



Sputtering with polyatomic ions: revisiting kinetic energy distributions of secondary ions

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Abstract

A new more accurate data processing procedure for calibration of kinetic energies of secondary ions measured in magnetic sector secondary ion mass spectrometers has been developed. The procedure was applied to reprocessing of raw data from previously published measurements of kinetic energy spectra of secondary atomic and cluster ions sputtered from Ta by 6 keV/atom Au⁻, Au₂⁻ and Au₃⁻ projectiles. Absolute energies of the sputtered Ta_n⁺ ions were determined more accurately, which permitted a fairer comparison of energy spectra for the same secondary ions measured under bombardment with different primary ions. Most probable and mean energies were determined for the sputtered ions, and their energy spectra were converted into distributions over inverse velocities. The reprocessed experimental results revealed strong differences between results for atomic and diatomic ions and those for larger cluster ions (consisting of more than seven atoms). In particular, the comparison of atomic and polyatomic bombardment showed that there are strong differences between atomic and diatomic sputtered species, while there were almost no changes between larger sputtered clusters. Results are discussed in terms of observed enhancements under polyatomic ion bombardment for the total sputtering efficiency and the ionization of sputtered species.

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PACS: 79.20.Rf; 34.50.Dy; 79.20.Rf; 68.49.Sf; 82.80.Ms

Keywords: Sputtering by atom, molecule, and ion impact; Ion-surface impact; Molecular beams interactions with solids; Secondary-ion mass spectrometry (SIMS)

1. Introduction

During the last decade, analytical applications of sputtering with polyatomic ions generated increasing interest in the ion-beam community, especially that part, which is engaged in secondary

ion mass spectrometry (SIMS) [1]. On the other hand, despite the fact that this ion bombardment regime has been long known to enhance yields of secondary ions [2], the mechanism of the enhancement remains poorly understood. It is presently unclear what actually increases under polyatomic ion bombardment: the total sputtering yield or the ionization probability of sputtered neutrals [3]. Moreover, for sputtered atomic and cluster ions, the emission enhancement observed in experiments might be due to different reasons, such

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as enhancement of ionization for atomic species and enhancement of sputtering for clusters.

In the present work, we will demonstrate that additional information on this process can be extracted from experimentally measured kinetic energy distributions of secondary atomic and cluster ions sputtered by atomic and polyatomic projectiles. We have recently developed a new data processing procedure for the calibration of kinetic energies of secondary ions measured in magnetic sector secondary ion mass spectrometers [4]. This procedure permits a better determination of the absolute energies and thus allows a more accurate comparison of the energy distributions of the same secondary ions measured under ion bombardment by different projectiles. We applied this new procedure to previously published data [5] by conducting a new processing of raw data. As a part of this re-examination, a conversion of the experimental kinetic energy distributions of secondary ions into distributions of velocities and inverse velocities was performed. Results of this effort revealed interesting trends as discussed below.

2. Experimental measurement and energy calibration procedures

Kinetic energy distributions of sputtered ions [5] have been measured using a magnetic sector SIMS instrument equipped with a cluster ion source [6], which generated 6 keV/atom polyatomic ions Au_m^- ($m = 1, 2, 3$). To keep the Ta sample surface clean of oxide films, sample temperatures of 2000 °C were maintained during the measurements. This was achieved by choosing the sample geometry as ~ 3 mm wide ribbon made of Ta foil whose two ends were connected to terminals of a floating power supply so that electric current through the ribbon could heat the sample. Secondary ions of a specific mass were selected by aligning the magnetic field to the maximum intensity of the ion signal while operating the instrument with a nominal accelerating voltage of 2000 V. To measure kinetic energy spectra, the accelerating voltage was altered by varying the target potential within the range of ± 300 V with 1 V increments. The energy resolution of the

