

Sputtering of thin benzene and polystyrene overlayers by keV Ga and C₆₀ bombardment

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Abstract

The mechanisms of ion-stimulated desorption of thin organic overlayers deposited on metal substrates by mono- and polyatomic projectiles are examined using molecular dynamics (MD) computer simulations. A monolayer of polystyrene tetramers (PS4) physisorbed on Ag{111} is irradiated by 15 keV Ga and C₆₀ projectiles at normal incidence. The results are compared with the data obtained for a benzene overlayer to investigate the differences in sputtering mechanisms of weakly and strongly bound organic molecules. The results indicate that the sputtering yield decreases with the increase of the binding energy and the average kinetic energy of parent molecules is shifted toward higher kinetic energy. Although the total sputtering yield of organic material is larger for 15 keV C₆₀, the impact of this projectile leads to a significant fragmentation of ejected species. As a result, the yield of the intact molecules is comparable for C₆₀ and Ga projectiles. Our data indicate that chemical analysis of the very thin organic films performed by detection of sputtered neutrals will not benefit from the use of C₆₀ projectiles.

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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. Understanding of these complex phenomena is not only of fundamental interest, but also could allow for the development of improved detection strategies for molecular surface characterization based on ion beam desorption techniques. Cluster ion beams are recognized as valuable sources for desorption of high mass ions in time-of-flight secondary ion mass spectrometry (TOF-SIMS) experiments [1,2]. For instance, the yield of the peptide gramicidin is enhanced by a factor of 1300 during C₆₀ impact when compared to Ga⁺ ion bombardment [3]. The reasons behind the unique properties of cluster ion beams are still not well-understood. Various degrees of enhancement of high mass secondary ions

have been reported, depending upon the type of projectile, target material and matrix [4]. For example, the experimental data show that thin polymer films on Ag do not seem to benefit from the use of polyatomic projectiles, while SIMS spectra from bulk polymers are dramatically improved [4].

To understand the signal enhancement in TOF-SIMS/SNMS experiments and to predict optimal experimental configurations, we have initiated a comprehensive series of MD investigations aimed toward understanding of collision cascades due to keV C₆₀ cluster bombardment [5–7]. The strategy involves utilizing well-defined model substrates to elucidate how the atomic motion and subsequent measurable quantities depend upon the nature of the incident particle, either an atomic species such as Ga or the cluster C₆₀. In our previous studies we have found that the C₆₀ projectile has several advantages as compared to Ga when used to analyze metallic samples [5,6]. Cluster bombardment can greatly enhance the yield over the atomic irradiation. The damage created by C₆₀ is much more confined than that induced by Ga. And finally, C₆₀ causes lower effective beam-induced contamination and leads to smaller surface roughening.

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The advantages of C_{60} ions were found to be much more limited when applied to a thin benzene overlayer [7]. For instance, only a very modest signal enhancement has been observed in this case. The lack of improvement was attributed to a limited number of weakly bound benzene molecules available for desorption. Essentially, both the Ga and C_{60} projectiles removed most of the material in the region of impact. Here, we focus on the study of 15 keV Ga and C_{60} interaction with polystyrene tetramer (PS4) overlayer deposited on the Ag{1 1 1}. Although PS4 molecules are also physisorbed to the Ag surface their binding energy is several times larger than for benzene. As a result, one may expect to achieve a lower rate of organic material removal which should allow for any differences associated with C_{60} and Ga bombardment to appear more readily.

2. Model

Molecular dynamics (MD) computer simulations have been used to elucidate the differences between Ga and C_{60} bombardment of thin organic overlayers. The details of simulations can be found elsewhere [8]. Briefly, the motion of the particles is determined by integrating Hamilton's equations of motion. The forces among the atoms are described by a blend of empirical pair-wise additive and many-body potential energy functions. The Ag–Ag interactions are described by the molecular dynamics/Monte Carlo corrected effective medium (MD/MC-CEM) potential for fcc metals [9]. The interactions with the impinging Ga atom are described using the purely repulsive Molière pair-wise additive potential. The adaptive intermolecular potential, AIREBO, developed by

Stuart and coworkers is used to describe the hydrocarbon interactions [10]. The interaction of C and H atoms with Ag is described by a Lennard-Jones potential [11,12].

