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Atoms, clusters and photons: Energetic probes for mass spectrometry

Barbara J. Garrison

104 Chemistry Building, Department of Chemistry, Penn State University, University Park, PA 16802, United States

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Abstract

The physical mechanisms underlying the surface based mass spectrometry techniques of atomic SIMS, MALDI and cluster SIMS are discussed along with the relation of the physics to the measured quantities. In particular, there are at least two types of motion resulting from cluster bombardment in SIMS. One scenario involves the individual atoms in the cluster initiating collision cascades similar to atomic bombardment. The second mechanism involves a mesoscale motion of the cluster as a whole. This mesoscale motion can induce an organized flow of the ejected material in a plume.

Keywords: Molecular dynamics; Simulation; SIMS; MALDI; Cluster SIMS; C_{60}

1. Introduction

The surface based mass spectrometry techniques, secondary ion mass spectrometry (SIMS) and matrix assisted laser desorption/ionization (MALDI), involve fast energy deposition processes at surfaces. In the case of SIMS, the energy is deposited by a particle with several 1000s of eV of kinetic energy. For MALDI, the energy is deposited via a pulsed laser. Even though the two techniques may appear similar, the physics driving the ejection process in each technique is quite different. In the case of SIMS, the motion of the atoms and molecules can be described by a sophisticated billiards or pool game [1,2]. As in a game of pool, the atomic motions following each ion event are variable. Laser ablation, i.e., MALDI, involves a phase transition of the material from a superheated liquid to a mixture of gaseous molecules and clusters of molecules [3–5]. The motion of particles following the phase transition is very organized and the material ablates in a plume.

The advent of cluster projectiles for use in SIMS and the corresponding computer simulations [6–8] open the question of whether cluster bombardment in SIMS should be discussed in the language of a collision cascade or whether the organized motion concepts from MALDI are more applicable. The motion giving rise to the crater formation [9] in cluster SIMS certainly implies a level of organized mesoscale motion. If cluster SIMS can have different basic physics than atomic SIMS, then one would expect ramifications on various measured quantities. Below we discuss atomic SIMS, MALDI and cluster SIMS and examine how the basic physics influences what is measured.

2. Essentials of surface based mass spectrometry

2.1. Atomic bombardment SIMS

The motion initiated in solids due to atomic ion bombardment is best described by a collision cascade although additional physics may be present for condensed rare gas solids [10,11] or molecular solids [12]. The time scale of the ejection process is a handful to tens of ps. The diameter of action in the surface can range from very small to several tens of nm. The implantation depth of a 15 keV atomic projectile can be up to 30 nm in materials:

- The number of particles ejected per incident ion varies over a large range. In particular, a few number of ejected particles per incident ion is often quite probable for most systems except weakly bound systems like rare gases [10]. A number of such distributions have been published over the years including two recent ones for 5 keV Ar bombardment of a polystyrene (PS) overlayer [13] on Ag and 15 keV bombardment of a silver surface [6]. Animations of high and low action events for the PS overlayer can be found on the web [9]. The consequence for the SIMS process is that

E-mail address: bjg@psu.edu.

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incident ions can bombard the surface and produce minimal useful signal.

- The collision cascade yields a kinetic energy distribution (KED) for amorphous and polycrystalline atomic solids that can qualitatively be described by the Thompson formula [14]. The high energy tail goes as $1/KE^2$ and the peak in the distribution is proportional to the binding energy. The KED of atomic clusters, e.g. Ag_2, tends to be narrow and peak at slightly lower energies [7,15]. The KED of molecules is distorted by dissociation of the molecules that might otherwise eject with large KE [16]. Of course, the KE and angular distributions of single crystals reflect the geometrical arrangement of the substrate [17].
- The large penetration depth causes significant damage in organic solids, thus the static limit of using a dose of less than 10^{12} ions/cm^2 must be followed rather rigorously.

