



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SCIENCE @ DIRECT®

Nuclear Instruments and Methods in Physics Research B 202 (2003) 168–174

**NIM B**  
Beam Interactions  
with Materials & Atoms[www.elsevier.com/locate/nimb](http://www.elsevier.com/locate/nimb)

# Molecular dynamic simulations of the sputtering of multilayer organic systems

Z. Postawa<sup>a,\*</sup>, K. Ludwig<sup>a</sup>, J. Piaskowy<sup>a</sup>, K. Krantzman<sup>b</sup>,  
N. Winograd<sup>c</sup>, B.J. Garrison<sup>c</sup>

<sup>a</sup> *Smoluchowski Institute of Physics, Jagiellonian University, ul. Reymonta 4, Krakow 30-059, Poland*

<sup>b</sup> *Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC 29424, USA*

<sup>c</sup> *Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA*

## Abstract

Sputtering of organic overlayers has been modeled using molecular dynamics computer simulations. The investigated systems are composed of benzene molecules condensed into one, two and three layers on an Ag{1 1 1} surface. The formed organic overlayers were bombarded with 4 keV Ar projectiles at normal incidence. The development of the collision cascade in the organic overlayer was investigated. The sputtering yield, mass, internal and kinetic energy distributions of ejected particles have been analyzed as a function of the thickness of the organic layer. The results show that all emission characteristics are sensitive to the variation of layer thickness. Although most of the ejected intact benzene molecules originate from the topmost layer, the emission of particles located initially in second and third layers is significant. The analysis indicates that the metallic substrate plays a dominant role in the ejection of intact organic molecules.

© 2002 Elsevier Science B.V. All rights reserved.

*PACS:* 31.15Q; 82.80M; 31.70Ks

*Keywords:* Molecular dynamics simulations; Organic overlayer; Sputtering

## 1. Introduction

The impact of an energetic ion on a metallic substrate covered with an organic overlayer triggers a chain of events that finally leads to the ejection of both substrate atoms and adsorbate molecules. An understanding of these complex phenomena is not only of fundamental interest, but also could contribute to the development of

improved technological applications as well as detection strategies for molecular surface characterization. The removal of surface-bound material by energetic particles forms the basis of surface-sensitive analytical techniques such as secondary ion, secondary neutral, and fast atom bombardment mass spectrometry (SIMS, SNMS and FAB, respectively) [1,2]. Mass spectral detection of the secondary species gives SIMS and SNMS the ability to characterize even non-volatile organic molecules on solid surfaces.

While the range of practical applications of desorption phenomena is spectacular, the theoretical understanding of underlying phenomena is still

\* Corresponding author. Tel.: +48-12-632-48-88; fax: +48-12-633-70-86.

E-mail address: [zp@castor.if.uj.edu.pl](mailto:zp@castor.if.uj.edu.pl) (Z. Postawa).

incomplete. One of the first molecular dynamics (MD) studies utilized pairwise potential to examine how a molecule such as benzene with chemical bond strengths of  $\sim 5$  eV adsorbed on a metal substrate could be ejected intact by a projectile with several keV of kinetic energy [3]. Since then remarkable achievements have been done both in experiments [4–8] and simulations of these complicated processes [9–15].

In this paper we report the results of a first systematic study of the phenomena taking place during buildup of organic layers on a metal surface. The ion-induced desorption of a benzene system composed from one, two and three monolayers deposited on Ag{111} and sputtered by 4 keV Ar projectiles is investigated. In particular, depth of origin and the contribution to the total emission of the processes stimulated by the projectile directly in the organic overlayer and in the metallic substrate is evaluated.

## 2. Model details

The Ar bombardment of multilayers of benzene molecules adsorbed on an Ag(111) surface is modeled using MD computer simulations. An extensive description of the MD scheme can be found elsewhere [16,17]. Briefly, it consists of integrating Hamilton's equations of motion over some time interval to predict the resulting position and velocity of each atom in the system. Experimentally observable properties such as total yield, mass spectrum, kinetic energy and angular distributions can be calculated from the final positions, velocities and masses of all the ejected species.