experimental apparatus and its response function, were determined by the measurement of the kinetic energy spectra of thermal ions of alkali metals, Na^+ and K^+ , formed on the hot sample surface in the absence of ion bombardment. The described experimental procedure matches the capabilities of the ion optics of the instrument, and, therefore, it is widely used for energy spectra measurements in magnetic sector mass spectrometers. Unfortunately, the procedure does not directly determine absolute values for secondary ion energies since the energy spectra maximums always correspond to the nominal accelerating voltage. To compare energy spectra measured under bombardment by different projectiles, a special calibration procedure was developed. This procedure, summarized in Fig. 1, is based on taking into account the fact that actual energy distributions are always distorted and smeared by the measurement process, which is characterized by the energy resolution function of the instrument with a finite width. The measured data are always related to the actual distribution through an integral of convolution. One straightforward but rather complicated, way of dealing with this would be processing the data

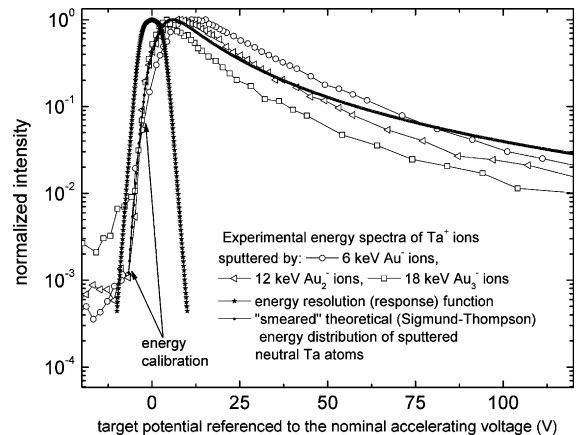


Fig. 1. How the energy calibration procedure works: experimental kinetic energy distributions of atomic ions Ta^+ sputtered by different 6 keV/atom Au_m^- ($m = 1, 2, 3$) projectiles are compared and aligned with the theoretical kinetic energy distribution computed for the same experimental energy resolution. The energy resolution, response function is determined by measuring kinetic energy spectra of thermal ions of alkali metals without ion bombardment.

using some sort of deconvolution technique. We did not choose this approach because the most probable and mean values that can be extracted from properly calibrated “smeared” experimental data are not necessarily less meaningful or accurate than those obtained from deconvolved data. Moreover, artifacts are easily introduced by deconvolution procedures due to noise, which is always present in experimental data. Therefore efforts were aimed at the development of an energy calibration procedure, which would perform convolution of analytical functions and compare them with the experimental data as described below.

First, a fitting function for the kinetic energy spectra of thermal ions was found. This was an asymmetric double sigmoidal function $\Phi(E)$,

$$\Phi(E) = \frac{A}{1 + \exp\left[-\frac{E+0.5\cdot w_1}{w_2}\right]} \cdot \left[1 - \frac{1}{1 + \exp\left[-\frac{E-0.5\cdot w_1}{w_3}\right]}\right], \quad (1)$$

where A , w_1 , w_2 and w_3 are fitting parameters.

Second, an assumption was made that kinetic energy distributions of neutral atoms sputtered by atomic ions are described by the Sigmund–Thompson formula [7,8],

$$F(E) = \frac{dN}{dE} \propto \frac{E}{(E + U_s)^3}. \quad (2)$$

The validity of this assumption for sputtering of pure metals has been proven experimentally many times during the three decades since the formula was introduced [9]. Thus, the kinetic energy distribution of neutral Ta atoms was calculated using the tabulated value of sublimation energy (taken as the first approximation of the surface binding energy) of $U_s = 8.1$ eV.

Third, the integral of convolution of the theoretical energy distribution of sputtered neutral atoms with the response function of the instrument was computed to produce the energy spectrum of sputtered neutral Ta atoms as if they were measured by the same SIMS instrument,

$$F_{\text{smeared}}(E) = \int_{-\infty}^{\infty} \Phi(\varepsilon) \cdot F(E - \varepsilon) d\varepsilon. \quad (3)$$

Overlapping and aligning the “smeared” theoretical spectrum $F_{\text{smeared}}(E)$ with the measured energy spectrum of sputtered atomic ions in the energy region to the left of the maximum (where intensities are sharply decreasing to zero) allowed us to determine the most probable energy of the sputtered ions. The position of the maximum of the “smeared” distribution $F_{\text{smeared}}(E)$ was considered to be the same as that of the original (Sigmund–Thompson) distribution $F(E)$ (Fig. 1). Using this energy calibration permitted a fair comparison between kinetic energy spectra of secondary ions measured under bombardment by different primary ions provided that the energy resolution of the instrument did not change.

