Internal and translational energy of sputtered silver dimers: a molecular dynamics study

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The ejection of Ag_2 molecules from a (111)-silver surface bombarded by normally incident Ar^+ ions was studied by a molecular dynamics simulation using a many-body embedded-atom interaction potential. First, the dependence of the translational energy distribution on the polar ejection angle was calculated and compared to corresponding experimental results. Then, the internal energy distribution as well as the vibrational and rotational state distributions of sputtered Ag_2 dimers were calculated and their correlation with the primary ion energy, the translational energy and the polar ejection angle was examined. It is found that the rotational–vibrational population can be well approximated by Boltzmann distributions revealing vibrational and rotational temperatures of 3000–5000 K and 8000–10000 K, respectively. The dependence of T_{vib} and T_{rot} on the primary ion energy, the translational energy and the polar ejection angle of the sputtered molecules is shown to be relatively weak.

1. Introduction

The ejection of diatomic molecules under keV ion bombardment of clean metal surfaces has been investigated extensively [1–3]. In particular, two classes of models describing the formation of sputtered dimers have evolved in the literature, which are based on two different ways to approach the problem. The *statistical* models [4–16] treat the molecule formation as a combination process involving two sputtered atoms with statistically distributed positions $r_{1,2}$ and velocities $v_{1,2}$ immediately after the ejection. While the probability distribution of $v_{1,2}$ can be readily obtained from analytical sputtering theory, the distribution of $r_{1,2}$ as well as the temporal correlation between the ejection of both atoms essentially have to be guessed. In addition, the question arises which potential energy function should be chosen to describe the interaction between the two sputtered atoms. In all statistical models, this function is taken to be that of the free molecule and hence, the interaction with the remaining surface atoms is assumed to be switched off instantaneously during the emission of a particle. Especially in cases where the equilibrium distance at the surface largely differs from that in the free molecule, this may lead to a serious overestimation of the internal energy of an ejected molecule.

In principle, these difficulties are circumvented by a *molecular dynamics simulation* (MDS) of the sputtering process. Here, in contrast to the statistical treatment, the classical equations of motion are integrated numerically for all atoms in the solid. Hence, besides the velocities, the method (automatically) delivers the spatial and temporal correlation between atoms sputtered throughout one collision cascade and the need to introduce artificial correlation parameters is eliminated. Furthermore, the smooth variation of the interaction potential governing the motion of particles during the ejection is accounted for, provided the potential function used in the simulation allows a proper description of the solid *and* the free molecule at the same time. This requirement, however, precludes the use of pairwise additive potentials which have been exclusively employed in early MDS studies on molecule sputtering [17–26]. We have recently shown that a many-body potential constructed by the embedded-atom method (EAM), which was originally designed to describe solid silver, provides a reasonable description of a gas phase Ag_2 dimer as well and, hence, enables a reasonably quantitative simulation of silver dimer sputtering [27]. In particular, absolute yields as well as angle integrated translational and internal energy distributions of sputtered Ag_2 dimers were calculated and compared to available experimental data. In the present paper, the influence of the primary ion energy E_B and the polar ejection angle θ on both the translational and the internal energy distribution of sputtered Ag_2 dimers is investigated. In addition, the interplay between transla-

tional and internal energy is examined and compared to results of statistical dimer formation models.

2. Description of the calculation

The molecular dynamics simulations have been discussed in detail elsewhere [28,29]. The interaction potential used for the present calculations as well as the procedure employed to identify sputtered dimers and determine their vibrational and rotational quantum state are described in ref. [27]. Briefly, the EAM potential published by Foiles et al. [30] was splined to a Molière potential at small internuclear distances. This was necessary since the original construction of the EAM potential did not take into account any data for extremely close encounters of the atoms. A pair of sputtered atoms was considered to be a dimer if its total internal energy (given by the sum of the relative kinetic and the potential energy at the time when the integration was stopped) was less than the dissociation energy and no bonds to third atoms were detected. This procedure neglects "secondary" dimers originating from dissociating trimers or higher multimers. The rotational quantum number was obtained from the angular momentum L of the molecule using the correspondence rule

$$L^2 = \hbar^2 N(N+1). \tag{1}$$

The quantization of the vibrational levels was performed by means of the WKB-approximation. A number of 1000 trajectories were run for each value of the primary ion energy E_B. The impact points were chosen to be uniformly distributed over the smallest irreducible surface cell, which is a triangle for the (111) surface.

