ELSEVIER

Applied Surface Science 203–204 (2003) 69–71

applied surface science

www.elsevier.com/locate/apsusc

Big molecule ejection—SIMS vs. MALDI

B.J. Garrison[a,*], A. Delcorte[b], L.V. Zhigilei[c], T.E. Itina[d], K.D. Krantzman[e], Y.G. Yingling[a], C.M. McQuaw[a,f], E.J. Smiley[a,f], N. Winograd[a,f]

[a]*Department of Chemistry, Penn State University, University Park, PA 16802, USA*
[b]*PCPM, Universite catholique de Louvain, 1 Croix du Sud, B1348 Louvain-la-Neuve, Belgium*
[c]*Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA 22904, USA*
[d]*LP3 CRNS, Universite d'Aix-Marseille II, Marseille, France*
[e]*Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC 29424, USA*
[f]*Materials Research Institute, Penn State University, University Park, PA 16802, USA*

Abstract

Using the results of molecular dynamics (MD) simulations, we discuss the question of whether the observed difference in mass limits in secondary ion mass spectrometry (SIMS) and matrix assisted laser desorption ionization (MALDI) are inherently related to the underlying physics of ejection or rather insufficient experimentation. The simulations show clearly that the physics of large molecule emission in SIMS and MALDI is very different. Consequently, we conclude that larger molecules can be ejected in MALDI than in SIMS.

Keywords: MALDI; Organic SIMS; Molecular dynamics; Computer simulation

1. Introduction

The ejection of large intact molecules underpins the applications of both secondary ion mass spectrometry (SIMS) and matrix assisted laser desorption ionization (MALDI). In some respects, the two processes appear quite similar as both are initiated by fast energy deposition events in the surface region. A high energy (5–25 keV) primary particle strikes the surface in SIMS, initiating a collision cascade that ultimately leads to the ejection of intact molecules. In MALDI, a laser irradiates the matrix and ultimately the large analyte molecules are ablated intact. In both experiments, ions are detected although neutral species generally dominate the ejected material. There is a big difference, however, in the size of the molecules that have been detected. Currently the upper mass limit for organic molecules in SIMS is in the range of 10–12 kDa [1]. The mass limit for MALDI, on the other hand, may be as high as ~1 MDa [2].

The ultimate question is whether these mass limits are inherently related to the underlying physics of ejection or rather insufficient experimentation. We have modeled both the SIMS [3–5] and MALDI [6–8] processes with molecular dynamics (MD) simulations. It is our belief that the physics of ejection is sufficiently different such that MALDI can ablate larger molecules than can be sputtered in SIMS. We describe the ablation process in MALDI ablation first as it is probably less familiar to the readers of these proceedings.

* Corresponding author. Tel.: +1-814-863-2103; fax: +1-814-863-5319.
E-mail address: bjg@psu.edu (B.J. Garrison).

0169-4332/02/$ – see front matter
PII: S0169-4332(02)00661-X

2. MALDI

The laser ablation process associated with MALDI is modeled with a novel breathing sphere approach. Each molecule in the system is represented by a particle with the true translational degrees of freedom but an approximate breathing mode that allows one to obtain a reasonable rate of energy transfer from the excited molecule to its neighbors [6]. This approximation is necessitated by a collective character of the ablation process that requires a large region of the irradiated sample to be included in the simulation. The properties of the laser including wavelength, pulse width and fluence are input into the simulation. Using a bead and spring representation of the analyte molecule in conjunction with the breathing sphere model we have observed in the simulation the ablation of analyte molecules up to a mass of 30 kDa [7,8].

Two time snapshots of the ablation of an analyte molecule with mass 11 kDa are shown in Fig. 1. At $t = 0$, the analyte molecule is beneath the surface. At $t = 150$ ps (or immediately after the 150 ps laser pulse has terminated), the plume containing the analyte molecule is 200 Å above the surface. The analyte molecule is entrained in the plume and is moving at a velocity of 490 m/s or a kinetic energy of 14 eV. Of note is that there is relatively little mass effect in the velocity of analyte molecules so a heavier molecule would be moving at a comparable velocity and thus an even higher kinetic energy.

In ablation, the laser energy is rapidly deposited in the sample. Depending on the laser pulse time, the speed of sound in the material, the thermal diffusivity and the penetration depth, the system can be in either stress or thermal confinement [6]. In the thermal confinement regime (UV MALDI), there is an overheating of the material and a phase explosion occurs. In the stress confinement regime (perhaps IR MALDI), there is a spallation of the material. In both situations, the physics of the laser ablation process demands that

