

## A microscopic view of secondary ion formation

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### ABSTRACT

The formation of secondary ions in sputtering is described by combining classical molecular dynamics of the particle kinetics with simple analytical treatments modeling the transfer of kinetic into electronic excitation energy, the transport of excitation away from the point of its generation and the charge transfer between the solid and a sputtered particle. For the simplest case of a metal atom sputtered from a clean metal surface, the predictions of such a model are used to answer a few fundamental questions regarding the ion formation process. The results indicate that the transient local excitation of the bombarded solid plays a dominant role in determining the charge state of a sputtered atom. Moreover, we find that the assumption of a sputtered particle being emitted from an ideal, undisturbed surface with a constant emission velocity – a picture which forms the physical basis of nearly all published secondary ion formation models – is not generally justified.

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### 1. Introduction

The formation of secondary ions in sputtering still represents an intriguing phenomenon which is only partly understood. In spite of the large significance of the process with respect to secondary ion mass spectrometry as one of the most versatile and widely used surface analysis techniques, and in spite of having been investigated for decades (see, for instance, numerous reviews of the subject [1–5]), the fundamental processes leading to the emission of a secondary ion are still not understood well enough to correctly predict the ionization probability of a sputtered particle even for the simplest cases. In a nutshell, the outcome of nearly all published analytical models describing the formation of a positively charged secondary ion can be summarized by [5,6]

$$\alpha^+ = F \cdot \exp\left(\frac{\Delta E}{\hbar\gamma v_{\perp}}\right) + G \cdot \exp\left(\frac{I' - \phi}{kT_e}\right) \quad (1)$$

where  $v_{\perp}$  denotes the normal emission velocity of the outgoing particle,  $I'$  its ionization energy at some distance away from the surface,  $\phi$  the surface work function, and  $\Delta E$  stands for a characteristic energy deficit which depends on the particular model invoked. While the first term arises from the non adiabatic passage of the outgoing atom across a zone of extension  $\gamma^{-1}$  above the solid surface, the second term refers to the so-called substrate excitation model put forward by Sroubek et al. [7], where the kinetic electronic excitation of the solid induced by the projectile impact is re-

tained by the outgoing atom and parametrized in terms of a temporally elevated electron temperature  $T_e$ . The quantity  $\gamma$  describes the decay length of the coupling matrix element between surface and atom states and is typically of the order of  $1 \text{ \AA}^{-1}$ . Typical values of the nominator in both exponentials are of the order of a few eV, rendering the characteristic velocity  $v_0 = \Delta E/\hbar\gamma$  of the order of several  $10^7 \text{ cm/s}$ . The parameters  $F$  and  $G$  are constants which depend on the chemical state of the surface and, for the case of metal atoms sputtered from a clean metal surface, can be assumed to be of the order of unity.

One of the major short comings of practically all published ionization models is that they do not account for the microscopic nature of the impact induced particle dynamics and their coupling to the electronic subsystem of the bombarded solid. As a consequence, the extremely localized nature of a solid's response to a projectile impact both in space and time is disregarded and relevant microscopic quantities like matrix elements describing the coupling between different electronic states, the morphology and excitation state of the surface during the emission event, the exact trajectory of the emitted particle etc. are being replaced by either averaged values or rather crude approximations. In particular, a few questions arise regarding the major assumptions behind nearly all analytical models describing secondary ion formation, namely

- How important is the transient electronic excitation of the solid (“substrate excitation”) as a consequence of the collision dynamics?
- How important is the fact that this substrate excitation following a projectile impact is strongly space and time dependent?

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- How justified is the assumption of a constant perpendicular emission velocity of an outgoing particle which forms the basis of practically all analytical predictions of secondary ion formation probabilities?
- How well defined is the “surface” (both geometrically and electronically) during a sputter emission event?

In order to address these questions, it is necessary to develop a microscopic picture of the sputtering and emission process which takes into account both the nuclear and electronic dynamics following a projectile impact. Since an *ab initio* treatment based on the solution of the coupled Schrödinger equation is still out of the question for a system large enough to enclose an entire collision cascade, we have tried to tackle the problem by means of a hybrid ionization model based on a combination of classical molecular dynamics describing the particle kinetics with simple analytical models describing the transfer of kinetic energy into electronic excitation energy. A crucial challenge in such simulations is the extremely rapid transport of excitation energy away from the point of its generation, which at least for metallic targets leads to a very efficient cooling of the cascade volume. In the prevailing version of our model, we describe this transport by means of a diffusive approach, using the diffusivity constant as a parameter which can vary locally and temporally and is coupled to the local crystallographic order as well as the lattice and electron temperature. Starting with the simplest case of a metal atom sputtered from a clean metal surface, the predictions of such a model regarding the ionization probability of sputtered atoms are found to reproduce corresponding experimental data at least in a semi-quantitative fashion. The calculations can therefore be used to discuss the questions raised above in terms of a microscopic view, thereby allowing us to assess the validity of some of the central assumptions behind the pertinent analytical secondary ion formation theory.