The model approximating the Ag{111} substrate consists of a finite microcrystallite containing 6300 Ag atoms arranged in nine layers of 700 atoms each. The crystal size was chosen to minimize edge effects on the dynamical events leading to ejection of molecules. Multilayers of benzene are formed by quenching benzene layers each consisting of 126  $C_6H_6$  molecules. The initial positions before quenching are obtained from X-ray diffraction data for a benzene crystal structure [18,19]. The final position of the benzene molecules is determined by allowing the system to equilibrate

at 0 K using a generalized Langevin algorithm with periodic boundary conditions along the sides and the bottom of the system. This procedure results in a " $(2 \times 2)$ " structure for a monolayer deposition. This case shall be referred as " $(2 \times 2)$ " because not all the molecules can be placed exactly in the correct location for a true  $(2 \times 2)$  arrangement. Moreover, a small number of the molecules in the equilibrated " $(2 \times 2)$ " overlayer do not lie parallel to the Ag{111} surface.

The 4 keV Ar atom is directed normal to the surface. A total of 185 trajectories are calculated to sample the appropriate impact zone shown schematically in Fig. 1. Each trajectory is initiated with a fresh sample with all the atoms in their equilibrium minimum energy positions. The trajectory is terminated when the total energy of all the atoms remaining in the solid is not sufficient for any further ejection. This time ranges between 5 and 13 ps and depends on the impact point of the primary particle and the manner in which the energy distributes within the solid. Open boundary conditions are used during sputtering so that energetic particles are allowed to escape the crystal.

The size of the system is always an important factor in computer simulations. To verify whether our system is large enough 20 trajectories were run on a twice larger crystal (in each direction). The calculations were very time consuming but the results obtained on the larger and the regular systems agree with each other within a statistical error. Also the same trends as for 4 keV irradiation were observed when a regular crystal was bombarded by 500 eV Ar atoms. We believe, therefore, that our system is sufficiently large to contain investigated phenomena. Data obtained with 4 keV projectiles are discussed because this energy is closer to the projectile's energy used in a typical experiment.

The forces among the atoms are described by a blend of empirical pairwise and many-body potential energy functions. The Ag–Ag interactions are described by the MD/Monte Carlo corrected effective medium (MD/MC-CEM) potential for fcc metals [20–22]. The Ar–Ag, Ar–C and Ar–H interactions are described using the purely repulsive Moli e pairwise additive potential.

The adaptive intermolecular potential, AIR-EBO, developed by Stuart and coworkers is used

