Mechanisms of Organic Molecule Ejection in SIMS and FABMS

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1. Introduction

Why is the study of organics on surfaces important? First, metal surfaces have long been known to promote certain organic reactions. These reactions can produce long-lived surface intermediates which can be studied by various techniques, including SIMS and FABMS. Another reason for studying organics on surfaces is based on the pioneering work of BENNINGHOVEN, where it was shown that large involatile organic molecules could be adsorbed and subsequently sputtered nearly intact [1]. This allowed the easy study of these large molecules by mass spectrometry. In the first case mentioned above, the adsorbed species undergo reactions to form different surface compounds. In the second case, one would like the initially adsorbed species and the surface species to remain essentially identical, so that the surface (and bombarding particle) during SIMS and FABMS act simply as a vehicle for obtaining gas phase ions. In both cases, however, one would like the detected ions (both parent and fragments) to be indicative of what was on the surface. It is this requirement that makes the study of what happens to the surface plus adsorbed species during the bombardment process very important.

In a recent review of the development of SIMS, HONIG [2] states that "at this time it seems that there are as many models (of organic ejection) as there are theoreticians studying the problem". Unfortunately, at first glance this statement appears true. However, along with the differences, certain underlying themes seem to be present in most models. The purpose of this review then, is to point out the differences and similarities between these models and how each model explains experimental results.

The models of organic ejection can be separated into two categories. The first approach is based on empirical interpretations of experimental results. Intuitive models are used here with very few actual calculations being performed. While important thoughts on the sputtering mechanism have come from these models, the results of several of the approaches mentioned next show that the interpretation of experimental results is not as simple as these ideas indicate. The other category of models is based more on the results of actual calculations, which are then interpreted in terms of experimental observables. Examples include classical molecular dynamics [3], Monte Carlo calculations [4], non-equilibrium thermodynamics [5] and kinetic rate theories [6]. Of this category, the classical dynamics, while still containing inherent weaknesses, provides the best feel for what physically occurs during the bombardment process, and so can act as a bridge between the two categories. Therefore, this review will focus on the similarities and differences between the intuitive ideas and the results of classical dynamics simulations. Finally, only low-energy primary particles are examined. This means that the nuclear collisions are important in transfering momentum and energy and that high-energy mechanisms (electronic stopping, electron-hole pairs, repulsive electronic states, etc.) for the most part can be ignored.

2. Experimental Results

Probably the most striking general experimental result is the fact that organic molecules, with bond strengths on the order of 4-5 eV, can be sputtered intact by primary particles with energies of a few keV. Another almost equally unexpected result is that the fragmentation patterns of the sputtered material are very similiar for seemingly different sputtering techniques. This seems to indicate that the sputtering process may be indifferent to the mechanism of energy transfer and chiefly dependent on the initial system. Both of these results are encouraging in view of the original goal of interpreting sputtering data in terms of what is on the surface.

Other general results have been seen which seem to yield more information on the actual sputtering process. First, the kinetic energies of sputtered fragments are higher than those of intact parent ions [7]. The angular distributions of parent ions are also different from those of the fragment ions [8]. These two results can be interpreted in several ways, as is discussed below.

3. Ejection Mechanisms

In order to follow the ejection mechanism in detail, we have broken it up into several steps. Each step is then examined in terms of what events can influence the experimental results.

3.1 The Initial System

As the incoming primary particle approaches the surface, it exchanges energy and momentum with the initial system. As this energy is dissipated through the crystal, surface species can begin to move and be ejected. This is an obvious start for any model of sputtering. However, the influence which this energy dissipation has on the ejected species is not agreed upon from model to model.

One school of thought is that ejected fragments are a product of direct impacts in the vicinity of the initial bombardment [9]. The intact parent ions, it is envisioned, then come from a region further away from the impact point where the energy has dissipated sufficiently, so that no fragmentation takes place, yet the intact surface species can still eject. This scenario accounts for the fact that the energy of the fragments is higher than that of the parents. It also accounts for the angular distributions, where analytic theories of sputtering predict broader cosine-like distributions for species sputtered by random collision cascades [10] similar to that seen for the intact ions.