## 2. Ionization model

The model calculation employed and discussed here has been described in great detail elsewhere [8]. Briefly, the impact induced particle dynamics are described by a classical molecular dynamics (MD) simulation employing a parametrized many body interaction potential fitted to the properties of solid silver. The kinetic electronic excitation induced by each moving particle is treated in terms of two different processes, namely (i) direct electron–atom scattering involving the valence electrons of the solid and (ii) close atom–atom collisions generating free electrons along with semi-localized holes. The excitation energy transferred to the electronic system is removed from the kinetic energy via (i) a velocity-proportional friction force and (ii) an artificial, sudden displacement of the atoms at the point of closest approach. The excitation generated this way is fed as a time and space dependent source term into a non-linear diffusion equation describing the transport of excitation, the numerical solution of which then yields a space and time dependent excitation energy profile. The resulting excitation energy density is parametrized in terms of a local electron temperature, which is then introduced into a simple non-adiabatic rate equation model describing the occupation probability of an outgoing atom’s valence level. This way, it is possible to calculate an individual ionization probability for each sputtered atom, taking into account its detailed trajectory as well as the temporal variation of the surface electron temperature during its passage away from the surface.

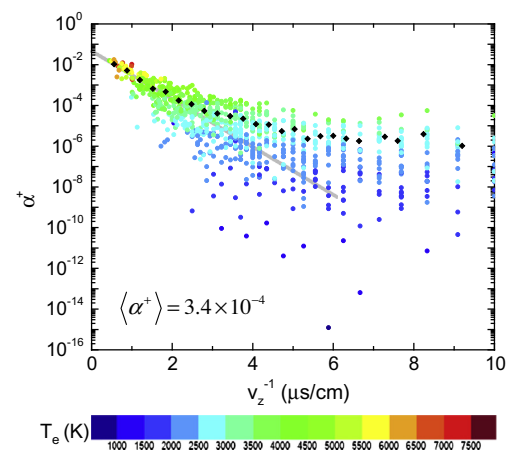
A few words are in order with respect to the target crystal used in these calculations. If we apply the model to the bombardment of an ideal single crystal at zero temperature, we find very low values of the ionization probability and a relatively strong influence of the

surface orientation on the calculated ionization probabilities [9]. This is understandable and caused by the fact that the heat diffusivity describing the electronic transport strongly depends on the crystallographic order: It is assumed to be large for an ideal single crystal and to decrease to smaller values once the target is dynamically amorphized in the course of a collision cascade. In order to study the influence of different model parameters and compare the calculated results with experimental data, we need to find a standard system on which all calculations are performed under otherwise identical conditions. We have therefore chosen to revert to an amorphous target as our standard system, since (i) the ionization probabilities calculated for such a target exhibit the best agreement with experimental data with respect to both the absolute magnitude and the emission velocity dependence (see below) and (ii) this is the only way we can study the dependence of the ionization probability on parameters like the projectile impact angle with reasonable computational effort.

## 3. Comparison with analytic theory

A typical result of such a calculation is depicted in Fig. 1, which shows the ionization probability of all atoms ejected from an amorphous silver surface under bombardment with normally incident 5-keV Ag atoms. In order to facilitate the comparison with analytic theory, the data have been plotted in a semi-log fashion against the inverse normal component of the particle’s velocity at infinite distance from the surface, since this would be the emission velocity which is measured in an experiment. The surface electron temperature “seen” by an outgoing particle at each point in time is determined by the temperature at that point of the surface which is closest to the particle at this time. This temperature is then averaged over time until the particle reaches a “detection plane” located 7 Å above the surface, since it was determined that the ionization probability does not change any more beyond that distance. The resulting average surface electron temperature experienced by the particle along its path away from the surface is depicted by the color of the respective symbol.

