Ro-vibrational population of sputtered metal dimers: the influence of unimolecular decomposition

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The vibrational and rotational states of metal dimers sputtered by keV ion impact were studied by a molecular dynamics simulation. Particular emphasis was put on the role of dimers originating from unimolecular decomposition of large unstable ejected clusters. It is seen that the contribution of these so called "secondary" dimers to the total dimer yield is non-negligible. In addition, secondary dimers are shown to be "cold" compared to "primary" dimers identified immediately after the sputtering event. Hence, the calculated vibrational and rotational temperatures are lowered if secondary fragmentation products are included into the treatment.

1. Introduction

For more than ten years, it has been the goal of a number of theoretical studies to predict the internal state population of sputtered molecules [1–11]. Among the various approaches used, molecular dynamics simulations (MD) seem to be the most promising methods to describe molecule sputtering [10], since many-body effects as well as correlations of the atomic motion within the sputtered flux are automatically included in the treatment. Early MD studies, however, were impaired by the exclusive use of pairwise additive interaction potentials which force to switch between "bulk" and "gas phase" potentials at some stage during the ejection. Only very recently, many-body potentials constructed by the embedded-atom method (EAM) became available which permit a description of the bombarded solid *and* ejected gas phase molecules *simultaneously* [10,12]. In addition, all sputtered molecules reported in earlier MD studies were identified immediately after the trajectory integration was stopped (i.e. when the atoms which were found to be sputtered did not interact with the surface any more). Molecules identified at that time, however, are not necessarily stable and, hence, may undergo unimolecular fragmentation as they travel away from the surface. We have

recently studied this phenomenon and found that the vast majority of trimers and larger multimers emitted from a metal surface is metastable, and they decompose on a time scale of picoseconds after the ejection [12]. Hence, only stable species can be expected to be found at distances larger than several hundred nanometers from the surface. Furthermore, it is seen that – depending on the kinetic energy of the impinging primary ion – the contribution of fragmentation products to the total yield of sputtered dimers may be as high as 50%. In the present work, we investigate the influence of fragmentation on the predicted vibrational and rotational state distribution of sputtered metal dimers.

2. Description of the calculation

The molecular dynamics simulation [13,14] as well as the treatment of unstable ejected multimers [12] has been described in detail earlier. Briefly, the classical equations of motion are solved numerically for all atoms of a crystallite containing approximately 1000 atoms. The interaction between target atoms is described by a many-body embedded-atom (EAM) potential. In order to establish some link to experimental data, a particular potential fit to known properties of solid silver [15] was chosen which was slightly modified for use in sputtering calculations [10]. It should be

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noted, however, that this potential was found to overbind small gas phase silver clusters [12] by amounts ranging from 60% (dimers, tetramers) to 90% (trimers).

The trajectory integration was carried on until those atoms which were found to be ejected did not interact with the solid surface any more. Then, the list of sputtered atoms was examined for emitted clusters. A cluster of n atoms was identified if its total (relative kinetic plus potential) energy was below zero. Sputtered multimers determined this way will in the following be called "primary clusters". Note that primary dimers are absolutely stable. For larger clusters, the internal energy E_{int} was calculated. If E_{int} was below the dissociation threshold (determined from the EAM potential), a cluster was considered to be stable. All unstable clusters, on the other hand, were input into a modified version of the MD code, where the motion of the n constituent atoms was followed further until the cluster had decomposed into stable fragments (or a maximum integration time limit of 200 ps was reached). Multimers originating from this unimolecular fragmentation will in the following be called "secondary clusters".

The quantum state of a sputtered primary or secondary dimer was determined semi-classically from the positions and velocities of the constituent atoms at a given time. As described in detail in ref. [10], the rotational quantum number N was obtained from the classical angular momentum, whereas the WKB approximation was utilized to calculate the vibrational quantum number v. The resulting non-integer N and v were rounded to the nearest integer values.

3. Results and discussion

The simulations described above were performed for 5 keV Ar^+ ions normally incident onto an fcc metal (111) surface. 1000 primary ion impact events were calculated, with the impact points being uniformly distributed over the smallest irreducible surface cell. In total 8128 atoms were found to be sputtered, among which 687 dimers, 48 stable and 150 unstable trimers and 190 unstable multimers of four or more atoms were identified as primary clusters. The largest ejected multimer found consisted of 31 atoms and contained an internal energy of 36 eV. With the exception of 28 trimers and four tetramers (including intermediate unstable fragmentation products from larger clusters), all unstable molecules could be followed until they had completely decomposed into stable fragments before the integration time limit (200 ps) was reached. This yielded 517 secondary dimers, 87 secondary trimers, eight secondary tetramers and one secondary pentamer.
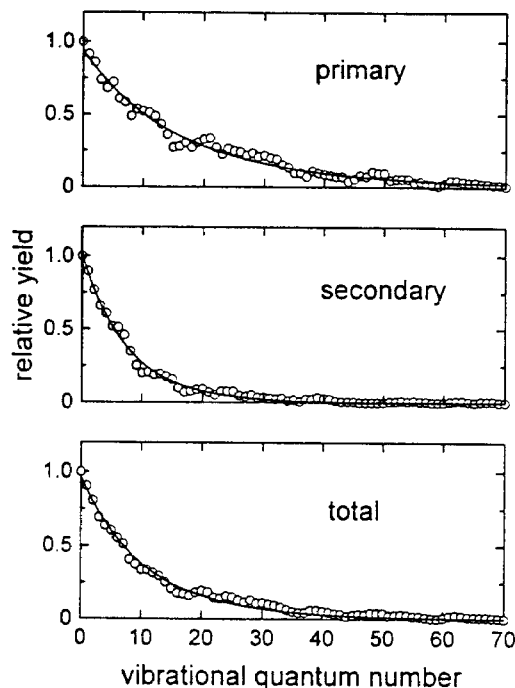

Fig. 1. Vibrational population distribution calculated for sputtered metal dimers. "primary": dimers identified immediately after ejection; "secondary": dimers originating from fragmentation of unstable species; "total": all dimers. Solid line: least-squares fit to thermal distribution.

