

Nanocraters, soft desorption and 3D-resolved organic mass spectrometry using cluster ion beams

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Arnaud Delcorte is a Research Director of the Belgian National Science Foundation (FNRS) and a Professor at the University of Louvain (UCL) and University Saint-Louis (Brussels). He heads the management board of the surface characterization facility of UCL. He has been active in Secondary Ion Mass Spectrometry for about 20 years. His current research activities encompass the theoretical and experimental study of energetic cluster ion-surface interactions, with an emphasis on soft molecular emission, and of plasma-surface interactions, as well as the 2D/3D molecular characterization of surfaces. Overall, he has published 5 book chapters, 150 articles in peer-reviewed journals and has received 50 personal conference invitations. He is the secretary of the International Committee of the biennial SIMS conference, a member of the SIMS Europe Workshop Advisory Board and a member of the International Scientific Committees of the ECASIA and ISI conferences. He co-chaired the SIMS XXI international conference in Cracow (Summer 2017).

Abstract:

Over the past decade, secondary ion mass spectrometry (SIMS) has moved from probing and imaging surfaces with keV atomic ions to small clusters such as SF_5^+ , C_{60}^+ or Bi_n^+ and, most recently, to nanoparticles like Ar_n^+ or $(H_2O)_n^+$ containing thousands of atoms. This shift in projectile size involved a shift of underlying physical processes, from linear collision cascades to collective atomic motions and macroscopic-like impact phenomena, and a step change in performance for the chemical and molecular analysis of solid samples at the nanoscale.

In this contribution, I first use our results of molecular dynamics (MD) simulations and experiments [1] to review the changes associated to this increase in projectile size, which translates in ever smaller projectile atom energies. The analytical consequences are illustrated, e.g. the possibility of soft desorption-ionization, “damageless” depth-profiling (Fig.1a,b) and 3D molecular imaging, giving unprecedented information on the chemistry of the top nanometers of organic films [2]. In addition, the MD models quantitatively describe the variations of sputter yield as a function of cluster size and energy, and serve as a guide for future developments [3]. The emission yield dependence on the molecular size and substrate nature are also observed in the experiments and explained by the models. While the issue of damage in sensitive molecular and organic materials (fragmentation and cross-linking, Fig.1a,c [4]) could be essentially

alleviated by using large Ar_n^+ clusters, two other important challenges are now being tackled. First, the very large sputter yield difference between inorganic and organic materials hampers 3D analysis of hybrid organic-inorganic samples. Second, though subcellular molecular imaging with excellent mass resolution and accuracy was demonstrated [5], the molecular ion yields often remain low for high lateral resolution mapping using Bi_n^+ and Ar_n^+ projectiles. New routes for improvement are envisioned.

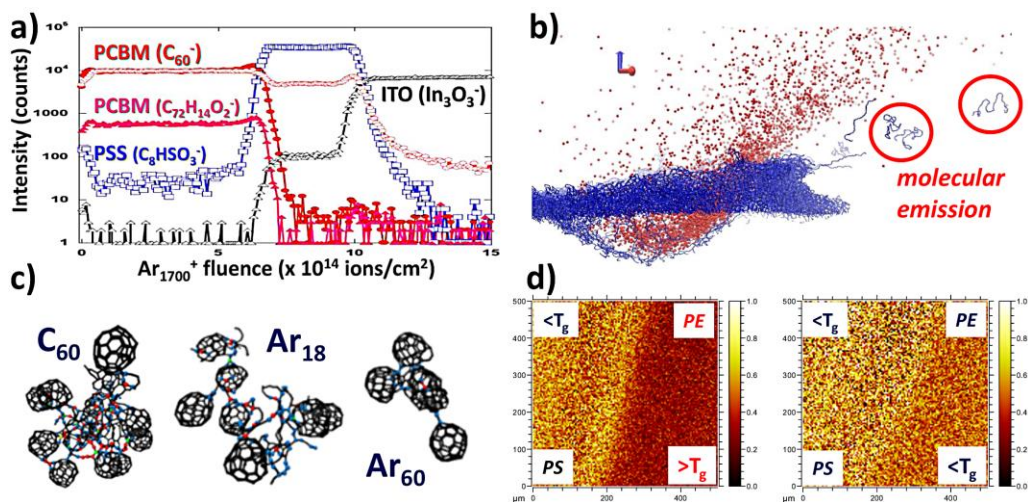


Fig. 1. (a) Molecular depth profiling of an organic photovoltaic multilayer device using Ar_{1700}^+ cluster sputtering. (b) Snapshot of the MD showing the cratering and molecular emission induced by a 5 keV Ar_{5000}^+ cluster in an organic sample (45° incidence). (c) MD Simulation of the crosslinking induced in fullerite by 2.5 keV clusters. (d) Images of the backscattered Ar cluster intensity ratio $\text{Ar}_2^+ / (\text{Ar}_2^+ + \text{Ar}_3^+)$ for a mixed polystyrene/polyethylene surface at room temperature and at -150°C .

Finally, I demonstrate that the backscattering of gas cluster ion fragments also provides information on the local physical properties of the bombarded organic surfaces, as illustrated with the glass transition of polymeric layers (Fig.1d) [6]. This potentially adds a new dimension to SIMS imaging with large clusters.

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