While Monte Carlo calculations have indirectly supported these ideas [4], molecular dynamics calculations predict a somewhat different conclusion [11]. For several types of organic molecules on clean surfaces, it has been shown that organic species can eject intact from areas both near and away from the initial impact. The dynamics calculations give three contributing explanations for intact ejection. First, it has been shown that the energy of the primary particle can be dissipated very quickly by the substrate.

Also, the molecular species contain many internal vibrational modes which are efficient in absorbing energy from an energetic collision. Finally, multiple atoms in the molecular species may be struck by a larger substrate atom,causing them to move away from the surface in a concerted fashion. Also in contrast to the qualitative model discussed above, the dynamics calculations show that the fragmented species can also arise from points away from the impact area. Not all direct fragments are from collisions with the primary particle.

Energy distributions from computer simulations also have shown higher energy fragments as compared to parent ions. This is due to the simple fact that the more energetic parent species fragment, thus depleting the distribution in the higher energy regions and increasing the number of high energy fragments. Calculated angular distributions also show a more cosine like distribution for ejected parent ions than for fragments [11]. This is because the smaller fragments formed at the surface are more susceptible to the influence of the matrix, which can change these distributions.

Another popular concept is that of a precursor or preformed ion pair [9,12]. In this model it is assumed that an initially charged surface species will retain its charge (and composition) during the bombardment process. While classical dynamics in its pure form does not include charge transfer, these calculations have indicated that the composition (and hence charge in some cases) can change during sputtering. This is discussed more below. Furthermore, other experiments and calculations involving charge transfer with inorganic systems clearly show that there is charge transfer between the surface and the ejected species as they leave the surface [13]. These ideas have also been generalized to organic systems [14]. While experimental results indicate that the idea of a precursor is somewhat valid [15], clearly the composition and charge of detected species in SIMS and FABMS is somewhat more involved.

3.2 The Near Surface Region

On the way to the detector, the ejected parent molecules, fragments and single atoms pass through the near surface region as highly reactive species. If more than one of these species are ejected in a single bombardment, there is a probability that reactions can take place, especially for fragments and single atoms. Here the nearby surface can act as an energy sink or source. There is also a high probability of electron transfer with the surface in this region. Both of these will clearly effect what is seen at the detector.

While computer simulations do show the ejection of intact molecules and clusters from the surface, they also show that ejected species can recombine in the near-surface region,so that their composition as seen at the detector is not what was on the surface. This has been seen in simulations of benzene on nickel [11], where ejected single Ni atoms combined with ejected intact benzene molecules above the surface. The single nickel atom can supply the charge necessary to be detected. Clearly no charged benzene molecule had to exist on the surface for the cationized species to be detected. This type of near-surface reaction is applicable to the transfer of other atomic species, including the gain or loss of hydrogens, the attachment of other cations or anions and combinations of each. Because of these types of reactions, both the charge and the composition of detected ions does not always give a direct indication of the surface species.

3.3 Away from the Surface

If a sputtered molecule leaves the near-surface region with sufficient internal energy, it may unimolecularly decay before it reaches the detector [16]. While this is generally accepted in all models of sputtering, the amount of fragmentation in this region,as compared to that in the previous two steps,has been debated. MOON [17] has shown by way of a simple classical description of the fragmentation of an ejected molecule away from the surface that the polar angle distributions of daughter ions from a single parent ion must peak at the same position. This principle was then applied to the sputtering of several organics on Ag(111) to show that gas phase unimolecular decay was not the chief mechanism for the formation of fragments. Experiments by CHAIT [16] and ENS et al. [16] clearly show, on the other hand, fragmentation on the way to the detector. The primary mechanism of fragmentation is still an open question.

4. Conclusion

Are the number of approaches and interpretations as different as the number of researchers in the field? As this review has shown, there are still some very fundamental questions which still need to be answered before the ejection mechanism is understood. It should be emphasized here that only charged species are detected experimentally, so a detailed comparison between theory and experiment is dependent on a thorough understanding of charge transfer during sputtering as well as the experimental detection of neutral species. Progress is currently being made in both of these areas [18]. As more experimental results become available and more sophisticated calculations are performed, the effect of the properties of the systems being sputtered on the experimental results are being better understood.

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