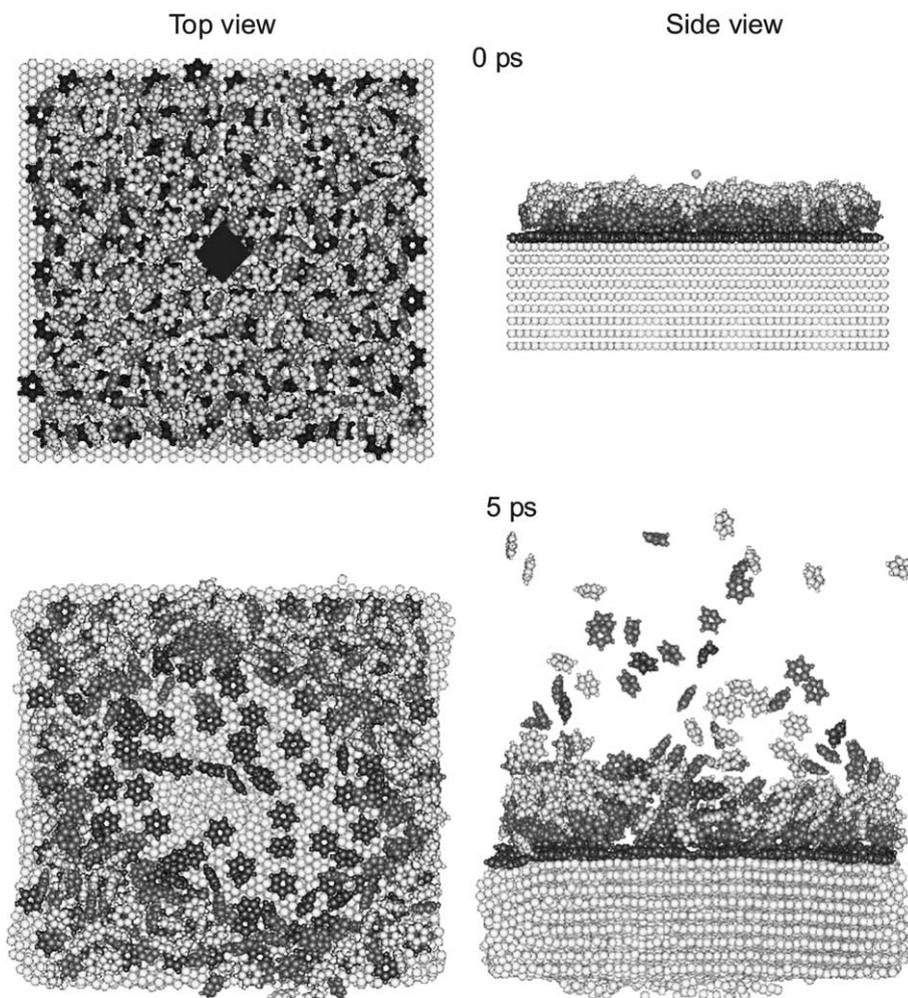


Fig. 1. Temporal snapshots of a typical sputtering event. A 4 keV Ar projectile bombards the three layer benzene system deposited on Ag{111}.

to describe the C–C, C–H and H–H interactions [23]. This potential is based on the reactive empirical bond-order (REBO) potential developed by Brenner for hydrocarbon molecules [24,25]. To overcome limitation of the REBO potential to short-range interactions, the AIREBO potential introduces non-bonding interactions through an adaptive treatment, which conserves the reactivity of the REBO potential. In the AIREBO potential, the strength of the intermolecular forces between pairs of atoms depends on their local chemical environment. The AIREBO potential yields a cohesive energy per benzene molecule of 0.40 eV.

The experimental cohesive energy of a benzene crystal depends on temperature of the crystal and ranges from 0.45 [18] to 0.507 eV [26].

Since the Ag–C<sub>6</sub>H<sub>6</sub> interactions are  $\pi$ -like in character, we choose to describe these potentials by Lennard-Jones potential functions which are pairwise additive for both the Ag–C and Ag–H interactions. The Lennard-Jones parameters are chosen such that the binding energy of C<sub>6</sub>H<sub>6</sub> to the Ag{111} surface is 0.4 eV for a single layer system [9]. The Ag–C and Ag–H distances of 2.3 Å are taken from a previously determined value for C<sub>6</sub>H<sub>6</sub>/Ag{111} [9]. The same set of parameters

was used when one, two and three layer systems were probed. In all investigated systems the mass of hydrogen was taken to be that of tritium ( $m = 3$ ) to increase the computational efficiency by allowing for a larger time step in the numerical integration. The mass of the benzene molecule is therefore 90 amu instead of 78 amu.

### 3. Results and discussion

The temporal evolution of a typical collision event leading to ejection of atoms and molecules is shown in Fig. 1. It is clearly visible that the benzene molecules in the overlayers are significantly desorbed by the ion impact. The central area around the ion impact point is almost entirely devoid of adsorbed molecules. Calculated mass spectra for one, two and three layer systems are shown in Fig. 2. The spectra are corrected for possible fragmentation by removing all molecules with internal energies greater than 5 eV, the value estimated to be the cutoff for dissociation. With this approach we found that almost 98% of all ejected benzene molecules are stable and will be detected. The mass spectra exhibit peaks for Ag, C, H, CH,  $C_2H_2$ ,  $C_5H_5$ ,  $C_6H_6$  along with other less pronounced species. In all cases, emission of intact molecules dominates the total ejection. This observation differs from the results published for tightly bound organic systems in which ejection of fragmented molecules is the most probable [11–13,27]. The yield of sputtered benzene molecules increases with the number of layers. Otherwise, there is no significant difference between the mass spectra. More careful inspection indicates, however, a slight increase in fragment emission as the thickness of the overlayer increases.

