Vacuum 83 (2009) S155–S158

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Sputtering of thin films of bariated molecules of arachidic acid by large noble gas clusters

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ARTICLE INFO

Article history:
Received 16 June 2008
Received in revised form
10 January 2009
Accepted 30 January 2009

Keywords:
Sputtering
Cluster bombardment
Organic overlayers
SIMS/SNMS
Molecular dynamics

ABSTRACT

Coarse-grained molecular dynamics computer simulations have been employed to investigate the sputtering process of a multilayer organic system composed of long, well-organized linear molecules induced by an impact of slow clusters composed of large number of noble gas atoms. The organic system is represented by Langmuir–Blodgett multilayers formed from bariated molecules of arachidic acid. The sputtering yield, surface modifications and the angular distributions of ejected species have been analyzed as a function of the kinetic energy of an Ar_{872} cluster projectile and the thickness of the deposited multilayer. It has been shown that the physics of ejection by these large and slow clusters is distinct from the ejection events stimulated by the popular SIMS clusters: C_{60}, Au_3 and SF_5. The organic molecules are not ejected by interaction with the energized substrate but by direct interactions with the projectile atoms.

1. Introduction

Stimulated desorption by cluster projectiles has become an important process in organic and biological mass spectrometry since it has been found few years ago that the sputtering yields can be enhanced when an atomic projectile is replaced by a cluster ion with the same incident energy [1]. A wide range of clusters ranging from Au_3 to micrometer size droplets have been tested in a quest to find the optimum size of the cluster projectile. A significant theoretical effort has been expanded to investigate molecular ejection from organic systems bombarded by small cluster projectiles [2]. Much less is known about processes initiated in organic systems by large cluster impact. In pioneering experiments with massive glycerol clusters Mahoney and co-workers have shown that desorption of large peptide and protein ions is possible [3]. Recently, Jiro Matsuo and co-workers draw their attention to the possibility of fragment-free desorption of biomolecular samples by large cluster ions formed from noble gas atoms [4,5].

Almost all modeling of large cluster bombardment have been done on inorganic samples [6]. In our recent study we have investigated the mechanism of molecular desorption from a monolayer of sec-butyl-terminated polystyrene tetramer (PS4) [7] and benzene (C_6H_6) molecules [8] by impact of large and slow Ar clusters. It has been found that the physics of ejection by these projectiles is distinct from the ejection events stimulated by small cluster and that fragment – free ejection of organic molecules can be achieved. The ejection of majority of intact molecules is initiated by direct interactions between the organic molecules and back-reflected projectile atoms.

Both benzene and PS4 molecules form thin and very open overlayers. In this study we would like to investigate the processes initiated in a well organized, thick and dense overlayer composed of long, linear organic molecules. The molecular ejection efficiency and the ejection angles are investigated and compared to the data obtained on PS4 and C_6H_6 monolayers.

2. Model

Details of molecular dynamics computer simulations used to model Ar_{872} bombardment are described elsewhere [2]. Briefly, the motion of the particles is determined by integrating Hamilton's equations of motion. In this study, we use a coarse-grained approach to model Langmuir–Blodgett (LB) films formed from bariated molecules of arachidic acid (BaAA) deposited on Ag{111}. The advantages of a coarse-grained approximation are that there are fewer particles, the potentials are simpler thus quicker to calculate, and the fast H-vibration is eliminated, which allows for a larger time step to be used in the integration [9]. On the other hand, however, chemical reactions are eliminated from the analysis, thus, any conclusions about the chemistry of the irradiated

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doi:10.1016/j.vacuum.2009.01.051

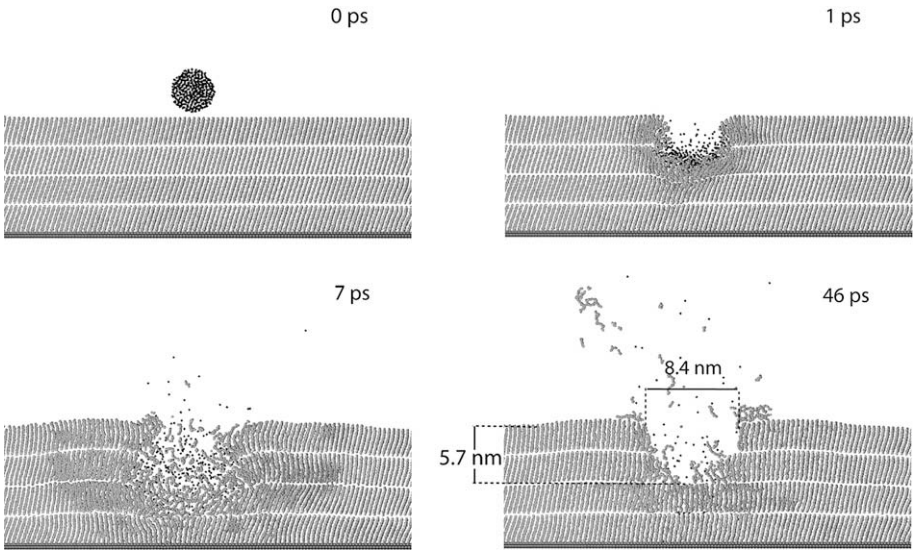

Fig. 1. Snapshots of the sputtering of a 4 layer system of the BaAA deposited on Ag{111} at 0, 1, 7, and 46 ps after 15 keV Ar_{872} impact at normal incidence.

