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Kinetic energy distributions of neutral In and In$_2$ sputtered by polyatomic ion bombardment

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Abstract

Kinetic energy distributions of neutral In monomers and In$_2$ dimers sputtered from a polycrystalline indium surface under bombardment with 5 keV/atom Au$_1$ and Au$_2$ projectiles have been investigated by means of laser postionization time-of-flight mass spectrometry. Results show that 5 keV Au$_1$ bombardment leads to results in full compliance with linear cascade sputtering theory. For polyatomic ion bombardment, we find a clear transition to a collisional spike dominated emission process. The spike contribution appears as a low-energy part in the sputtered flux which increases with increasing projectile nuclearity and energy. We show that, the velocity spectrum associated with the low-energy contribution is virtually identical for sputtered monomers and dimers. This finding has important implications with respect to the particle emission mechanism under polyatomic projectile bombardment.

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1. Introduction

When a solid is bombarded with energetic ions, surface species are released (sputtered) in various charge, excitation and binding states. The underlying physics of the process when atomic projectiles implemented is reasonably well understood and described by collisional cascade theory [1]. Sputtering in linear cascade mode leads to the emission with strongly non-thermal kinetic energy distributions (KED) of atoms verified both experimentally (see Ref. [2] for a review) and in computer simulations [3]. Linear cascade theory is applicable when the energy density deposited by the impinging projectile is dilute enough that condition of binary collisions (linearity) is fulfilled. Experimentally, however, deviations from the theory were observed when projectiles containing more than one atom were used [4]. This effect manifested as a non-additive enhancement of the sputtering yield per constituent atom in the projectile [5–8]. The qualitative interpretation of this observation is that the projectile disintegrates upon impact, and the collision cascades initiated by the individual constituent atoms overlap to form a dense collisional spike, which does not satisfy the linearity condition. Recent results [9,10] showed large yield enhancement effects scaling with projectile nuclearity. The effect is interpreted in the terms that, in addition to a linear cascade, a spike developed at later times must evolve.

KED of sputtered neutrals must carry a characteristic signature of the sputtering process. So far, only few experiments have been conducted where the KED of sputtered species were measured under polyatomic ion impact. Most of them were taken for secondary ions, where the observed energy spectra are influenced by a velocity dependent ionization mechanism. The information regarding the influence of non-linear spike contributions on the emission energy distribution of sputtered neutral particles ejected under polyatomic projectile is still lacking. In the present work, we use gold cluster ions Au$_m$ with $m = 1, \ldots, 3$ and impact energies of 5 and 10 keV to bombard a clean, polycrystalline indium surface. KED of In and In$_2$ species emitted along the surface normal are presented. The resulting spectra are compared with the prediction of linear cascade sputtering theory. The results show a strong non-linear yield enhancement under polyatomic projectile bombardment, which originates from a spike emission mechanism predominantly leading to low-energy ejection. Comparison of the result with published spike models reveals that evaporation from a thermal spike cannot explain the data. In contrast, the data constitute strong evidence for “microexplosion” [11] emission...
mechanism involving a quasi-free expansion of an over-critically heated subsurface volume.

2. Experimental

The experimental setup used for mass and energy spectrometric detection of sputtered neutral particles has been described in detail elsewhere [12]. The system consists of an ion source generating cluster ions of a desired element and a laser postionization time-of-flight (ToF) mass spectrometer used to detect the neutral species sputtered from the sample surface.

The sputter ion source generating the projectile ions is described in detail elsewhere [13]. In the present work, mass selected $\text{Au}^+$, $\text{Au}_2^-$ and $\text{Au}_3^-$ projectile ions of 5 and 10 keV impact energy were used with beam currents around 150 nA ($\text{Au}^+$) and 20 nA ($\text{Au}_2^-$ and $\text{Au}_3^-$), respectively. The projectiles impinge onto a polycrystalline indium surface under an angle of 45° with respect to the surface normal.