The model approximating the Ag{1 1 1} substrate consists of a finite microcrystallite containing 166530 atoms arranged in 39 layers. Organic overlayers are represented by three layers of benzene [7] and a monolayer of 112 sec-butyl-terminated polystyrene tetramers (PS4) adsorbed on the Ag{1 1 1}. The adsorption scheme and the potential parameters for PS4 molecules were adopted from Ref. [12], however, the crystallite size was significantly enlarged to contain more energetic processes induced by 15 keV projectiles. In all the considered systems, the mass of hydrogen is taken to be that of tritium (3 amu) to increase computational efficiency. The mass of the C_6H_6 is 90 and the mass of PS4 is 559 amu instead of 78 and 474 amu, respectively. Prior to projectile impact, the entire system is relaxed to a minimum energy configuration. This procedure yields the resulting binding energy of 2.1 eV for the polystyrene tetramer which is several times larger than the binding energy of the adsorbed benzene overlayer (~ 0.4 eV) [7]. Special care was taken to eliminate the artifacts associated with the pressure waves generated by the C_{60} bombardment as described in Ref. [5].

3. Results and discussion

Snapshots of the temporal evolution of typical collision events leading to ejection of an average number of intact PS4 molecules due to 15 keV Ga and C_{60} bombardment of PS4 monolayer are shown in Fig. 1. A comparable portion of the PS4 monolayer is altered upon the impact of either projectile.

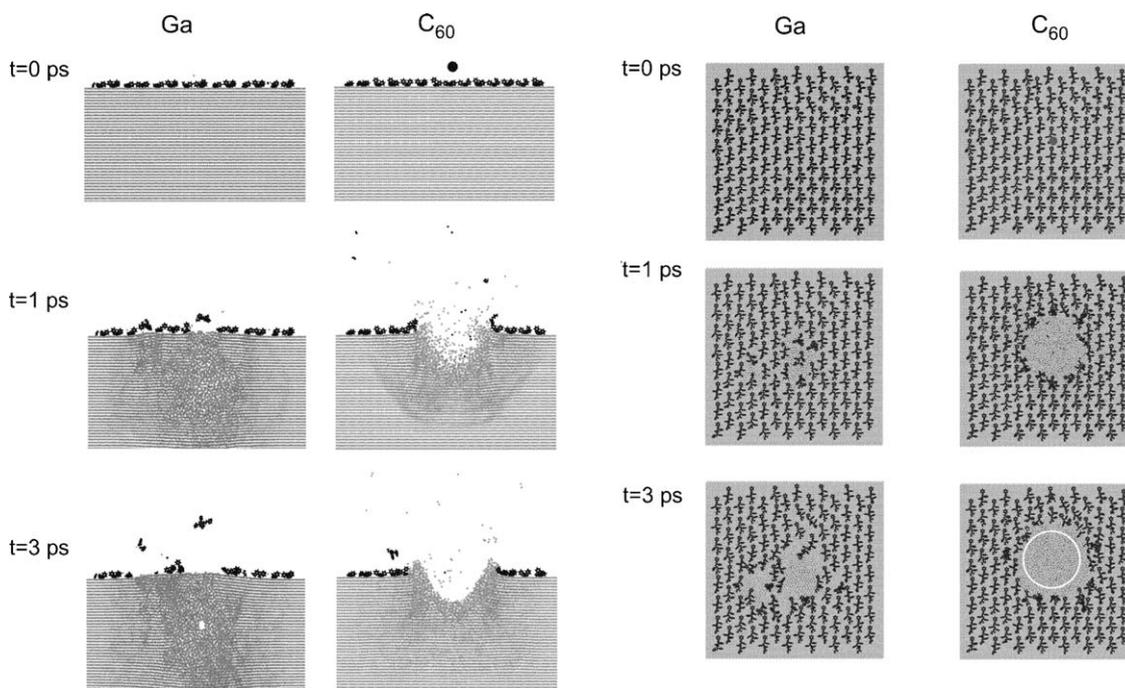


Fig. 1. A cross sectional view and top view of the temporal evolution of a typical collision event leading to the ejection of an average number of intact PS4 molecules due to 15 keV Ga and C_{60} bombardment at normal incidence of a PS4 monolayer deposited upon a Ag{1 1 1} surface. A slice 1.5 nm wide of the system centered at the impact point is shown. The white circle denotes the outer rim of the crater formed in the Ag substrate by C_{60} impact.

