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ELECTRONIC SPUTTERING OF BIOMOLECULES

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A review of results on electronic sputtering of biomolecules, induced by fast heavy ions like fission fragments, obtained by the Uppsala group the last two years is given. The readily determined yields of ions in electronic sputtering have been compared to total sputtering yields in a collector experiment. The results indicate that the neutral yield of the amino acid leucine is of the order of 10^4 times that of the ion yield. Studies of yield vs sample thickness, where samples were prepared with the Langmuir–Blodgett technique, show that intact molecular ions are sputtered from depths in the range 100–200 Å. These two results support the idea that craters of sizes of the order of 100 Å are formed in electronic sputtering induced by e.g. 90 MeV ^{127}I ions. Furthermore, recent results indicate that the angular distribution of ejection of large molecular ions is peaked at an angle related to the direction of the incoming ion rather than being peaked perpendicular to the sample surface or being isotropic. Finally, all the mentioned results have been qualitatively demonstrated in a molecular dynamics simulation of the desorption process.

1. Introduction

Sputtering phenomena, i.e. the ejection of surface material due to particle impacts on solids, can be divided into two main categories: nuclear and electronic sputtering depending on the velocity of the impinging particle. Below the so-called Bohr velocity, $v_B \approx 0.22$ cm/ns, the particle slows down mainly due to nuclear stopping, i.e. energy is transferred to the target atoms via collisions between screened nuclei giving rise to a collision cascade in the target which causes *nuclear* sputtering at the surface.

For velocities above v_B the main energy loss is through ionizations and excitations of target electrons. Here also sputtering occurs as a secondary effect, in this case only for insulating materials; *electronic* sputtering. It is only during the last decade that electronic sputtering has been an intense field of research aiming at a basic understanding of the processes via which the primary energy deposition results in the secondary sputtering effect. This work has also been highly motivated by the fact that electronic sputtering has been used successfully to produce gas phase ions of intact large organic molecules for time-of-flight mass spectrometry [1]. In particular biomolecules with masses up to 34 000 amu [2] have been studied with this technique.

Fission fragments from ^{252}Cf sources are now commonly used as primary ions in such mass-spectrometric applications. However, in research aiming at an elucidation of the sputtering process, in particular tandem accelerators are used to produce well defined beams of fast heavy primary ions. In such studies [3] the yield of secondary ions (the number of ions ejected per impinging primary particle) has been studied as a function

of a variety of primary ion parameters and sample types.

This paper gives a review of results obtained in this field at the Division of Ion Physics at Uppsala University over the last two years.

2. Neutral yields and sample thickness dependencies

As mentioned in the introduction, most of the experiments in electronic sputtering have been concerned with secondary *ion* yields. In a collector experiment in 1986 [4] it was shown that the yield of *neutrals* is about 10^4 times that of positive molecular ions for 78 MeV ^{127}I ions impinging on a target of the amino acid leucine (molecular weight 131 amu), demonstrating the need for knowledge of neutral yields in studies of the electronic sputtering process. The neutral yield was found to be about 1000 leucine molecules per primary ion. In this experiment the ejected neutrals are collected on an etch-cleaned silicon surface situated close to the bombarded target. The collected amounts can then be analysed quantitatively using amino acid analysis. The relative amount of collected material for different primary ion species can be obtained with a mass-spectrometric analysis of the collector.

In such a relative measurement the neutral yield of the amino acid leucine was found to vary with electronic stopping power as $(dE/dX)^3$ [5] whereas the ion yields vary roughly linearly for positive ions and quadratically for negative ones.

In a measurement of yield vs sample thickness [6], using Langmuir–Blodgett films [7], it was found that molecular ions from depths varying from 100 to 200 Å

were ejected for primary ions ranging from 7.4 MeV ^{12}C to 78 MeV ^{127}I . In combination with the neutral yield results this indicates that craters of sizes of the order of 100 Å are formed due to impacts by these primary ions.