Layer resolved analysis shows that most of ejected intact benzene molecules originate from the topmost layer. However, a relative contribution from deeper lying molecules is also significant. For a 4 keV Ar bombarded three layer system almost 48% of all the emitted intact molecules are ejected from the topmost layer, 32% from the second and 20% from the third layer. With the 500 eV projectile, these numbers are different but still the emission of subsurface molecules is much larger

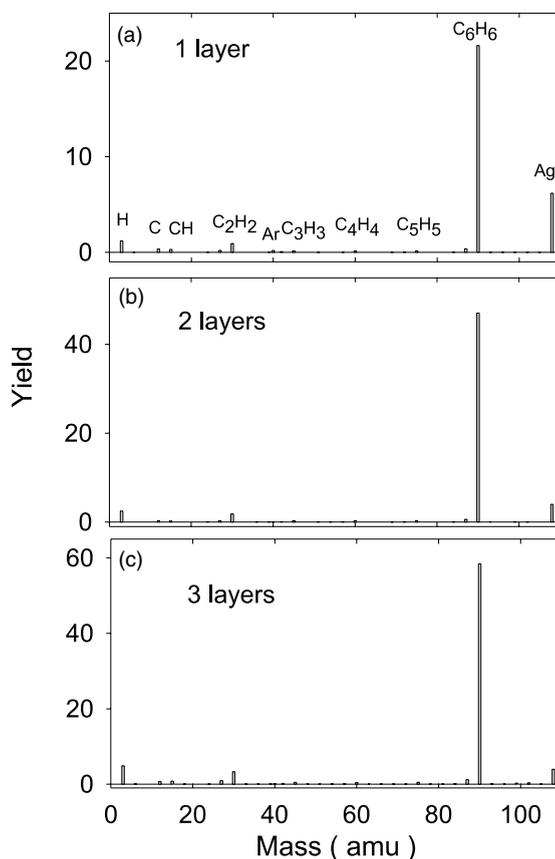


Fig. 2. Mass spectra of molecules and fragments sputtered from 4 keV Ar bombardment: (a) one, (b) two and (c) three layer system of benzene adsorbed on Ag{111}.

than reported for metals, where more than 90% of all atoms are ejected from the topmost layer [28]. Such behavior should be, however, characteristic of loosely bound systems in which a significant amount of material is ejected by a single projectile.

The mass spectra shown in Fig. 2 indicate that sputtering of benzene system is very efficient. The benzene sputtering yield of almost 22 is obtained for a single layer system and increases with the overlayer thickness. This result does not seem to comply with experimental findings reported in literature, where a maximum in the yield versus thickness dependency was seen for ions and neutrals [8,29,30]. This maximum was attributed to a formation of a complete monolayer. The reason for this discrepancy is not clear at the moment.

For measurements with secondary ions the variation of the ionization probability with the layer thickness may be important. This phenomenon should not be present in experiments in which the neutral flux was probed. However, it should be pointed out that the layer thickness was not precisely determined in [8,29,30]. For instance, in measurements performed on adenine [29,30] the correlation between the yield maximum and formation of a monolayer was not shown but arbitrary assumed. Our preliminary data indicate that the sputtering yield is lower for benzene solid than for 3L system. The appearance of a maximum seems, therefore, to be undisputable. However, the correlation of this quantity with a formation of a monolayer is not justified. Our preliminary calculations performed on atomic overlayer deposited on metal substrate show, for instance, that the height and position of a maximum depends on the relative strength of interactions within the overlayer and the interactions between the overlayer and the substrate [31].

When Ar bombards the benzene/Ag(111) system, both molecules and molecular fragments are ejected. In general, several processes responsible for ejection could be identified. From previous studies on a monolayer  $C_6H_6/Ag(111)$  system [9] it is known that collisions between ejecting substrate atoms and the adsorbed benzene molecules is a dominant process leading to emission of intact molecules. The analysis of particle trajectories identifies another mechanism that can contribute to desorption of multilayer systems. The molecules that are directly struck by the impinging projectile do fragment. Energetic fragments can hit neighboring molecules. At the initial stages most of these fragments have sufficiently high energy to break covalent bonds, and cause further fragmentation. Some low energy fragments will collide with neighboring molecules, imparting sufficient energy to initiate motion without fragmentation. In result, a quasi-atomic collision cascade develops inside the overlayer. The high energy cascade cools down relatively fast and after several ps mostly intact molecules take part in collisions. The inspection of particle trajectories shows also that fragments may react to form new species. Chemical reactions between particles release energy that

can be slowly transferred to molecules in the top-most layer, which are subsequently desorbed. The contribution from these two processes is very small for a monolayer system. However, such processes become more and more significant as the thickness of the overlayer increases and should become major mechanisms for sputtering of benzene solids [15].