3. Results and discussion

3.1. Kinetic energies

Experimental raw data from [5] were recalibrated as described above. Then additional data processing was performed to determine most probable and mean kinetic energies of secondary ions and to compare these values for the same secondary ions sputtered by different primary ions. Results of these calculations are presented in Fig. 2. Before determining most probable energies, the spectra were smoothed using the fast Fourier transform (FFT) filtering algorithm. No smoothing was needed to calculate the mean energies as

$$\bar{E} = \int E \frac{dN}{dE} dE / \int \frac{dN}{dE} dE. \quad (4)$$

The error propagation from experimental data into the calculated mean values was computed assuming the errors to be defined by the Poisson statistics, typical for the pulse counting mode used in these measurements.

Comparing sputtering from atomic and polyatomic ions, for the results shown in Fig. 2, one can see that the most probable energies and the mean energies of secondary ions reveal significant differences for Ta^+ atomic ions, slight differences for Ta_2^+ diatomic ions and practically no differences (within the experimental confidence intervals) for larger cluster ions. Compared to atomic

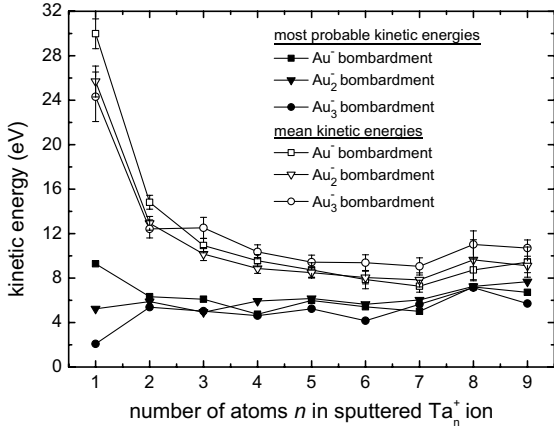


Fig. 2. Most probable kinetic energies and mean kinetic energies of Ta_n^+ ($n=1-9$) secondary ions sputtered by 6 keV/atom Au_m^+ ($m=1, 2, 3$) primary ions determined from the calibrated kinetic energy distributions dN/dE .

projectiles, the polyatomic ones cause a significant decrease in kinetic energies of sputtered atoms and dimers. It is commonly believed [7] that the most probable energy of sputtered atomic ions is defined both by energy of sputtered neutral atoms and their ionization probability, which also depends on kinetic energy of the neutrals. The most probable kinetic energy of neutral atoms correlates with the surface binding energy of the material the ion was sputtered from, as expressed in Eq. (2). Decreases of the most probable energies we observe for atomic ions sputtered by polyatomic projectiles may indicate the decrease of the surface binding energy, which is the factor that defines the sputtering process efficiency [10]. It is logical that lowering the surface energy barrier would increase the emission probability of recoils with lower energies. In general, this should cause an increase of the sputtering yields. On the other hand, the trend we observe may suggest that the ionization probability for slower sputtered neutrals increased, or equivalently, that the neutralization probability for slower ions decreased, which would increase the yield of sputtered ions. This may indicate that the efficiency of the ionization mechanisms for atomic and diatomic sputtered species changes under ion polyatomic bombardment. Unfortunately, based on SIMS measurements only, it

would be prematurely to conclude which effect is dominating.

Another interesting trend seen in Fig. 2 is that energies of larger cluster ions $Ta_7^+ - Ta_9^+$ increase, in comparison to the smaller clusters. This might suggest either some difference in the process of cluster formation or changes in ionization probability of these larger cluster ions compared to smaller ones. What is important and clearly seen from the mean energies of these cluster ions is that changing the bombarding projectile from atomic to polyatomic does not have a strong influence on the mean energy.