The nature of the collision events leading to these changes, however, is different for Ga and C₆₀. The Ga projectile easily penetrates through the organic overlayer. Direct collisions between Ga and organic molecules lead to the formation of energetic organic fragments. After passing through the organic overlayer, the Ga projectile penetrates into the substrate depositing most of its kinetic energy at a considerable depth similar to the motion induced without the overlayer [5,6]. The energy is subsequently redistributed within the crystal and a highly excited cylindrical volume is formed. Only a small portion of the primary energy is deposited near the Ag surface leading to ejection of substrate particles. Large intact organic molecules can, in principle, be ejected by a collision with an ejecting energetic substrate atom. However, collective action of several low energy atoms is a much more favorable scenario [7,11–13]. The size of the collision cascade generated in the substrate is large and the molecules located far from the impact point can be ejected as shown in Fig. 1.

Ejection of PS4 molecules induced by 15 keV Ga occurs in a relatively short time and the emission usually terminates around 2 ps. Similar processes take place in the benzene overlayer [7] with some notable differences. The ejection process extends to much longer times, as even after 2 ps there is still enough energy in the substrate to eject the loosely bound benzene molecules. The amount of ejected organic material and the extent of the damage is larger as the layer is thicker and less energy is needed to uplift the loosely bound benzene molecules.

A different scenario takes place during C₆₀ impact of the PS4 monolayer. Due to its much larger size, C₆₀ always interacts with the organic overlayer losing a portion of its primary energy. Again, formation of small fragments is the main result of this interaction. After impact on the Ag substrate the spatial correlation of C atom movements is lost. Due to the heavier mass of the substrate Ag atoms, most of the C atoms originating from the projectile are reflected towards the organic

overlayer. Consequently, the energy of the cluster projectile is deposited in a shallow volume of the substrate in a short time leading to the ejection of many substrate particles. As a result a crater is formed. The process is almost mesoscopic in character and only weakly depends upon the initial impact point of the C₆₀ on the surface. Crater formation leads to a temporally and spatially correlated motion of metal substrate particles as shown in Fig. 1. These particles collectively interact with the adsorbed organic molecules, uplifting the molecules by a catapult-like action [14]. As in the case of Ga bombardment the ejection of organic molecules is completed at around 2 ps, although there is still a lot of energy deposited in the crater region to eject silver particles with low kinetic energy. Again, similar processes take place during irradiation of the benzene overlayer. However, due to lower molecular binding energy the altered area is larger. In addition, due to larger thickness and density of the benzene layer, C₆₀ projectile loses almost half of its primary kinetic energy when penetrating this overlayer [7]. Part of this energy leads to the formation of a planar pressure wave that moves the adsorbed molecules aside from the point of impact. Because a significant amount of kinetic energy is drained out of a C₆₀ projectile a typical crater formed in the substrate is smaller than for PS4/Ag system.

The mass distributions of ejected particles are shown in Fig. 2. Emission of intact C₆H₆ is the main result of Ga bombardment of benzene. Ejection of intact PS4 is also an important channel for PS4 monolayer irradiated by Ga. In this case, however, there is a significant contribution of substrate particles as the layer is thin and open. A significant number of substrate particles and small hydrocarbon fragments ejects for the C₆₀ irradiation of both overlayers. The number of ejected parent molecules is slightly enhanced by application of the C₆₀ instead of the Ga projectile on C₆H₆/Ag{111} system. However, the opposite trend is visible for PS4. The mass spectrum shown in Fig. 2 is not corrected for a possible post-

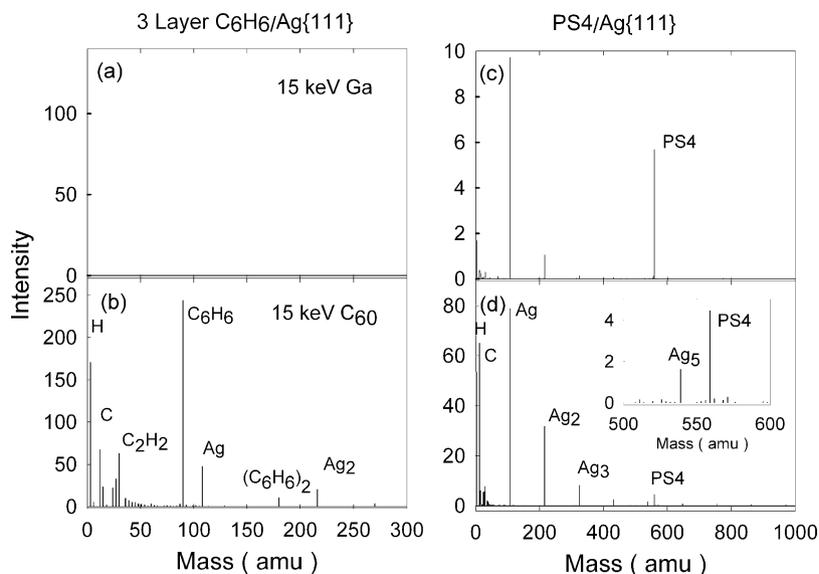


Fig. 2. Mass distributions of particles ejected by 15 keV Ga (top) and 15 keV C₆₀ (bottom) bombardment of benzene (left) and PS4 (right) systems collected ~15 ps after the projectile impact. The enlarged fragment of a mass spectrum around PS4 molecule is shown in the inset.