A three layer system was used to estimate the role of the energy deposited by the primary projectile into the organic overlayer and into the substrate. Simulations in which interactions between Ar and hydrocarbons or between Ar and silver are selectively switched on and off were done to accomplish this goal. For instance, when the Ar–Ag interaction is turned off and Ar–C, Ar–H are turned on, the ejection is stimulated only by the processes that begin in the organic overlayer. On the other hand, when Ar–Ag interaction is turned on and Ar–C, Ar–H interactions are turned off, all ejections will be initiated by the portion of projectile energy deposited in the metallic substrate. The mass distributions of particles sputtered from such systems are shown in Fig. 3. It is

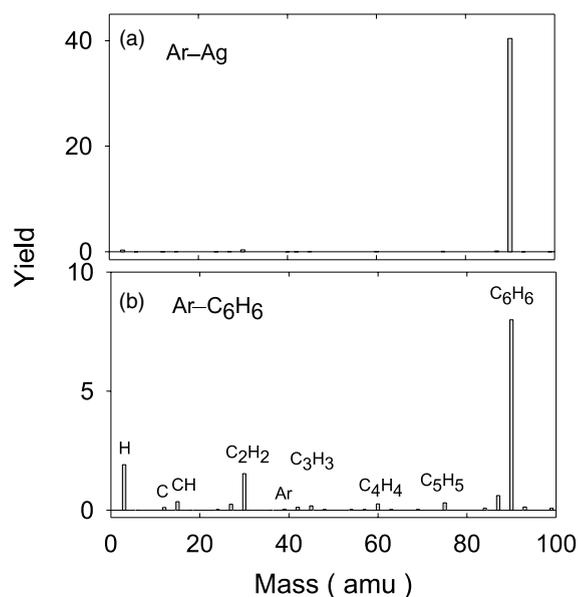


Fig. 3. Mass spectra of molecules and fragments emitted from a three layer system bombarded by 4 keV Ar projectiles interacting selectively with (a) substrate (Ar–Ag) atoms and (b) an organic overlayer (Ar– $C_6H_6$ ).

clearly visible that most of intact molecules are ejected due to processes initiated in the substrate. Even for the thickest investigated system, the primary energy deposited in the substrate plays the dominant role in ejection of intact molecules. Ejecting silver particles collide with benzene molecules leading to direct and indirect (through development of molecular collision cascade) ejection of intact benzenes. Since the average kinetic energy of these particles is relatively low (the most probable kinetic energy  $\sim 3$  eV) the fragmentation is minimal. Only approximately 20% of all benzenes are directly ejected due to processes stimulated by the energy deposited into the thickest organic overlayer investigated here. These processes are more energetic. It is shown in Fig. 3(b) that most of fragments are ejected due to these collisions.

#### 4. Summary

Desorption of a multilayer benzene system deposited on a metal substrate by energetic projectiles was investigated. In all cases, emission of intact molecules dominates the total ejection. The ejected molecules can originate from a significant depth. Most of sputtered intact molecules are emitted due to processes initiated in the metallic substrate. The contribution from direct interactions between the benzene molecules and the Ar projectile is responsible only for 20% of the total emission in the thickest investigated system. Although some transitions observed experimentally are visible in our data as the number of layers is increased, it is evident that this system is not thick enough to reproduce behavior of an organic solid.

#### Acknowledgements

The financial support from the National Institutes of Health, the National Science Foundation and the Office of Naval Research, as well as the Polish Committee for Scientific Research, Cooperation Programme between Flanders and Poland, and CYFRONET are gratefully acknowledged.

