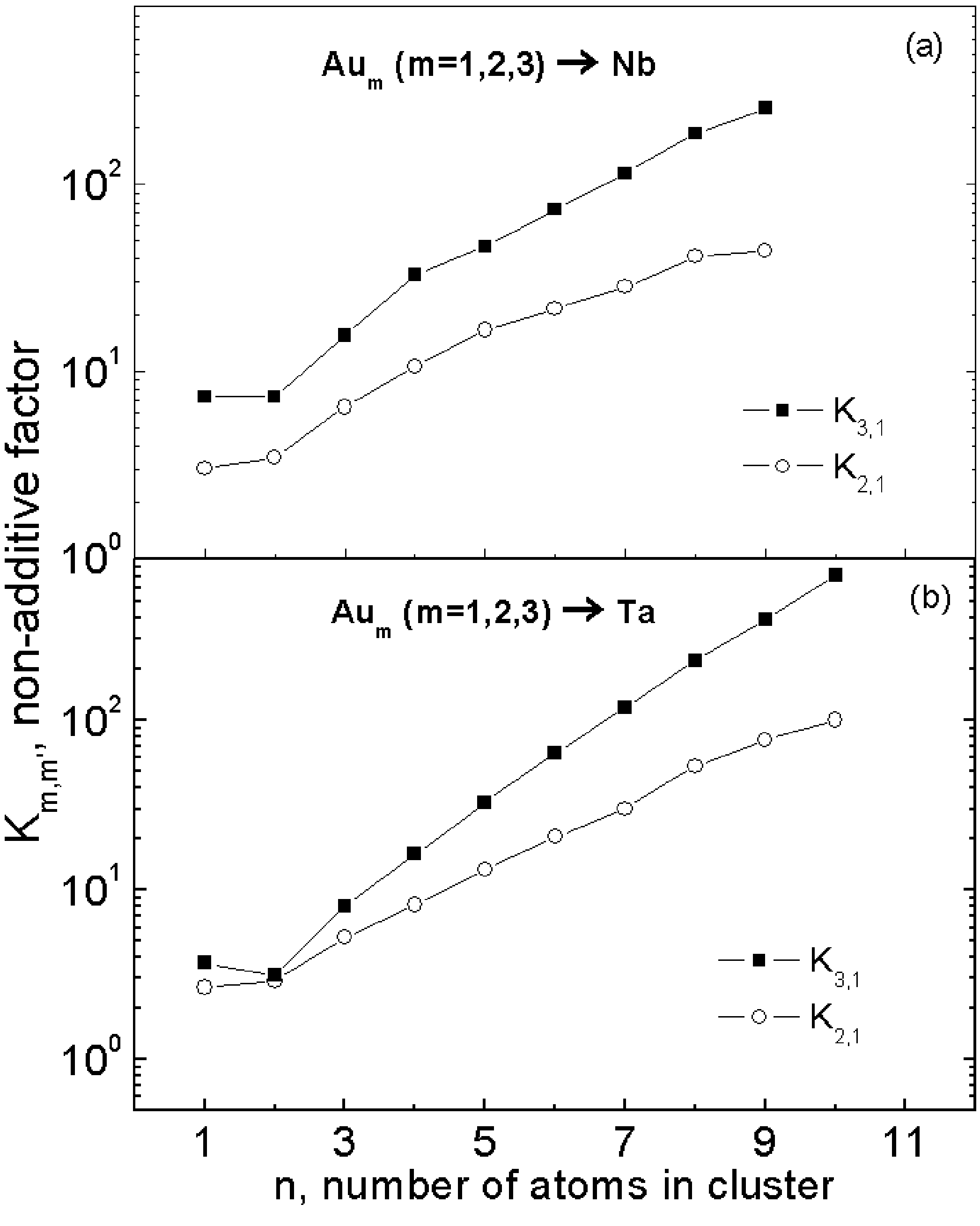

Figure 2.

Integral enhancement (non-additivity) factors $K_{m,m'}$ calculated using Eq.1 from the dependencies of total yields of sputtered particles shown in Fig.1.