The overall ionization probability averaged over all sputtered particles regardless of emission velocity and angle is calculated to be of the order of  $10^{-4}$ , a finding which is in surprisingly good agreement with corresponding experimental data measured for

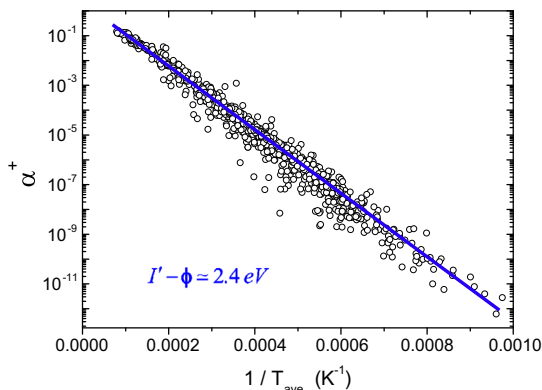


**Fig. 1.** Calculated ionization probability of Ag atoms sputtered from an amorphous silver target under bombardment with 5-keV Ag projectiles vs. inverse normal component of the emission velocity. The color of the symbols reflects the average electron temperature “seen” by the particle throughout its trajectory away from the surface as indicated by the color bar. Black symbols: Average values binned over equidistant  $1/v_z$  intervals. Grey line: Least square fit to black symbols. Insert: Ionization probability averaged over all sputtered atoms.

silver atoms sputtered from a polycrystalline silver surface under bombardment with 5-keV  $\text{Ar}^+$  ions ( $\alpha_{\text{Ag}}^+ \sim 3 \times 10^{-5}$  [10]). In judging this result, it should be kept in mind that – due to the exponential nature of Eq. (1) – only very small changes of the model parameters, the calculated temperatures and the emission trajectories may result in tremendous changes of the predicted ionization probability – often by many orders of magnitude. Moreover, it is clear that polycrystalline target material is not equivalent to an amorphous crystal as used here, since the volume affected by a single projectile impact is much smaller than a typical crystallite size. In the experiment, each impact will therefore occur onto single crystalline material, however, due to the random orientation of the crystallites, the influence of surface orientation will be averaged out. In addition, any real target material is (i) not free of defects and (ii) not at zero temperature. For these reasons, we feel that experimental data should be more closely approximated by a model calculation performed on an amorphous crystal, even though the transport of electronic excitation may be underestimated in that case. In this respect, it appears reasonable that the results obtained on an amorphous system tend to slightly overestimate the measured average ionization probability, while it is underestimated by several orders of magnitude if ideal single crystal targets are being used.

At first sight, the data depicted in Fig. 1 appear to be in rather good agreement with the prediction of Eq. (1). In the limit of high emission velocity, the ionization probability roughly exhibits an exponential dependence on the inverse emission velocity as illustrated by the straight line in Fig. 1. Such a behavior is predicted by non-adiabatic and tunneling ionization models and represented by the first term in Eq. (1). From the slope of the indicated line, one determines a characteristic velocity  $v_0 \simeq 5 \times 10^5$  cm/s, which, however, is much lower than a theoretically expected value ( $\sim 10^7$  cm/s [5]). In the limit of small velocity, we find a deviation from the exponential behavior that has been observed experimentally and is in principle predicted by the second term in Eq. (1). It is, however, apparent that different emitted particles experience very much different average electron temperature along their path away from the surface, leading to vastly different ionization probabilities.

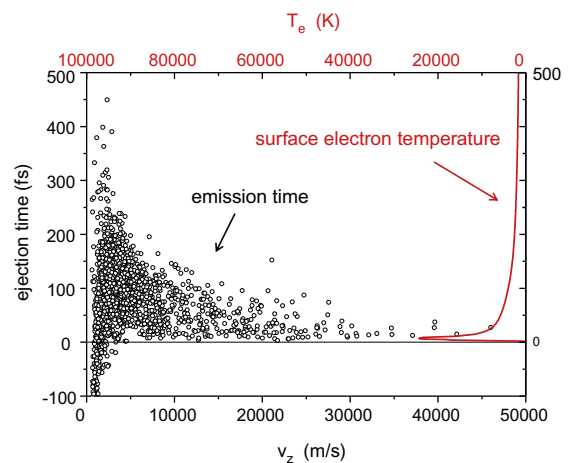
In order to examine the correlation between calculated ionization probability and electron temperature, we re-plot the data of Fig. 1 in an Arrhenius-type manner as shown in Fig. 2. It is quite obvious that the correlation is rather good, suggesting that substrate excitation plays a dominant role in determining the ionization probability of a sputtered atom. The straight line indicated in the figure represents a least square fit which corresponds to the second term in Eq. (1). From the slope, one can determine



**Fig. 2.** Calculated ionization probability of Ag atoms sputtered from an amorphous silver crystal under bombardment with 5-keV Ag projectiles vs. average electron temperature “seen” by the particle throughout its trajectory away from the surface.

the characteristic energy  $I' - \phi$  in Eq. (1) as 2.4 eV. In connection with the known work function  $\phi \simeq 4.6$  eV of silver, this translates into an effective ionization potential  $I' = 7.0$  eV, which is reduced by about 0.6 eV with respect to the value of isolated silver atoms. Assuming that the level is being shifted solely by the image potential  $e^2/4z$ , this means that the charge state of the sputtered atoms is determined at a distance of about  $z^* = 6 \text{ \AA}$  away from the surface.