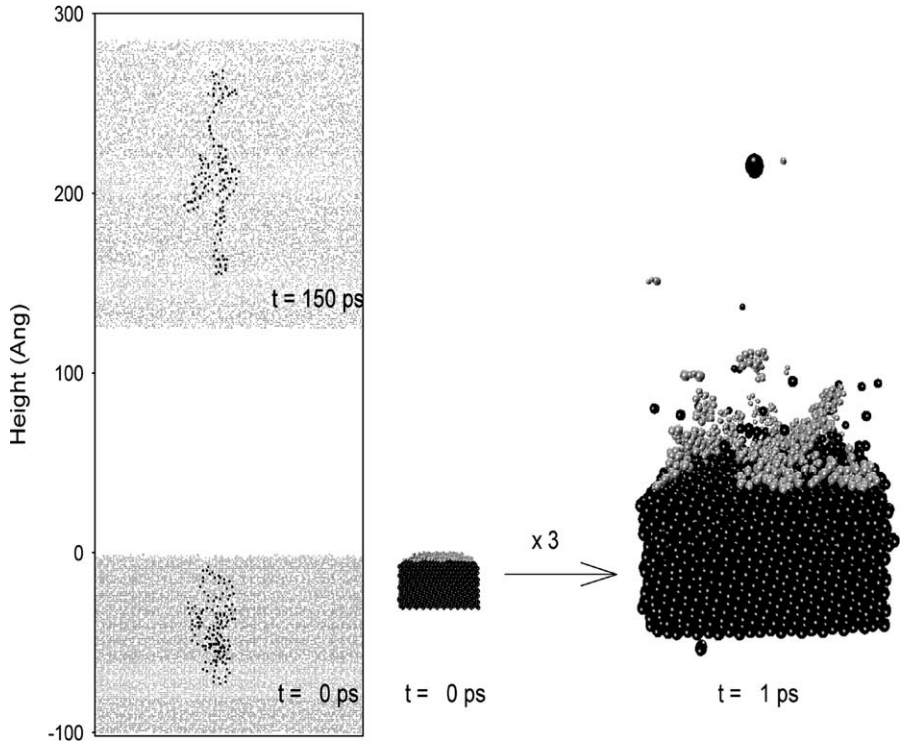

Fig. 1. Snapshots from the MALDI and SIMS MD simulations. The MALDI snapshots are on the left. Each matrix molecule is shown as a gray dot. The beads comprising the analyte molecule are shown as black dots. Only a portion of the simulation cell and plume are shown. The SIMS snapshots are shown on the right. The $t = 0$ snapshot is at the same length scale as the MALDI snapshots. The Ag atoms are shown as black spheres and the atoms in the PS molecules as gray spheres.

there be a cooperative motion of material towards the vacuum.

3. SIMS

The Ar bombardment of *sec*-butyl terminated polystyrene (PS) oligomers on a Ag{1 1 1} surface is modeled using atomistic MD computer simulations [4]. The sample consists of 13 PS tetramers (four styrene repeat units) placed on the Ag crystal. The mass of the PS tetramers using a tritium isotope of hydrogen in the simulations is 559 Da.

The MD simulations predict for sputtering that a diversity of actions can occur in the solid [4]. Some of the primary particle impacts result in very little material being removed from the surface. Other impacts give rise to tremendous motion, a phenomenon termed megaevent [5]. Shown in the figure are two snapshots of an impact event in which a total mass of 10 kDa was ejected. The initial time frame is shown at approximately the same scale as the MALDI simulations. Our simulations show that there is a cooperative upward motion pushing the molecule towards the vacuum. The atoms involved in the cooperative uplifting arise, however, from only three to five atomic layers or $\sim$10 Å beneath the surface. Moreover, the most probable kinetic energies of the ejected molecules are typically on the order of $\sim$1 eV. In another trajectory similar to the one shown in the figure, two PS hexadecamers (2001 Da each) are ejected.

4. Discussion and conclusions

The figure is designed to give a reasonable sense of perspective to the two experiments. We feel that our system sizes in the SIMS simulation are ''reasonable'' for modeling sputtering of 5 keV bombardment of an organic film on a metal surface. The system shown in the figure is $\sim$60 Å $\times$ 60 Å in width and $\sim$25 Å in depth. For the laser ablation calculations, we have chosen a laser penetration depth of 400 Å. This value is about a factor of two to five smaller than penetration depths typically encountered in UV MALDI. The experimental systems would have an even larger volume of material moving in a concerted manner than we have in our simulations.

The physics of large molecule emission in SIMS and MALDI is clearly very different. In SIMS there are high action events (megaevents) that lead to cooperative uplifting of the molecules from the surface. The upward motion occurs in only several Angstroms near the surface. Most importantly, the physics of the collision cascade does not demand that the atoms move in a concerted fashion. Rather, sometimes the atoms do move together. The physics of ablation requires that a rather large amount of material (tens of nanometer to microns in size) move in a concerted manner towards the vacuum. Because of the difference in the physics of material removal, we believe that the differences observed in maximum molecule size in SIMS and MALDI are real.

Acknowledgements

We gratefully acknowledge financial support from the Medical Free Electron Program (Air Force Office of Scientific Research) and the Chemistry Division of the National Science Foundation. The computational support for this work was provided by the IBM Selected University Research Program and the Center for Academic Computing at Penn State University. More results including papers, graphics and animations can be found on the group web page http://galilei.chem.psu.edu/.

References

[1] J.C. Vickerman, D. Briggs, A. Henderson, The Static SIMS Library, SurfaceSpectra Ltd., Manchester.
[2] S. Berkenkamp, C. Menzel, M. Karas, F. Hillenkamp, Rapid Commun. Mass Spectrom. 11 (1997) 1399;
C. Menzel, S. Bevkenkamp, F. Hillenkamp, Rapid Commun. Mass Spectrom. 13 (1999) 26.
[3] B.J. Garrison, A. Delcorte, K.D. Krantzman, Acc. Chem. Res. 33 (2000) 69.
[4] A. Delcorte, B.J. Garrison, J. Phys. Chem. 104 (2000) 6785.
[5] B.J. Garrison, in: J.C. Vickerman, D. Briggs (Eds.), ToF-SIMS: Surface Analysis by Mass Spectrometry, SurfaceSpectra Ltd. and IM Publications, 2001, p. 223.
[6] L.V. Zhigilei, B.J. Garrison, J. Appl. Phys. 88 (2000) 1281.
[7] L.V. Zhigilei, Y.G. Yingling, T.E. Itina, T.A. Schoolcraft, B.J. Garrison, J. Mass Spectrom. Ion Process., Franz Hillenkamp (special issue), submitted for publication.
[8] T.E. Itina, L.V. Zhigilei, B.J. Garrison, J. Phys. Chem. 106 (2002) 303.