#### References

- [1] A. Benninghoven, F.G. Rudenauer, H.W. Werner, Secondary Ion Mass Spectrometry, Wiley-Interscience, New York, 1987.
- [2] P.A. Lyon (Ed.), Desorption Mass Spectrometry, American Chemical Society, Washington, DC, 1985.
- [3] B.J. Garrison, J. Am. Chem. Soc. 104 (1982) 6211.
- [4] R. Chatterjee, D.E. Riederer, Z. Postawa, N. Winograd, J. Phys. Chem. 102 (1998) 4716.
- [5] R. Chatterjee, D.E. Riederer, Z. Postawa, N. Winograd, Rapid Commun. Mass Spectrom. 12 (1998) 1226.
- [6] E. Vandeweert, C.A. Meserole, A. Sostarecz, N. Winograd, Z. Postawa, Nucl. Instr. and Meth. B 164 (2000) 820.
- [7] Ch. Meserole, E. Vandeweert, Z. Postawa, Brendan C. Haynie, N. Winograd, J. Chem. Phys. B 106 (2002) 12929.
- [8] Ch. Meserole, Ph.D. Thesis, The Pennsylvania State University, 2002.
- [9] R. Chatterjee, Z. Postawa, N. Winograd, B.J. Garrison, J. Phys. Chem. B 103 (1999) 151.
- [10] B.J. Garrison, A. Delcorte, K. Krantzman, Accts. Chem. Res. 33 (2000) 69.
- [11] A. Delcorte, X. Vanden Eynde, P. Bertrand, J.C. Vickerman, B.J. Garrison, J. Phys. Chem. B 104 (2000) 2673.
- [12] A. Delcorte, P. Bertrand, B.J. Garrison, J. Phys. Chem. B 105 (2001) 9474.
- [13] A. Delcorte, B.J. Garrison, Nucl. Instr. and Meth. B 180 (2001) 37.
- [14] C.A. Meserole, E. Vandeweert, Y. Dou, Z. Postawa, B.J. Garrison, N. Winograd, Nucl. Instr. and Meth. B 180 (2001) 53.
- [15] K.D. Krantzman, Z. Postawa, B.J. Garrison, N. Winograd, S.J. Stuart, J.A. Harrison, Nucl. Instr. and Meth. B 180 (2001) 159.
- [16] B.J. Garrison, Chem. Soc. Rev. 21 (1992) 155.
- [17] B.J. Garrison, in: J.C. Vickerman, D. Briggs (Eds.), ToF-SIMS: Surface Analysis by Mass Spectrometry, Surface-Spectra Ltd. & IMPublications, 2001, p. 223.
- [18] E.G. Cox, Proc. R. Soc. A 135 (1932) 491.
- [19] E.G. Cox, D.W.J. Cruickshank, J.A.S. Smith, Proc. R. Soc. A 247 (1958) 1.
- [20] M.S. Stave, D.E. Sanders, T.J. Raeker, A.E. DePristo, J. Chem. Phys. 93 (1990) 4413.
- [21] T.J. Raeker, A.E. DePristo, Int. Rev. Phys. Chem. 1 (1991) 10.
- [22] C.L. Kelchner, D.M. Halstead, L.S. Perkins, N.M. Wallace, A.E. DePristo, Surf. Sci. 310 (1994) 425.
- [23] S.J. Stuart, A.B. Tutein, J.A. Harrison, J. Chem. Phys. 112 (2000) 472.
- [24] D.W. Brenner, Phys. Rev. B 42 (1990) 9458.
- [25] D.W. Brenner, C.T. Harrison, C.T. White, R.J. Colton, Thin Solids Films 206 (1991) 220.
- [26] H.P. Steinrck, Surf. Sci. 218 (1989) 293.
- [27] K.S.S. Liu, C.W. Yong, B.J. Garrison, J.C. Vickerman, J. Phys. Chem. B 103 (1999) 3195.

- [28] R. Maboudian, Z. Postawa, M. El-Maazawi, B.J. Garrison, N. Winograd, *Phys. Rev. B* 42 (1990) 7311.
- [29] R. Möllers, A. Schnieders, A. Benninghoven, in: *Proc. SIMS X*, 1995, p. 943.
- [30] A. Schnieders, R. Möllers, A. Benninghoven, *Surf. Sci.* 471 (2001) 170.
- [31] J. Piaskowy, K. Ludwig, M. Szewczyk, B.J. Garrison, Z. Postawa, in press.