3. Results and discussion

3.1. Translational energy distributions

We have already compared the angle integrated (i.e. integrated over the whole 2π solid angle) energy distribution calculated for sputtered Ag atoms and Ag_2 dimers with experimental curves determined on a polycrystalline silver target [27]. In the present work, we investigate the influence of the ejection angle θ (measured with respect to the surface normal) on the energy distribution of sputtered molecules. Fig. 1 shows the results calculated for Ag_2 dimers sputtered from Ag(111) under bombardment with normally incident Ar^+ ions of 1 keV. As immediately seen from the figure, the energy distribution remains virtually unchanged in the region $0 \leq \theta \leq 40°$ and for $\theta > 40°$ peaks at lower energies and falls off more steeply with
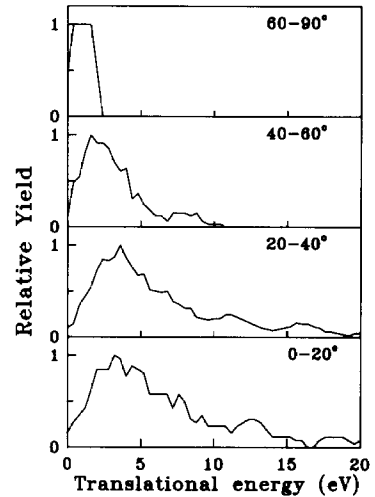

Fig. 1. Polar ejection angle dependence of the translational energy distribution calculated for Ag_2 dimers sputtered from Ag(111) by normally incident Ar^+ ions of 1 keV. The data were integrated over the azimuthal angle.

increasing energy. This predicted behaviour agrees well with experimental results available on metal dimer sputtering: For Cu_2, V_2 and Nb_2 sputtered from polycrystalline metal targets bombarded by 2 keV Ar^+ ions under normal incidence, the translational energy distribution was found to vary only very little if the ejection angle was changed from $\theta = 0°$ to $\theta = 45°$ [31]. The same observation was reported for various metal dimer energy distributions obtained at ejection angles of $\theta = 0°$ and $\theta = 40°$, respectively [32]. Unfortunately, experimental data are lacking for polar ejection angles larger than $45°$ and, hence, our prediction of lower peak energies and narrower energy distributions cannot be examined at this point. This, however, would be of particular interest since recent calculations of Snowdon [33] based on a statistical model predict a somewhat different behaviour of the dimer energy distribution than our present results. In ref. [33], the molecule formation process is subdivided into the so-called "double collision" and "single collision" mechanism, the former leading to a slight shift of the peak energy towards higher values and the latter predicting a less steep fall off towards higher ejection energies with increasing θ (cf. fig. 7 in ref. [33]). Both effects point in the opposite direction as the variation displayed in fig. 1. This deviation may in part be due to the fact that the Monte Carlo calculations reported in ref. [33] were performed for amorphous targets, whereas the present simulation was done for a single crystal surface. In order to account for this difference, MDS simulations for other low index silver surfaces are under way, which, if averaged, will allow a better comparison both

with Monte Carlo calculations and with experimental data taken on polycrystalline surfaces [34].

3.2. Internal energy distributions

The angle integrated internal energy distribution of Ag_2 dimers sputtered from a (111)-silver surface by 1 keV Ar^+ ions has been presented earlier [27]. In the present work, the main interest was focused on the correlation between the internal and translational (= center of mass) energy of the ejected molecules. Fig. 2 shows the distribution of the internal energy calculated for dimers with selected translational energy. The average internal energies calculated from these distributions are displayed in table 3. It is clearly seen that a correlation exists in such a way that dimers ejected with low translational energy preferably possess low internal energy as well. This finding is easily understood since in order to form a stable diatomic molecule of high translational and low internal energy the two constituent atoms have to be ejected with high individual kinetic but low *relative kinetic* energy. Hence, their ejection has to be increasingly aligned which becomes less probable with increasing translational energy. It should be noted that a similar type of correlation is predicted from statistical models as well [8,9].