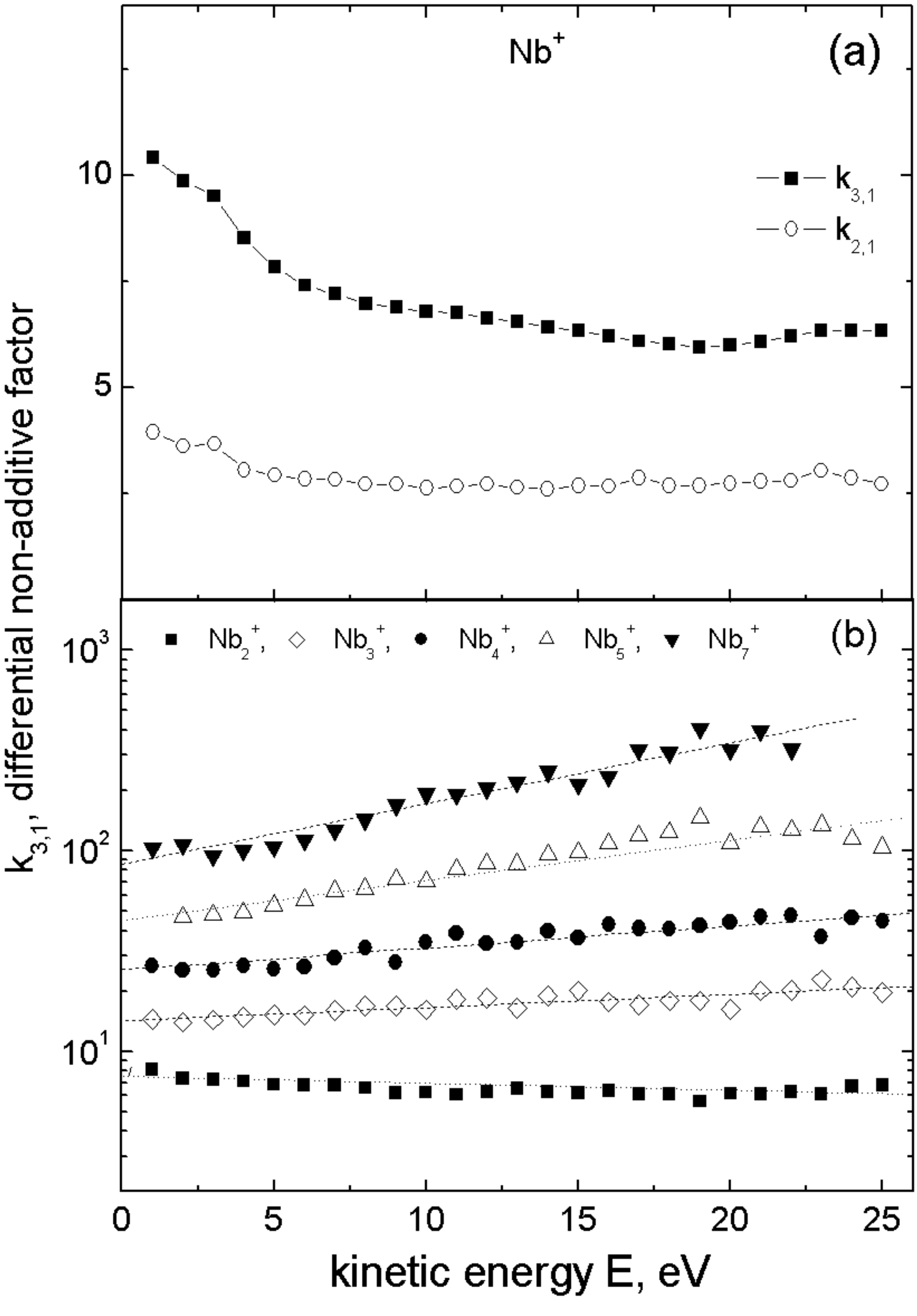

Figure 3.
Differential non-additivity factors calculated using Eq.3 from kinetic energy spectra of ions sputtered from Nb: factors $k_{2,1}$ and $k_{3,1}$ for atomic ions Nb$^+$ (a) and factors $k_{3,1}$ for cluster ions Nb$_n^+$ (n=2-5,7).