2.2. MALDI

The physics driving ablation of molecules in UV MALDI is a phase explosion or explosive boiling [3–5]. The rate of energy deposition is sufficiently fast that the system heats, melts and expands. Once the system reaches approximately the spinodal temperature, then the rate of homogeneous nucleation of vapor bubbles increases exponentially. At this point the system converts to a gaseous mixture of individual molecules and clusters of molecules [5,18]. This phase explosion drives off the material and entrains the analyte molecules in the expanding plume of the matrix molecules. The expansion of the plume into the vacuum cools the system. The time scale is multiple ns. The lateral diameter of the laser is microns and the penetration depth can be hundreds of nm. Animations of the ablation events are available on the web [19]:

- The yield on *every* laser shot can be more than 10^{10} molecules. (No statement is implied here about the consistency of emission of analyte ions, and thus the issue of sweet spots in MALDI.) The analyte molecules are entrained in the expanding plume of matrix molecules. This mandatory large scale motion is the basis for the observations that much larger molecules are observed in MALDI mass spectra compared to SIMS mass spectra.
- The velocity distribution is characterized by a Maxwell–Boltzmann distribution with a range of flow velocities in the axial direction [20,21]. The more massive analyte molecules are moving at essentially the same axial velocities as the matrix molecules. The radial velocity distributions are characterized by a temperature, thus the heavier analyte molecules are moving slower than the matrix molecules in the direction perpendicular to the flow. Consequently, angular distributions of the molecules are highly forward peaked ($\cos^n \theta$ with n between approximately 10 and 30) with the analyte molecules more forward peaked than the matrix molecules [22].
- Even though there is rapid heating of the matrix close to the spinodal temperature, the cooling due to the phase transition and expansion undoubtedly helps to cool the internal vibrations of the molecules. To my knowledge no direct experimental evidence is available, however, to support this statement.

2.3. Cluster bombardment SIMS

There are two concepts and languages that have been used to describe cluster bombardment in SIMS. The first language speaks of non-linearity in the sputtering yield due to cluster, e.g. Ag_2, bombardment relative to what two monomers, Ag, at the same velocity would eject [23]. This language suggests that each constituent atom creates a collision cascade similar to atomic bombardment. In the traditional concepts of atomic bombardment and especially the binary collision approximation, the incident projectile strikes one (or more) target particles. Each of the moving particles can go on to collide with other target particles. For cluster bombardment, since the two or more particles strike the surface within Å of each other, the collision cascades can overlap, causing an enhancement in the yield.

Alternatively, simulations for cluster bombardment by buckyball [6–8] and gold [24,25] clusters portray an initial mesoscale motion of the cluster as a whole followed by a relatively low energy motion of individual particles that formed the cluster. A detailed analysis of a 20 keV C_{60} collision on water shows clearly that at very early time, there are multiple occurrences where more than one carbon atom can come within about 1 Å of a single water molecule. In other words, there is a many-body collision with several projectile atoms hitting the same target molecule. The water–water collisions then ensue before many of the C atoms have collided with any water molecule. The individual atoms in the cluster are not initiating their own collision cascades, rather they are working cooperatively to move the water molecules. From this concerted motion, a portion of the energy of the projectile transmits through the sample in a pressure wave [6]. Sample animations are available on the web [9]. It is not completely clear as yet what factors are important for inducing this mesoscale motion. Clearly, the size of the cluster must be larger than atomic spacing within the substrate. There is possibly a relative mass effect but that is yet to be determined. The compressibility of the substrate may also play a role.

Thus, there are at least two mechanisms by which incident cluster ions can interact with the substrate in SIMS. In the first case, each particle in the cluster behaves similarly to a single incident ion but with possible overlap of the cascades. In the second case, all atoms in the cluster collectively induce a mesoscale motion. Since the concept of the mesoscale motion being relevant to cluster SIMS is relatively new, we focus on it in the remaining discussion. Moreover, it is the opinion of the author that many of the new, exciting results from cluster bombardment are directly related to the mesoscale motion.

The mesoscale motion induced by clusters such as C_{60} alters the nature of the ejection process relative to atomic bombardment SIMS. There is high action on every impact

[6,7,24,25]. There are no longer incident ions that eject very little material. Moreover, recent calculations of the onset of the plume development in simulations of C_{60} on water ice show a clear organized motion similar to a nozzle [26]. This organized motion may, in fact, bring in elements of the laser ablation language and physics to the SIMS community.

The advantage to us, at least, in using the language and concepts from the simulations of laser ablation (UV MALDI) is that the simulations have made numerous specific predictions that have compared favorably with experimental data [27,28] and have in a couple of cases predicted experiments to perform [29]. The lesson also learned from the laser ablation simulations is that the analytic models and ideas can have the essence of the correct physics but simplification misses many important details.

