

Looking at surfaces with cluster ion beams

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Various mass-spectrometry-based techniques are widely used to characterize the near-surface region of a solid. The idea is to stimulate the desorption of surface species with some type of energetic input, such as an intense laser pulse, strong electric field, or energetic ion beam. Detection of the elemental or molecular species by mass spectrometry can provide a selective and sensitive measure of surface chemistry, with applications ranging from nanotechnology to biology.

Ion-beam techniques are associated with secondary ion mass spectrometry (SIMS). As the name implies, desorbed ions are created as the incident ion beam collides with the sample. Since the kinetic energy of the incident ion is usually several thousand electron volts, a value much greater than typical chemical bonds, complicated mass spectra consisting of many atomic and molecular fragment ions are observed. With molecular surfaces, the rapid accumulation of chemical damage changes the composition of the surface layers. This effect creates a limit to the ion fluence, greatly reducing the amount of material available for detection. High sensitivity and high lateral resolution for imaging may be achieved using a liquid metal ion gun (LMIG) as a focused probe and time-of-flight (TOF) detection for the mass spectrometry. The ion beam can be scanned over an area, acquiring mass spectra on the fly. This development marked the birth of molecule-specific TOF-SIMS imaging, which was quickly adopted by the community. However, matrix-assisted laser desorption ionization (MALDI) mass spectrometry has been more widely employed in biology than TOF-SIMS, since it yields simple mass spectra for high molecular weight molecules (i.e. peptides and proteins), and has made strong inroads into the biological community.

The development of cluster ion beams could alter this balance and allow SIMS to provide molecular information of a quality approaching that of MALDI, yet retain its unique surface sensitivity and imaging properties. Interestingly, it has been known since at least 1989 that cluster bombardment greatly enhances the yield of molecular ions¹. The idea is that each atom in the cluster carries only a fraction of the total kinetic energy. When the projectile collides with the sample, it immediately breaks apart into its atomic components. Each atom

initiates its own cascade of moving particles, but with lower kinetic energy. Hence, the energy is deposited closer to the surface and in a more concentrated fashion. As a result, desorption yields can be enhanced by an order of magnitude or more.

During the 1990s, interest in these sources developed but was fragmented, perhaps because of the high maintenance requirements of cluster sources and the inconsistency of the enhancement effects, which confused the field. The big breakthrough came with the introduction of a Au cluster LMIG^{2,3} and a gas C₆₀⁺ source⁴ that could be focused to a probe size of a few microns. Both of these sources were commercialized and the LMIG, also now available using Bi clusters, was rapidly adopted by the community. The C₆₀⁺ source was shown to exhibit superior SIMS spectra in most cases, but its poorer imaging quality and expense have limited its acceptance. It is particularly appealing, however, because of the large number of atoms in the cluster. Each C atom in a 20 keV beam has an energy of just 333 eV. In any case, a large majority of TOF-SIMS machines have incorporated various cluster ion sources, and the activity level in the field is growing rapidly. The number of cluster-beam related talks at the recent international SIMS conference held in Manchester, UK was over ten times the number just two years earlier.

With more players come more results. New rules for the implementation of cluster SIMS are emerging that suggest it may complement MALDI experiments in many research domains. For example, the physics of the cluster-solid interaction has a mesoscopic character with a size between the collision cascades associated with atomic bombardment and the macroscopic ablation phenomenon associated with MALDI. Molecular dynamics computer simulations of the bombardment event show the formation of a crater that looks very much like the feature that is formed when a meteor strikes the earth. A representative simulation of the process, comparing atomic and polyatomic bombardment, is shown in Fig. 1. Perhaps it is the collective motion associated with the formation of this crater that leads to such effective molecular desorption. A lot of basic science still needs to be completed to fully understand this interesting phenomenon. Many groups have shown that the buildup of chemical damage associated