These results will be discussed in the molecular dynamics section below.

3. Ejection angles of secondary ions

In a recent experiment, a correlation of the angle of ejection of various secondary ions to the angle of incidence of the primary ions was found [8]. In this experiment two pairs of deflection plates were introduced in the field-free region of the mass spectrometer, behind the acceleration gap (see inset in fig. 1). Fission fragments at normal incidence on the back side of a thin Al foil were used as primary ions. The sample molecules were deposited on the front side. By applying appropriate voltages to the deflection plates an ion ejected at a certain angle with respect to the axis of the spectrometer will be deflected back to the axis at the stop detector and the angular distribution of secondary ions can thus be determined.

It was found that the yield of molecular ions of insulin (molecular weight 5733) has a minimum in the forward direction of the angular distribution, as illustrated in fig. 1. The distribution peaks at voltages corresponding to an ejection angle of about 45° to the normal. In contrast, the distribution for light fragments (that of CH_3^+ is plotted in the figure) peaks in the forward direction.

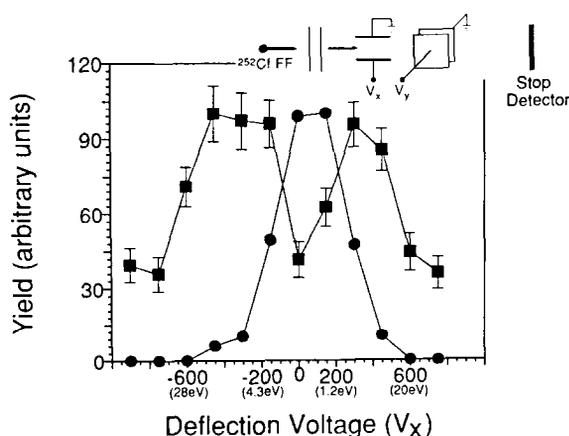


Fig. 1. Relative yields of positive molecular ions of bovine insulin (squares) and CH_3^+ ions (circles) as a function of deflection voltage. Primary ions: fission fragments. The numbers in parentheses on the horizontal scale are the energies corresponding to the radial velocities which can be associated with the different deflection voltages.

These results support the idea that large molecular ions are ejected as a result of a cylindrical pressure wave emanating from the primary ion track, whereas the lighter fragments are ejected in the direction of the track much like a gasjet expansion. To test this idea and in an effort to explain the results in the previous sections, a molecular dynamics study of the sputtering process was performed.

4. Molecular dynamics simulations

Several mechanisms for the transfer of the energy primarily deposited as excitations and ionizations have been proposed over the last several years. In the ion explosion model [9] repulsion between ions in the charged track core gives rise to atomic and nuclear motion.

In a model proposed by Watson and Tombrello [10] the local excitation of the electron gas around the primary ion path leads to a decrease in the electronic binding forces of the nuclear lattice, resulting in an expansion of the lattice and hence motion of atoms and molecules.

Recently, Williams and Sundqvist [11] suggested the so-called "popcorn model". In this picture the low-energy secondary electrons ejected from the track core excite low-lying vibrational levels in molecules close to the track. The average length of a vibrationally excited bond is larger than that of the ground state leading to an expansion of these molecules and thus to molecular motion. Molecules situated at the surface can "pop off" due to this sudden excitation and expansion in analogy with the cause of events when making popcorn.

In addition, thermal models have been proposed [12] where heat diffuses cylindrically from an initially hot core around the ion path. This approach is however not compatible with, in particular, the directional effects in the ejection of large molecules discussed above.

The three former mechanisms all give rise to molecular motion propagating initially cylindrically from the region of the track core. It could well be that a combination of several mechanisms is involved in this first stage. Thus, it is interesting to study the propagation of the initial molecular motion, even though a detailed knowledge of its cause is lacking. We have chosen to do this in a molecular dynamics simulation aiming at a quantification of the resulting ejection of molecules at the surface.