The ideas and predictions presented below are still in the early stages of conceptualization and verification by experimental data. The sorting out of whether the underlying action in the solid exhibits motion characteristic of individual atom bombardment with non-linear enhancement, the mesoscale motion or some other essential physics is still in progress. It is already clear that the nature of the projectile and the substrate are both important. It is doubtful that one experimentally measured quantity will be a definite signature of a particular type of motion. One possible signature might be the yield enhancement of the cluster projectile relative to atomic bombardment. Recent simulations have shown mesoscale motion and crater formation in C_{60} bombardment of three layers of benzene on an Ag surface. There is no enhancement, however, in benzene yield relative to Ga bombardment at the same 15 keV incident energy [8]:

- Stapel et al. [30,31] and Gillen et al. [32] have measured ion yields for a Langmuir–Blodgett film and tryptophan, respectively, as a function of cluster size for incident molecules containing up to18C (or F) atoms. They show that the yield increases with cluster size until approximately C_6 when the yield levels off. I propose that for the smaller clusters that atoms in the cluster are creating individual collision cascades and that there is a non-linear enhancement. Once the cluster attains a critical size, then the mesoscale motion dominates the physics and impacts from all cluster sizes are similar.
- During mesoscale motion, the cluster deposits much of its energy in the near surface region. Consequently, the yield of particles ejected in cluster SIMS is considerably larger and more consistent than for atomic SIMS. For example, Szakal et al. have measured water ice yields for Au, Au_2, Au_3 and C_{60} bombardment at 20 keV [33]. They report total yields of 100, 575, 1190 and 2510 water equivalents for the four projectiles, respectively. Although there is a significant enhancement using C_{60} (factor of 25) relative to Au, the total yield is not the same order of magnitude as in MALDI.
- The organized motion of the plume development [26] in the cluster bombardment process implies that one should compare velocity distributions as in MALDI rather than KE distributions in atomic SIMS. Moreover, one should distinguish between axial velocities and radial velocities [20,21]. This specific analysis has not as yet been done. The KEDs of Ag and Ag_2 from experiment and calculation for C_{60} bombardment show the Ag_2 KED to be broader than the Ag KED, the reverse of the distributions for Ga bombardment [7,15]. Sun et al. have subsequently analyzed the experimental total velocity distributions of the ejected Ag and Ag_2 particles and likewise concluded that they are characteristic of a flow motion [34]. There is a slight discrepancy with the concepts of a flow in that the fastest particles are Ag_2 species rather than Ag monomers whereas in laser ablation simulations, the fastest particles are the lightest ones [21]. A big caveat on the comparison between MALDI and cluster SIMS, however, is the fact that in laser ablation a true thermal equilibrium is established in the evolving plume and there is massive material removal. At least in the simulation of C_{60} bombardment of water ice that shows the organized motion, no thermal equilibrium is established [26].
- For molecular solids such as the water ice system where the velocities are characterized by the flow motion, the angular distributions are forward peaked [26] although not as forward peaked as the angular distributions in MALDI. For systems of thin overlayers on metal substrates, the angular distributions can be influenced by the uplifting motion of the crater rim [8].
- The big inference from the simulations of C_{60} bombardment of Ag [7] that has rocked the SIMS community is that there might be minimal damage to the substrate due to the C_{60} bombardment [35]. If, in fact, the sputtering yield is larger than the remaining damage [36], then the static limit can be abandoned. Several recent experiments suggest that with C_{60} bombardment on organic films [37–43] that these conditions can be realized. The initial mesoscale motion of the crater formation pushes the substrate downward in a concerted manner. It is conceivable that this type of motion causes less strain on the molecules and that they are damaged less than with atomic beams. Further simulations and experiments are needed to test the range of applicability of this concept.
- One aspect of the physics of the organized flow motion that has not as yet been investigated is whether the organized motion can entrain large molecules as in MALDI. Will cluster SIMS give rise to the ejection of larger molecules than atomic SIMS, especially if they are embedded in a matrix of smaller molecules?
- Another aspect of the organized flow motion is the suggestion that the expanding plume will cool the molecules. Certainly, one of the complications of doing post-ionization experiments on the sputtered molecules in SIMS is the fact that the molecules eject with high internal energies [44]. The post-ionized mass spectra are thus very messy [38]. Based on the suggestions of cooling from the simulations, post-ionization experiments of cluster SIMS bombardment might have potential.

3. Conclusions

Cluster bombardment has introduced the potential of new physics to the SIMS process. By understanding the new physics and its consequences, the community will be better positioned to exploit the full potential of the technique.

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