sample must be drawn with caution. Nevertheless, this technique has proven to significantly decrease simulation time while giving the results similar to the data obtained with a full atomistic model [10]. In the coarse-grained approach each BaAA molecule is represented by a sequence of one COOBa (mass 182 amu), 18 CH_2 (mass 14 amu each) and one CH_3 (mass 15 amu) beads. With this arrangement, the total mass of a bariated AA molecule is 449 amu. The forces among the particles are described by a blend of pair-wise additive and many-body potential energy functions. The Ag–Ag interactions are described by the MD/MC-CEM potential for fcc metals [11]. A Lennard–Jones potential is used to describe the interactions of the particles located in different molecules and the interaction between the molecules and the metal substrate. The values of ϵ and σ have been chosen from previous studies describing linear hydrocarbons [12,13]. A Morse potential has been selected to describe interactions between adjacent particles (nearest neighbors) in the molecule. The parameters of this potential were selected to reflect the bond strength and equilibrium distance in linear hydrocarbons [12,13]. The same potential with a small well depth is also used to model interactions between particles separated by one particle (next nearest neighbors). As a result the particles are allowed to interact if the molecule is dissociated and the molecules adopt the appropriate zigzag shape in an equilibrium configuration. Finally, a Lennard–Jones potential is used to describe interactions between particles of a molecule that are separated by two or more particles. These types of interaction have been preferred to an angle bend term adopted in studies of lipid film configurations which does not allow for dissociation and is, therefore, inappropriate for sputtering simulations [9]. Finally, the interactions between Ar atoms in the projectile and between Ar atoms and all other particles in the system are described by a Lennard–Jones potential splined with KrC potential to properly describe high-energy collisions [14].

The model approximating LB films consists of coarse-grained molecules arranged in 1, 2, 4 and 6 layers deposited on Ag{111}. In the experiment, BaAA LB films are not prepared on silver but on clean Si substrate [15]. In our studies, however, a metal substrate was selected due to a simpler form of the potential, which results in much faster calculations. Silver was selected as a substrate because adsorption sites of BaAA on the Ag{111} surface could be arranged very close to the sites measured for BaAA/Si{100} system [16,17]. However, it should be noted that, although not a proper substrate was used, both the geometrical arrangement of the molecules, the adsorption sites and the value of the molecular-surface binding energy were selected to reproduce the experimental data obtained for bariated arachidic acid adsorbed on Si{100} [16,17]. Finally, a special care was taken to eliminate artifacts associated with a possible backreflection of a pressure wave generated by impact of such massive clusters, as described in Ref. [18].

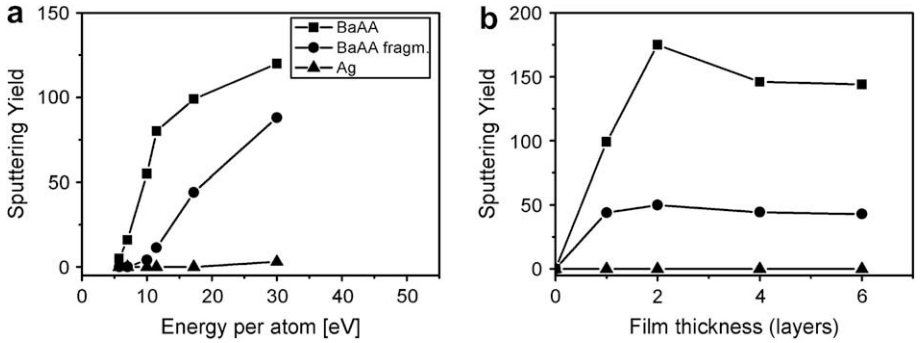

Fig. 2. Total sputtering yield of silver atoms, fragmented and intact molecules of BaAA ejected by Ar_{872} impact at normal incidence. Dependence of the yield (a) from a monolayer system on the kinetic energy of a projectile; and (b) on the film thickness for 15 keV ($\sim$17 eV/atom) projectile.

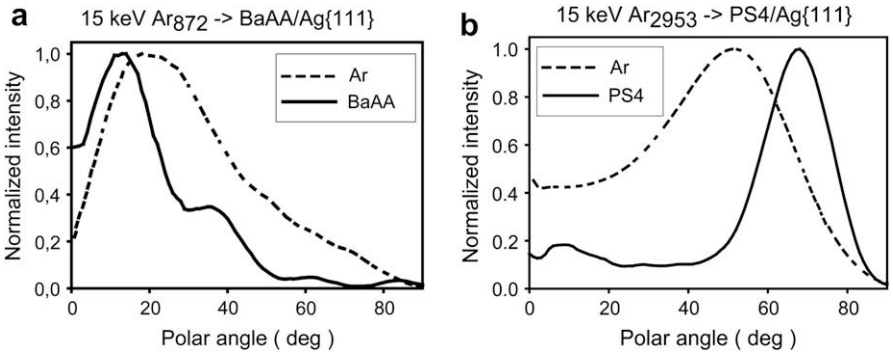

Fig. 3. Energy-integrated polar angle distributions of intact molecules (solid line) and back-reflected Ar atoms (dashed line) ejected by 15 keV (a) Ar_{872} bombarding a monolayer of BaAA and (b) Ar_{2953} bombarding a monolayer of PS4 [7].