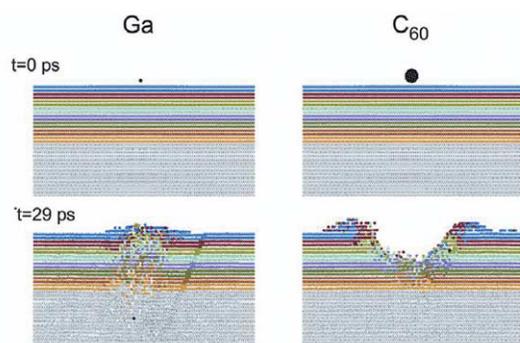


Fig. 1 Cross-sectional view of the temporal evolution of a typical collision event leading to ejection of atoms in 15 keV Ga and C_{60} bombardment of a Ag{111} surface at normal incidence. The atoms are colored by original layer in the substrate. The projectile atoms are black. (Reprinted with permission from⁵. © 2004 American Chemical Society.) Note the increased subsurface damage associated with the Ga impact. Animations of these two trajectories are available elsewhere⁶.

with atomic bombardment is not nearly as severe when using cluster beams. This observation raises the possibility that complex materials, such as multilayer polymers, simple organic thin films, and biofilms can be examined beneath their surface by using the cluster beam to peel away molecular layers, one layer at a time⁷⁻¹³. Fundamental measurements suggest the sputtering yield of these materials can be very high – several hundred to several thousand molecules per projectile^{7,10}, and that the molecular ion yield can also be enhanced by a built-in chemical ionization mechanism. Under the correct circumstances, cluster bombardment also reduces the formation of topography during sputtering¹⁴, with little interlayer mixing. Surface roughening has been a big problem with atomic bombardment and has inhibited this type of depth-profiling experiment.

An example of the power of this approach is shown in Fig. 2. A small peptide molecule Gly-Gly-Tyr-Arg (GGYR) was dissolved at the 1% level into an aqueous solution of trehalose. Trehalose is a simple sugar that is known to protect the peptide structure¹⁵. The solution was then spin-coated onto a Si substrate for analysis. This sugar has the remarkable property of forming a uniform glassy film of thickness 350 nm with a roughness of order 1 nm. So it makes a wonderful platform to study the erosion properties of molecular films. Fig. 2a shows that bombardment with C_{60}^+ eventually removes the entire film, as indicated by the mass peaks at 325 (trehalose) and 452 (peptide). After the removal of the film, the mass 28 peak (Si) increases. Note that the width of the

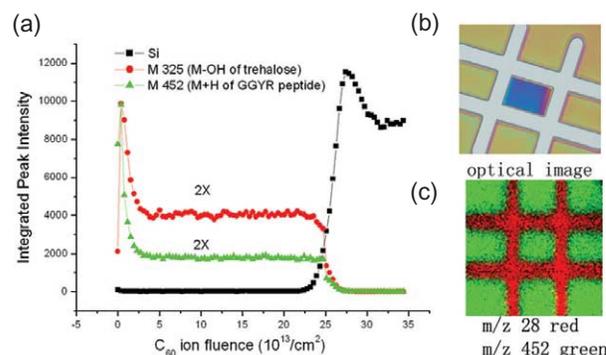


Fig. 2 (a) Depth profile of secondary ion intensities against C_{60}^+ ion fluence of a 350 nm trehalose film doped with 1% Gly-Gly-Tyr-Arg (GGYR). (b) Optical image of the film in an array format. The central square has been etched to 150 nm. The change in color is a result of optical interference. (c) Mass spectral image of (b). Note the intense signal from $m/z = 452$, the molecular signal of the peptide. The field of view is 520 μm .

Si/peptide interface is less than 15 nm, so that the depth information is largely preserved in this experiment. The intensity fluctuations near zero fluence are not yet completely understood, but probably result from the buildup of some chemical damage and matrix ionization effects that are well known with this technique. Molecular imaging is possible for these films, as shown in Figs. 2b and 2c. The result illustrates the power of this approach, since the image was taken by consuming several layers of the sample, leading to many orders of magnitude more sensitivity than was previously possible. Moreover, three-dimensional information can be achieved, since images can be recorded at any point along the profile shown in Figs. 2a and 2c.

The cluster SIMS field is generating a great deal of excitement in the community right now but there are still many unresolved issues. For example, it is not yet clear if any one of the many possible projectiles is the best one. Only a limited range of materials have been investigated, and it is not clear how general the molecular depth profiling experiments will prove to be. But, with many challenging surface analysis problems in nanotechnology, biosensing, and drug discovery, to name just a few, these new mass-spectrometry-based desorption probes are being scrutinized by a growing segment of the materials community. [ml](#)

Acknowledgments

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