To determine the emission velocity distribution of sputtered neutral particles, the projectile ion beam is operated in a pulsed mode with a pulse duration of 200 ns. The postionizing laser beam is positioned at a distance of 2 mm in front of the surface and focused to a cross-section of about 0.3 mm $\times$ 0.5 mm (FWHM) with the short dimension along the surface normal. Moreover, the laser intensity is attenuated to a peak power density of about $2 \times 10^6$ W/cm$^2$ in order to avoid saturation of the photoionization process. The emission velocity of the detected neutral particles is selected via their flight time from the sample surface to the ionization volume by a controlled variation of the time delay $t_d$ between the projectile ion pulse and the laser pulse [14].

3. Results and discussion

3.1. Energy distributions

The resulting kinetic energy spectra of neutral In atoms ejected along the surface normal under bombardment with different projectiles are displayed in Fig. 1. These data can now be compared with the distribution expected from linear cascade theory [15]

$$f(E) \propto \frac{E}{(E + U_0)^3}$$

where $U_0$ denotes the surface binding energy of the ejected atoms. In principle, minor corrections to the exponent in the denominator have been proposed [1] which are neglected here. Taking $U_0$ as a fit parameter, we obtain the best fit for $U_0 = 2.4$ eV slightly below the respective value of 2.6 eV for indium. The resulting curve, normalized to the maximum of the 5 keV $\text{Au}^-$ data, is indicated by the solid line. It is apparent that the linear cascade prediction is in almost perfect agreement with the energy distribution measured for impact of 5 keV $\text{Au}^-$ projectiles. In the case of $\text{Au}_2^-$ bombardment with energy of 10 keV, deviations from the linear cascade distribution are found which manifest as an additional contribution at low emission energies.

Qualitatively, this observation is in agreement with results of earlier energy distribution measurements performed under impact of heavy, high-energy monoatomic projectiles [4]. As discussed in Andersen’s review [4], this contribution is attributed to particle emission from a so-called “collisional spike”, i.e., a subsurface region where a very dense collisional cascade is propagating. Here, the linear cascade condition – low density of moving particles – is not fulfilled any more, leading to a non-linear enhancement of the sputter yield. In that sense, the data depicted in Fig. 1 represent clear evidence that particle emission initiated by impact of heavy polyatomic projectiles onto a metallic surface is completely dominated by such a spike which shows no resemblance with a linear cascade any more.

So far, only the atomic species among the flux of sputtered particles have been considered. As it turns out, another interesting piece of information on the sputtering mechanism is gained by comparing the emission velocity spectra of ejected monomers and clusters. As an example, corresponding data measured for sputtered neutral In$_2$ dimers are plotted in Fig. 2 along with those of the monomers. Under 5 keV $\text{Au}^-$ bombardment, a dimer spectrum is produced which peaks at lower emission velocity and falls off more steeply towards high velocities than that of the monomers. This result is in accordance with a number of similar studies [16,17] and represents another manifestation that this case clearly falls into the linear collision cascade regime of sputtering. Upon transition to 10 keV $\text{Au}_2^-$ bombardment, we find a dominating low-velocity component also for sputtered dimers. The corresponding data in Fig. 2 reveal a striking change of the measured spectra in such a way that now the sputtered monomers and dimers exhibit almost identical velocity distributions. This is particularly true in the low-velocity range (below 2 km/s), where the spike emission mechanism is operative. At high velocity, on the other hand, the data show that a superimposed linear cascade emission process remains active. Translated to emission energy, the data in Fig. 2 mean that the dimer energy spectrum peaks at higher kinetic energies than that.
experimental data slightly better than Eq.(2), it is evident that this functional dependence is not capable of describing the measured distributions. The striking observation is in marked contrast to the case of atomic ion bombardment. This observation is in marked contrast to the case of atomic ion bombardment. While bombardment of monomers under polyatomic projectile bombardment.