3. Results and discussion

Snapshots of a 4 layer system bombarded with 15 keV Ar_{875} taken at 0, 1, 7 and 46 ps are shown in Fig. 1. The impinging projectile is deformed after the impact on the organic layer. Ar atoms slow down penetrating the layer, however, no collision cascade is generated in the sample. The organic molecules and fragments are ejected by direct interaction with the projectile atoms. The extent of the damage is localized in relatively narrow volume (8×6 nm) implicating a possibility of achieving a good spatial resolution in depth profiling experiments.

The dependence of the sputtering yield on the initial kinetic energy is shown in Fig. 2a for Ar_{872} cluster impact at normal incidence at 1 layer system. At very low kinetic energy no material is removed from the samples. As the energy exceeds approximately 5 eV/atom, the ejection of intact BaAA molecules is initiated and the yield steeply increases with the kinetic energy. Up to approximately 11 eV/atom only intact molecules are emitted. At higher kinetic energy the ejection of molecular fragments sets in. Emission of intact molecules saturates around 20 eV/atom for a monolayer system, while no indication of saturation is visible for a 4 layer system even at 30 eV/atom (not shown here). The ejection process is quite efficient. As shown in Fig. 2b, 15 keV Ar_{872} cluster leads to emission of 100, 175, 150 and 148 BaAA molecules from a 1, 2, 4 and 6 layer system, respectively. As a strong signal is always a beneficiary factor for SIMS/SNMS spectrometry, these characteristics could make large, slow Ar clusters potentially attractive for chemical analysis of organic samples. As shown in Fig. 2b, for a constant primary kinetic energy, the sputtering yield goes through maximum and finally saturates as the LB layer becomes thicker. The analysis of energy transfer pathways indicate that such behavior is caused by a competition between signal enhancement due to increasing number of organic molecules and the signal decrease due to lowering of the amount of the primary energy being back-reflected into the organic overlayer by the receding organic/metal interface. When the sample thickness becomes much larger than the penetration depth of the projectile, the sputtering yield is independent of thickness.

The results presented in Fig. 2a are qualitatively very similar to data obtained for a monolayer of PS4 [7] and benzene [8] deposited on Ag{111}. There are, however, significant differences in thresholds of the emission of both intact molecules and substrate particles. For C_6H_6/PS4, the emission of intact molecules is initiated below 1 eV/atom [8], while intact BaAA molecules are not ejected up to 5 eV/atom. Second difference is associated with the emission of substrate particles. For C_6H_6/PS4, onset of ejection of silver occurs around 5 eV [7,8]. For AABa system, no ejection of Ag particles was recorded within investigated energy range for multilayer system. For monolayer system only four substrate atoms were ejected at the highest investigated energy (30 eV/atom), while no emission occurs for lower energies. This difference can be explained by a much more open structure of both C_6H_6 and PS4 monolayers as compared to a monolayer of BaAA, and a larger thickness of the latter. Projectile atoms lose their energy penetrating the BaAA overlayer. As a result, when they arrive near the metal substrate they do not have sufficient energy to stimulate ejection of substrate atoms.

A significant difference in sputtering of C_6H_6/PS4 and BaAA systems is also visible in directions of ejection. The kinetic energy-integrated polar angle distributions of intact molecules and back-reflected Ar atoms ejected from a monolayer of bariated arachidic acid and PS4 molecules by Ar cluster are shown in Fig. 3. While spectra calculated for PS4 show that these molecules are emitted at almost glancing polar angles, the ejection of BaAA molecules peaks at polar angles close to the surface normal. The analysis performed on C_6H_6 and PS4 systems shows that direct interactions between the atoms that streams from the sides of deforming large cluster and the organic molecules are responsible for molecular ejection [7,8]. Similar process takes place also in the BaAA system (see Fig. 1). However, in this case, the possible ejection angles are limited by the resistive action of a thick and dense overlayer.

4. Conclusions

Coarse-grained molecular dynamics computer simulations have been employed to investigate the sputtering process of a multilayer of bariated arachidic acid system composed of long, well-organized linear molecules induced by an impact of slow clusters composed of large number of noble gas atoms. The results were compared to the data collected on more open and thinner monolayer systems [7,8]. It has been found that in both cases ejection of intact molecules is initiated by direct interactions between organic molecules and the projectile atoms. However, different density/thickness of the BaAA layer influences the ejection thresholds of intact molecules and substrate particles, and the directions of molecular emission.

Acknowledgments

The financial support from the Polish Ministry of Science and Higher Education programs no. PB 0935/B/H03/2008/35 and PB 4097/H03/2007/33, and the National Science Foundation grant #CHE-0456514 are gratefully acknowledged.

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