It is interesting to note that the temperature correlation also holds for those particles which are emitted with high velocities. A close inspection of Fig. 1 reveals that high emission velocity of a sputtered atom often coincides with a high electron temperature at the point and time of its emission from the surface. One possible reason for such a correlation may be given by the time structure of the emission and excitation processes. Fig. 3 shows the correlation between an atom’s ejection time and its emission velocity. In this context, we define the emission time as that time following the projectile impact when a sputtered particle is set in motion and leaves the surface. This quantity, however, is not easy to determine. At first, one can look for the time at which the particle crosses the detection plane located at a fixed distance (here: 7 Å) above the initial surface. However, this definition can be strongly misleading, since it disregards the particle’s travel time from its original location in the crystal to the detection plane. In order to attempt a first order correction, one can estimate this time under the assumption of a constant particle velocity and subtract it from the detection time, yielding a “corrected emission time” which is plotted on the ordinate of Fig. 3 (left axis). Two observations are immediately evident. First, and most important, particles with high emission velocity (where the flight time correction is relatively unimportant) are predominantly emitted at rather short times after the projectile impact. Second, an abundant number of particles appear to have *negative* corrected emission time and therefore cannot have traversed the 7 Å zone at a constant emission velocity. Instead, these particles must have been slowed down during their passage from the surface to the detection plane. Inspection reveals that this holds true for at least 18% of all sputtered atoms, a finding which clearly demonstrates that the general assumption of a constant perpendicular emission velocity is not generally justified. It is evident that the emission time correction is incorrect for these particles, and therefore the corresponding data points in Fig. 3 should be disregarded.



**Fig. 3.** Black symbols: Emission time of Ag atoms sputtered from an amorphous silver crystal under bombardment with 5-keV Ag projectiles (left axis) vs. normal component of their emission velocity (bottom axis). Solid line (red curve): Average electron temperature at the surface (top axis) vs. time after the projectile impact (right axis). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In order to examine the correlation with electron temperature, the time dependence of the surface temperature following a projectile impact is of interest. As an example, we plot the electron temperature determined at a specific surface point – in this case the impact point where the projectile hits the surface – averaged over all calculated trajectories (red curve and upper axis in Fig. 3.) vs. time after the projectile impact (right hand axis of Fig. 3). Note that the exact location of this point is not important since practically all relevant surface points exhibit a similar time dependence albeit different absolute magnitude of the electron temperature. The important observation is that the surface electron temperature reaches its maximum value almost immediately after the projectile impact and then decays with increasing time. In connection with the velocity–time correlation noted above, this leads to the effect that high emission velocities apparently coincide with a larger average surface electron temperature experienced by the outgoing particle, leading to a higher average ionization probability.

#### 4. Conclusions

The ionization model presented here provides a microscopic insight into the processes leading to secondary ion formation. Based on the analysis of the conceptually simplest case of a metal atom sputtered from a clean metal surface of the same element, we find the following answers to the questions raised in the introduction:

- The results strongly indicate that local and temporal *substrate excitation* following a projectile impact plays a dominant role in determining the charge state of a sputtered particle. More specifically, we find an astonishingly clear correlation between the ionization probability and the average electron temperature seen by the particle during its trajectory away from the surface.
- The *dynamics* (i.e., time and space dependence) of the generated excitation profile are extremely important in order to understand observations like the apparent emission velocity dependence of the ionization probability.
- The assumption of a sputtered particle leaving a static, undisturbed surface with constant perpendicular emission velocity is not generally justified.

The last conclusion is significant, because it reveals that the physical basis of nearly all published models describing secondary ion formation, i.e., the assumption of an emitted particle interacting with an ideal, intact surface, is not generally justified for a realistic description of a secondary ion formation process in sputtering. In particular for events induced by the impact of a cluster projectile, measured ionization probabilities can therefore not be expected to be described by simple analytical formulae like Eq. (1) [11]. In order to understand secondary ion formation under these conditions, it is mandatory to account for the local and temporal modification of the surface during the emission process.

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