3.2. Comparison with theoretical spike models

The energy spectra depicted in Fig. 1 are now compared to predictions from published spike sputtering models. We first examine the thermal evaporation approach which has been cast in a variety of different formulations. In its simplest form, the energy spectrum of atoms emitted by thermal evaporation from a locally heated surface spot is predicted as a Maxwell–Boltzmann distribution according to:

\[ f(E) \propto E \exp\left(\frac{-E}{kT}\right) \]  

(2)

Corresponding fits have been made to some published experimental data and were claimed to agree quite well [19–21]. If we fit Eq. (2) to the data presented in Fig. 1, we obtain the results included as dotted line. It is immediately evident that the measured spectra cannot be explained by such a model, since the Maxwell–Boltzmann distribution severely underestimates the data in the energy regime above 0.3 eV. Least square fits of the more sophisticated energy distribution predicted, for instance, by the Sigmund–Claussen model [22] are therefore also included in Fig. 1 (dashed line). Although the results fit the experimental data slightly better than Eq. (2), it is evident that also this functional dependence is not capable of describing the measured distributions. The striking observation is in Fig. 1 is the very low most probable emission energy of 0.1 eV, which corresponds to a spike temperature of about 1000 K. Based on the prevailing model description of thermal spike emission [22] this value can be used to estimate the relative magnitude of the non-linear yield contribution arising from the spike. As a result, the model [22] predicts a ratio between the thermal spike and linear cascade yield contributions \( Y_{S}/Y_{lin} \sim 10^{-11} \), which is by many orders of magnitude at variance with the data in Fig. 1. As a consequence, one has to conclude that the experimental results obtained here cannot be consistently interpreted in terms of a thermal spike emission mechanism.

A sputtering model based on concepts of hydrodynamics in a superheated gas has been proposed to explain the emission characteristics found during sputtering of condensed rare gases [23]. This “gas flow” model treats the emission process as a quasi-free expansion of a sub-surface sample volume which has been heated to temperatures above the critical point and, hence, become gasified in the course of the collision cascade. Since the density is still close to that of the solid, immense pressure builds up which leads to a complete disruption of the surface, typically followed by the formation of a crater [23–25]. In principle, such a scenario should develop under conditions where the energy density in the collision cascade greatly exceeds the sublimation energy per atom. For rare gas targets, due to the low sublimation energy this situation is already reached under low-energy impact of rare gas atoms. For metallic targets, a similar situation is apparently realized under heavy polyatomic projectile impact.

The model in its published form makes an explicit prediction of the kinetic energy spectrum of emitted particles, and can therefore be compared to our experimental data. In particular, we fit KED of In monomers sputtered under polyatomic ion bombardment using the initial spike core temperature \( T_0 \) and the “recondensation temperature” \( T_{con} \) as fitting parameters. The resulting fitting curve is shown as a dash dot line in Fig. 1. It is clearly evident that our experimental data are in much better agreement with the prediction from the gas flow model in comparison with the thermal spike model. The best fit is found for \( T_0 = 18000 \) K (and \( T_{con} = 700 \) K).

The high energy density in the spike volume leads to a fundamentally different situation where the criteria for the applicability of phase explosion dynamics described, for instance, by the gas flow model appear to be fulfilled.

4. Conclusion

The energy distributions of neutral particles sputtered from a metal surface under bombardment with heavy gold cluster projectiles present clear evidence for the formation of collisional spikes. Our results show the contribution of a spike-induced emission mechanism to grow with increasing nuclearity and energy of the projectile. While bombardment of indium with 5 keV \( \text{Au}_1 \) still leads to results which are in excellent agreement with the prediction of linear cascade sputtering, the impact of 10 keV \( \text{Au}_2 \) apparently generates completely spike-dominated dynamics. However, it is also evident that the particle emission mechanism prevailing under these conditions cannot be interpreted in terms of thermal
evaporation from a locally heated solid. This finding is easily rationalized by the fact that spike temperatures producing the observed non-linear yield enhancement would necessarily have to be of the order of $10^6$ K, i.e., larger than the critical temperature of the target material. Therefore, the material in the core of the developing collision cascade is rapidly transformed into a gas-phase state, leading to a phase explosion of the overheated and, hence, strongly pressurized spike volume. The gas flow model explains the experimental observation of most probable emission energies to be much lower than both the “thermal” energy in the spike volume and the sublimation energy of the target material. The gas expansion scenario is even more corroborated by the fact that under spike conditions the emission velocity distributions of sputtered monomers and dimers are found to be practically identical. This result, which would be highly atypical for linear cascade sputtering, appears to be another key feature of collisional spikes developing under polyatomic ion bombardment of metal targets.

References