3.2. Inverse velocities

In an attempt to gain insight into the ionization process, we converted kinetic energy distributions of sputtered ions dN/dE into distributions of velocities dN/dv and distributions of inverse velocities $dN/d(v^{-1})$ using the Jacobians corresponding to these transformations:

$$\frac{dN}{dv} = \frac{dN}{dE(v)} \cdot \frac{dE(v)}{dv} = \frac{dN}{dE(v)} \cdot Mv, \quad (5a)$$

$$\begin{aligned} \frac{dN}{d(v^{-1})} &= \frac{dN}{dE(v^{-1})} \cdot \frac{dE(v^{-1})}{d(v^{-1})} \\ &= \frac{dN}{dE(v^{-1})} \cdot \left[-\frac{M}{(v^{-1})^3} \right], \end{aligned} \quad (5b)$$

where M is the mass of the sputtered particle.

When considering inverse velocities, one should remember that multiplying them by some distance produces the time necessary to move over that distance. The distributions in such times, dN/dt , are proportional to the distributions in inverse velocities, $dN/d(v^{-1})$. If we choose a crystal lattice parameter as a (characteristic) distance, then the distributions dN/dt will show the time required for sputtered atoms and clusters to move away from the sample surface a distance of one lattice parameter. Distances of this order are often considered in models of charged state formation in sputtering [11] as the ones that limit the electron exchange processes between a departing sputtered particle and the surface. This is why knowing how long it takes a sputtered species to reach this dis-

tance may be a good indication of what processes on the surface can contribute to formation of secondary ions observed in experiments. For Ta, the lattice parameter is estimated as 0.33 nm. Three sets of distributions, dN/dv , $dN/d(v^{-1})$ and dN/dt , were calculated for atomic and cluster ions sputtered from Ta by 6 keV/atom Au^- , Au_2^- and Au_3^- primary ions. As in the case with kinetic energy distributions, in order to compare so many different curves, we calculated mean values of the velocity, the inverse velocity, and the time needed to travel one lattice parameter away from the surface:

$$\bar{v} = \int v \frac{dN}{dv} dv / \int \frac{dN}{dv} dv, \quad (6a)$$

$$\overline{v^{-1}} = \int v^{-1} \frac{dN}{d(v^{-1})} d(v^{-1}) / \int \frac{dN}{d(v^{-1})} d(v^{-1}), \quad (6b)$$

$$\bar{t} = \int t \frac{dN}{dt} dt / \int \frac{dN}{dt} dt. \quad (6c)$$

Fig. 3 shows the dependencies of mean inverse velocities, $\overline{v^{-1}}$, and mean times, \bar{t} , on the number of atoms, n , in the detected sputtered ion.

The weak trend seen is that values of $\overline{v^{-1}}$ and \bar{t} become undistinguishable for all three projectiles

Au_m^- ($m = 1, 2, 3$) at $n = 4$. In the region of atoms, dimers and trimers these values increase while m increases, i.e. secondary ions produced by molecular bombardment are slower, on average. In the region of larger clusters $\overline{v^{-1}}$ and \bar{t} show the opposite behavior, i.e. secondary ions produced by molecular bombardment are faster. The whole picture may suggest that polyatomic ion bombardment of tantalum does not cause any dramatic changes in the ionization probability of sputtered species larger than atoms and dimers as compared to atomic ion bombardment.