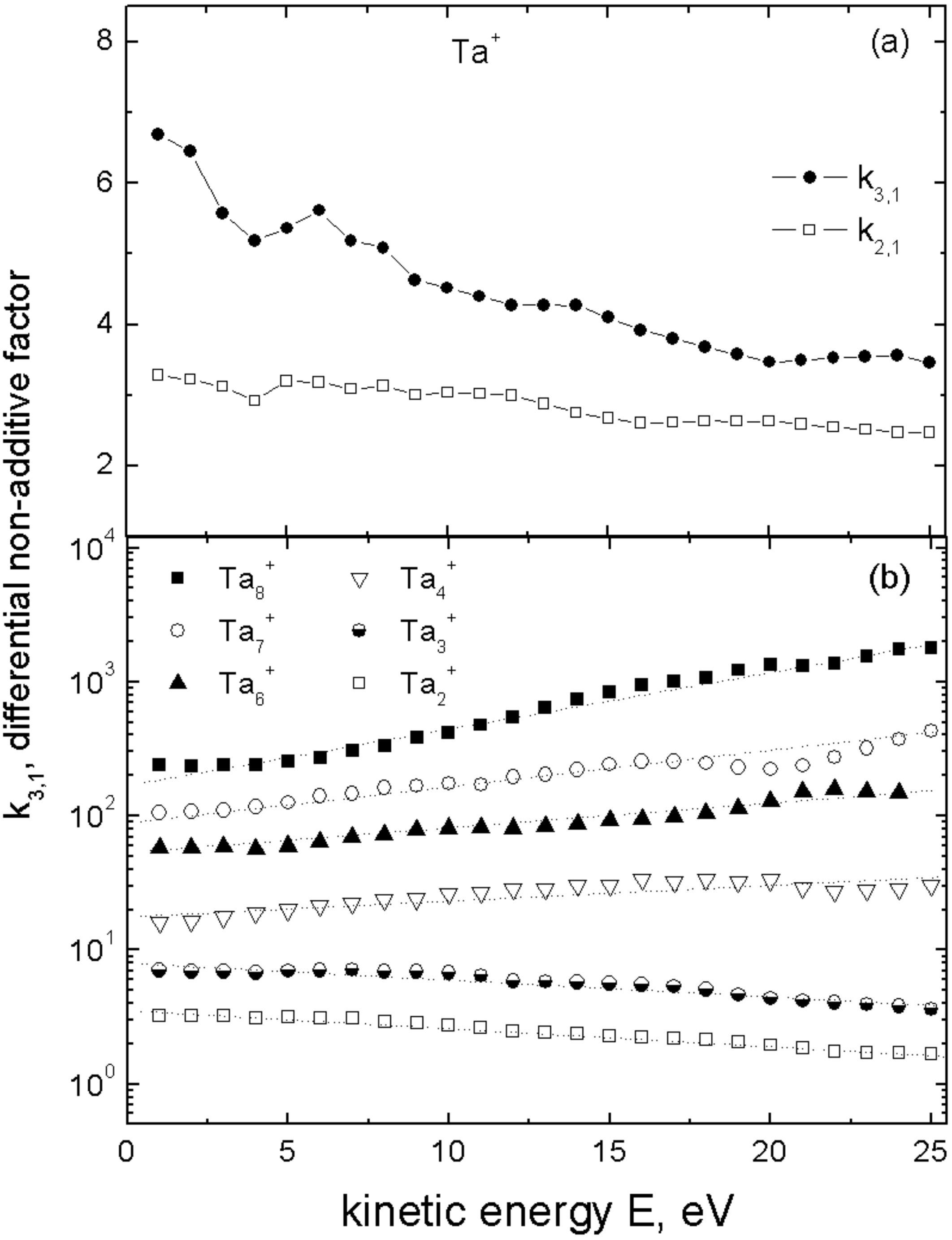

Figure 4.
Differential non-additivity factors calculated using Eq.3 from kinetic energy spectra of ions sputtered from Ta: factors $k_{2,1}$ and $k_{3,1}$ for atomic ions Ta^+ (a) and factors $k_{3,1}$ for cluster ions Ta_n^+ (n=2-4, 6-8).