In these simulations [13], the popcorn approach was chosen in which molecules within a distance of 20 Å from the track were given vibrational excitations corresponding to expansions of $\approx 10\%$ for 90 MeV ^{127}I primary ions, in accordance with estimates given in ref. [11]. It was further assumed that the increase in potential energy due to the expansion is proportional to the

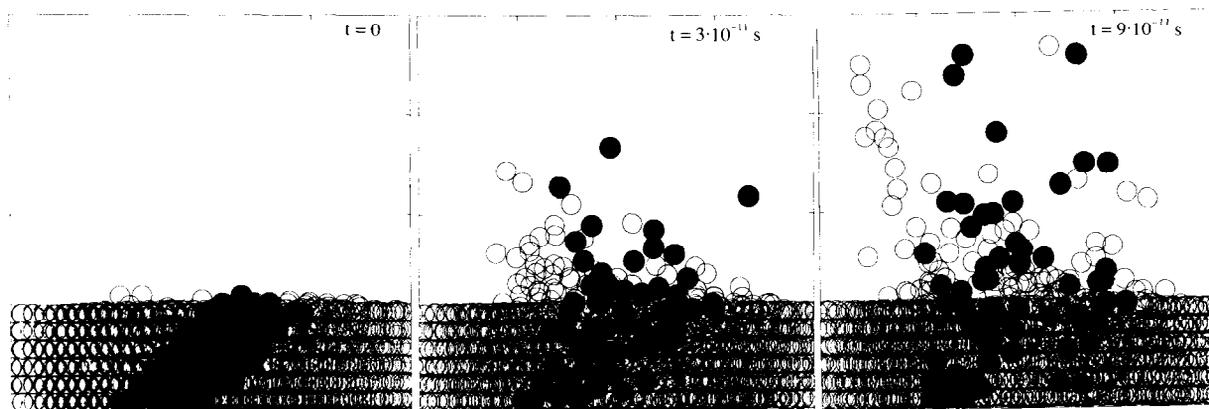


Fig. 2. The sample at 0, 30 and 90 ps after the expansion of a cylindrical track. Expanded and nonexpanded molecules are shown as filled and unfilled circles, respectively. A side projection of the cylindrical matrix is shown. The angle of incidence of the fast ion is here 45° .

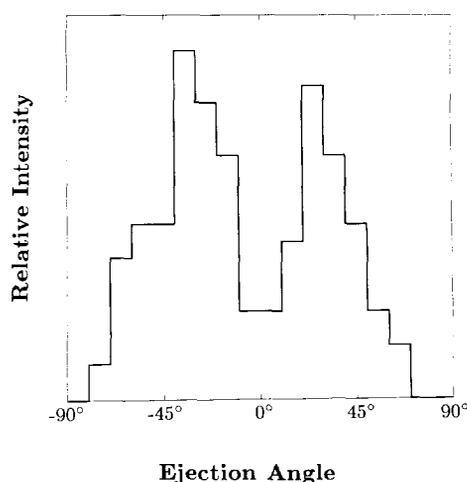


Fig. 3. Angular distribution of nonexpanded ejected molecules having a kinetic energy larger than 0.1 eV for normal incidence of the primary ion.

electronic stopping power of the primary ion. The molecules, of mass 10 000, were assumed to interact via Lennard–Jones two-body potentials.

The preliminary results of the simulations (figs. 2 and 3) show that

- (a) the total yield varies roughly as $(dE/dX)^3$,
- (b) molecules from depths of the order of 100 Å are ejected in the sputtering process, and
- (c) for normal incidence the angular distribution of ejected molecules agrees qualitatively with what was observed in the experiment discussed above.

5. Conclusions

We conclude that existing experimental data, in combination with the results of the molecular dynamics

simulations, strongly support the picture that molecular motion initiated in the region of the primary track core propagates roughly as a cylindrical pressure wave, resulting in ejection of molecules at the surface. Several mechanisms for the initial stage of motion have been suggested and it remains unclear which one is mainly responsible.

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