The trend clearly seen in Fig. 3 is the difference in behavior of atomic and diatomic ions, on one hand, and $\text{Ta}_7^+ - \text{Ta}_9^+$, on the other hand. The times these larger clusters need to depart from the emission spot appear to be about the same, around 4×10^{-13} s. Such long times may indicate that the localization of electronic excitations around the emission spot [12] do not contribute to ionization mechanisms of these clusters. Such electronic excitations have lifetimes about one order of magnitude shorter than the time needed for large clusters to depart from the near-surface region. As a consequence, these electronic excitations may have much stronger influence in the ionization of atomic and diatomic ions than in that for larger clusters. Considering this, one should keep in mind that using the inverse velocity multiplied by the lattice parameter as a parameter indicating how long the sputtered species spend near the surface and participates in electron exchange becomes rather questionable for larger clusters. This is because velocities determined from experiments correspond to the center of mass of the sputtered particle. When the size of the particle increases, the position of its center of mass does not describe well the distance at which the electron exchange process ends. This distance may be better estimated using the scaling law of cluster properties [13], which expects them to scale linearly with the inverse cluster radius estimated as a reciprocal of the product of a lattice parameter and a cubic root of number of atoms in the cluster. Doing this with the dependencies shown in Fig. 3 will shift the effective times needed for larger clusters to depart from the surface into a picosecond range, where internal vibrational excitation of the clusters may start

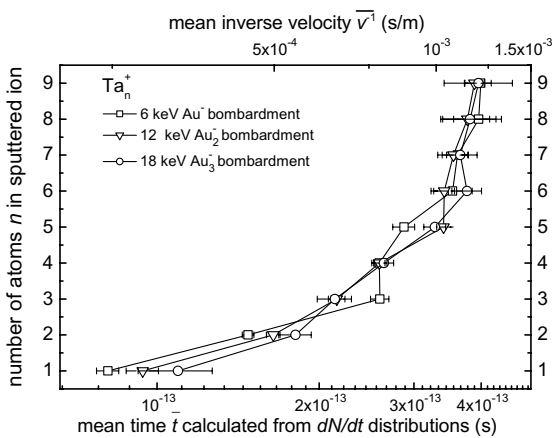


Fig. 3. Mean inverse velocities and mean times needed to travel the distance of one lattice parameter determined for Ta_n^+ ($n = 1 - 9$) secondary ions sputtered by 6 keV/atom Au_m^- ($m = 1, 2, 3$) primary ions.

contributing to the cluster ionization. For example, speaking in terms of the characteristic distance that enables electron exchange with the surface, one can imagine these vibrations alternating the probability of this process just due to the change in the physical dimension (size) of large clusters slowly moving away from the surface. And this does not yet take into account the possibility that internal energies of large clusters may be sufficient for their ionization in vacuum, without participation of the surface. This can occur, for example, due to the thermo-electron emission from clusters [14]. The above considerations demonstrate the complexity of charge state formation of sputtered atomic and cluster species.

4. Conclusion

Developing a more accurate energy calibration procedure and reprocessing the experimental raw data for kinetic energy spectra of ions previously reported [5] allowed us to determine and to compare important characteristics of secondary ion emission from a Ta sample sputtered by atomic and molecular ions Au_m^- ($m = 1, 2, 3$). Similar trends were observed in the secondary ion distributions over velocities, inverse velocities, and characteristic times needed for particles to travel one lattice parameter away from the sample surface. It can be summarized, as follows:

- (1) Strong differences in most probable and mean energies of atomic and diatomic ions sputtered by different projectiles may indicate both a decrease in surface binding energy under polyatomic ion bombardment and a change in the energy dependence of the ionization probability of atomic and diatomic sputtered species so that the probability increases for ions with lower energies.
- (2) No strong dependence on the size of the projectile is observed for sputtered cluster species.
- (3) For larger cluster ions Ta_n^+ ($n > 6$), the time needed to move away from the sputtered spot

to a distance of one lattice parameter are significantly longer (an order of magnitude) than those for atomic and diatomic ions. This indicates significant differences between mechanisms of their ionization.

Acknowledgements

Authors would like to thank Drs. Wallis Calaway, Igor Wojciechowski and Alexander Zinoiev for fruitful discussions and useful comments related to the results presented in the manuscript.

This work is supported by the US Department of Energy, BES-Materials Sciences, under contract no. W-31-109-ENG-38 and by the Belgian Federal Services for Scientific, Technical and Cultural Affairs (DWTS/SSTC) of the Prime Minister's Office through IUAP-5.

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