As reported earlier [27], the rotational–vibrational state population of sputtered Ag_2 dimers can be well fitted by Boltzmann distributions revealing vibrational and rotational temperatures of several thousand K with roughly $T_{vib} : T_{rot} \simeq 1 : 2$. Our present calculations show that this statement also holds if only dimers ejected with selected translational energies or emission
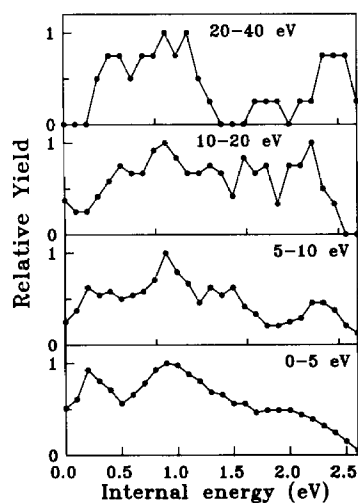
Table 1
Dependence of vibrational and rotational temperature and average internal energy of sputtered Ag_2 dimers on primary ion energy E_B ($Ar^+ \rightarrow Ag(111)$)

E_B [eV]	T_{vib} [K]	T_{rot} [K]	E_{int}^{av} [eV]
250	4128	10236	1.17
500	5111	10779	1.22
1000	4233	8506	1.13
5000	4693	8639	1.16

Table 2
Dependence of vibrational and rotational temperature and average internal energy of sputtered Ag_2 dimers on molecule ejection angle θ (1 keV $Ar^+ \rightarrow Ag(111)$)

θ	T_{vib} [K]	T_{rot} [K]	E_{int}^{av} [eV]
0°–20°	4693	10067	1.24
20°–40°	4128	7671	1.09
40°–60°	3688	9090	1.12

Table 3
Dependence of vibrational and rotational temperature and average internal energy of sputtered Ag_2 dimers on molecule translational energy E (1 keV $Ar^+ \rightarrow Ag(111)$)

E [eV]	T_{vib} [K]	T_{rot} [K]	E_{int}^{av} [eV]
0– 5	3688	8603	1.07
5–10	4128	8165	1.14
10–20	4822	9298	1.26

Fig. 2. Translational energy dependence of the internal energy distribution calculated for Ag_2 dimers sputtered from Ag(111) by normally incident Ar^+ ions of 1 keV.

angles are considered. The dependence of T_{vib} and T_{rot} on the different parameters, as extracted from least-squares fits to the calculated population distributions, are displayed in tables 1–3. First, no significant influence of the primary ion energy E_B on the internal energy distribution, represented by the average internal energy, and the rotational–vibrational state population of the sputtered dimers is detected for values of E_B between 250 eV and 5 keV. This finding is to be expected as predominantly the low energy part of the sputtered atom energy distribution contributes to dimer formation which, in turn, has been shown to be independent of the bombarding energy [11]. Second, from tables 2 and 3 it is seen that the dependence of T_{vib}, T_{rot} and E_{int}^{av} on the ejection angle θ and the translational energy E is predicted to be relatively weak. In particular, the vibrational temperature is found to decrease slightly with increasing θ and with decreasing E. While the weak θ-dependence is in accordance with

similar results given by statistical models [9], a much stronger dependence on E is predicted by the Monte Carlo calculation [16]. An experimental determination of the vibrational temperature of sputtered S_2 dimers yielded $T_{vib} = 1500$ K, independent of the translational energy [16]. This finding, which at the time being could not be understood in terms of the Monte Carlo model, perfectly matches our present results. The agreement is not as good, however, if the dependence of T_{rot} on the translational energy is considered. While the experimental finding of ref. [16] shows a strong increase of T_{rot} with increasing vibrational quantum number and E, our present simulation reveals only a very weak dependence of the rotational temperature on both parameters.

4. Conclusion

We have shown that a molecular dynamics simulation of metal dimer sputtering leads to similar correlations between the translational and internal energies of the ejected molecules as do the published statistical models. The dependence of the translational energy distribution on the polar ejection angle, however, is calculated to be different from the prediction of the statistical calculations at high ejection angles. Hence, in order to clarify this point it would be very much desirable to obtain experimental data on angular resolved energy distributions of sputtered dimers for polar ejection angles larger than $45°$, which are currently not available.

Concerning the rotational–vibrational population of sputtered metal dimers, we find thermal distributions with vibrational and rotational temperatures being essentially independent of the primary ion energy, the polar ejection angle and the translational energy E. In particular the weak dependence of T_{vib} on E is found to be in good agreement with published experimental data on sputtered S_2 molecules which cannot be explained by any statistical model so far. On the other hand, the rotational temperature dependence calculated here disagrees with the experimental finding obtained on sulphur dimers. Hence, we conclude that there must be some difference between the processes leading to ion bombardment induced ejection of S_2 from amorphous sulphur and the sputtering of metal dimers. Such differences are to be expected since the former involves the ejection of a strongly bound molecule which is only very weakly bound to the surface, whereas for the case of Ag_2 dimers studied here both the dimer dissociation energy and the surface binding energy are of the same order. To elucidate this point, however, further experimental data on the rotational–vibrational state population of sputtered metal dimers are badly needed.

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