Fig. 1 shows the distribution of vibrational states determined for sputtered primary and secondary dimers, respectively. In order to improve the statistics, the calculated data have been integrated over all rotational states and, in addition, a sliding average over three next-neighbour values of v was performed for smoothing. It is seen that in both cases the simulated vibrational population can be well approximated by Boltzmann distributions. The vibrational temperatures obtained from the corresponding least squares fits are displayed in table 1. The calculated rotational state distributions are shown in fig. 2. Here, each data point displayed for a specific rotational quantum number N represents the sum of the population calculated for

Table 1
Vibrational and rotational temperature of sputtered metal dimers. "Primary": dimers identified immediately after ejection; "secondary": dimers originating from fragmentation of unstable species; "total": all dimers

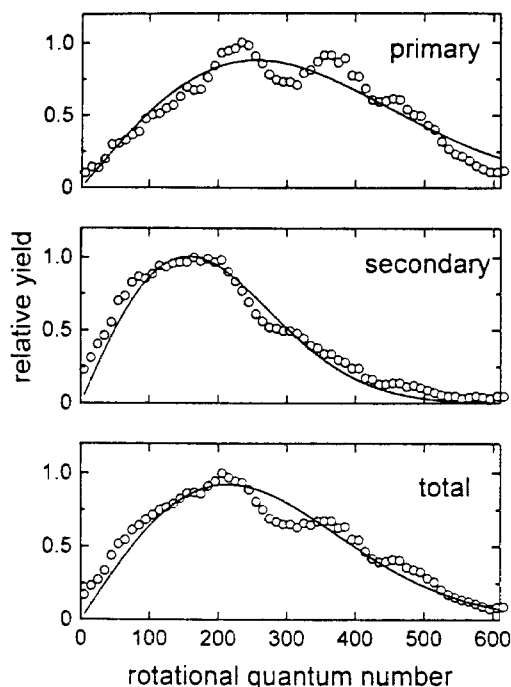|	T_{vib} [K]	T_{rot} [K]
Primary	5174	9881
Secondary	2461	3674
Total	3521	6818

Fig. 2. Rotational population distribution calculated for sputtered metal dimers. "primary": dimers identified immediately after ejection; "secondary": dimers originating from fragmentation of unstable species; "total": all dimers. Solid line: least-squares fit to thermal distribution.

rotational quantum numbers between $N - 5$ and $N + 5$. In addition, due to the limited statistics of the calculation, the population was integrated over all vibrational quantum numbers. As indicated in fig. 2, also the rotational population of sputtered dimers can be fit to thermal distributions. As seen from table 1, however, the resulting rotational temperatures are significantly higher than the corresponding vibrational temperatures, thus emphasizing the non-equilibrium nature of the sputtering process. At the same time, characteristic deviations from the Boltzmann curves are observed, leading, for instance, to population minima at rotational quantum numbers around $N = 300$. From our previous work we know that these structures depend on the crystallographic orientation of the investigated surface [10]. Although less pronounced (due to poorer statistics), similar features like those observed in fig. 2 were found in ref. [10] when the (111) surface was bombarded with Ar^+ ions of 1 keV. Hence, we conclude that the "wiggles" in fig. 2 represent a characteristic of the atomic arrangement at the surface.

From figs. 1 and 2, it is apparent that secondary dimers are "cold" compared to those primarily identified in the sputtered flux. We attribute this finding to the fact that secondary dimers constitute the end prod-

ucts of sometimes long fragmentation chains. From a detailed analysis of the dissociation kinetics involved, we find that a significant amount of internal energy stored in the original unstable cluster is carried away in form of kinetic energy by the fragmentation products.

As already stated in the introduction, the dissociation reactions described here occur on a picosecond time scale. During such times, the clusters can on the average escape about several hundred nanometers away from the surface. Experimental detection of these species, on the other hand, is only possible at much larger distances. Hence, experimental detection schemes will not be able to distinguish between sputtered primary and secondary clusters. In order to allow a comparison of the present results with experimental data, all multimers of a given size should be analyzed. First, from the numbers given above, relative yields of sputtered clusters (i.e. the total number of multimers normalized to that of sputtered monomers) can be calculated. The resulting values are 2.3×10^{-1} (dimers), 2.6×10^{-2} (trimers), 1.5×10^{-3} (tetramers) and 1.9×10^{-4} (pentamers). It should be noted that if these values are to be compared with corresponding experimental data obtained for sputtered sputtered silver clusters, care should be taken due to the fact that the EAM potential overbinds these clusters (for a detailed discussion of possible correction schemes see ref. [12]). Nevertheless, the calculated data reproduce the experimentally observed decay in cluster yields by approximately one order of magnitude per additional constituent atom [16–18]. Second, total vibrational and rotational distributions calculated from all sputtered dimers have been included in figs. 1 and 2. Due to the large contribution of secondary dimers to the total dimer yield, the corresponding internal temperatures which are also displayed in table 1 are significantly lower than those determined exclusively from primary dimers. As a consequence, we conclude that unimolecular decomposition of unstable species present within the flux of sputtered particles plays a non-negligible role and must under any circumstances be included into molecular dynamics simulations predicting yields and internal state distributions of sputtered clusters.

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