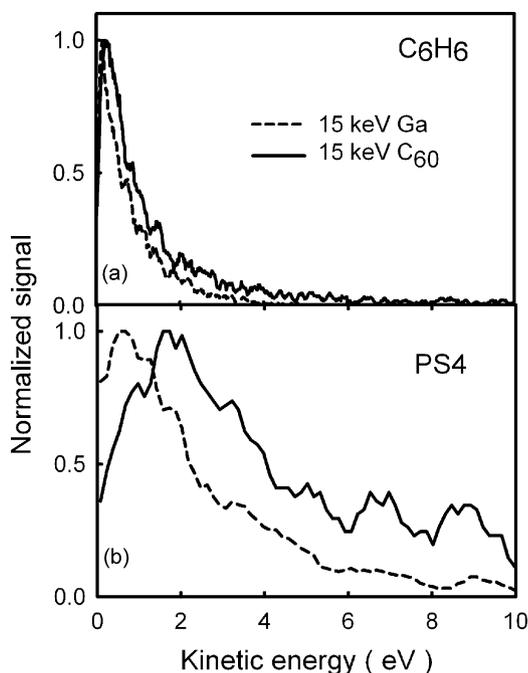


Fig. 3. Peak normalized kinetic energy distributions of (a) C₆H₆ and (b) PS₄ molecules sputtered at normal incidence by 15 keV Ga (broken line) and C₆₀ (solid line).

ejection unimolecular decomposition of molecules and clusters [12]. To take this process into account a constant threshold of internal energy is used to estimate whether organic molecules will dissociate. Unimolecular decomposition theory predicts that more than 90% of C₆H₆ and PS₄ molecules will be detected on a μ s time scale if their internal energy does not exceed 4.6 and 28 eV, respectively [12]. Approximately 9% C₆H₆ and 5% of PS₄ molecules have an internal energy higher than the assumed dissociation thresholds for Ga projectile bombardment. At the same time, \sim 21% of C₆H₆ and \sim 14% of PS₄ molecules ejected by C₆₀ impact have internal energies exceeding the threshold values. All of these molecules will dissociate and, consequently, they would not be detected experimentally. Because of the decrease in benzene and PS₄ yields due to dissociation, the final enhancement factor is reduced from 1.8 to 1.4 for benzene and from 0.8 to 0.7 for PS₄.

The kinetic energy distribution of ejected particles is a quantity that can be measured and, at times, can be used to help understand the mechanisms responsible for emission. Angle integrated kinetic energy distributions of C₆H₆ and PS₄ molecules ejected due to 15 keV Ga and C₆₀ projectiles are displayed in Fig. 3. The kinetic energy distributions are consistent with the picture in which more energetic processes are involved in ejection of organic molecules due to C₆₀ bombardment versus Ga bombardment. In addition, it is obvious that more strongly bound PS₄ molecules are ejected with higher kinetic energy. Recent measurements performed by Delcorte and collaborators show that the kinetic energy distribution of parent and parent-like molecular ions ejected from an overlayer of polystyrene oligomers is indeed broader when using 15 keV C₆₀ instead of Ga as primary ions [15].

4. Conclusions

The presented data indicate that there is no gain in application of C₆₀ projectiles in chemical analysis of both benzene and PS₄ thin overlayers. Although emission of substrate particles is significantly enhanced, there is little to no enhancement of the ejection of intact molecules and the mass spectrum contains more molecular fragments. This conclusion agrees with experimental observations reported by Kotter and Benninghoven of bombardment of thin polystyrene layers [4]. Several factors can be responsible for such behavior. First, in weakly bound thin organic layers there is a limited number of physisorbed organic molecules available for desorption and the processes taking place after Ga and C₆₀ impact are energetic enough to desorb most of the adsorbed molecules. In addition, in these systems the impact of the C₆₀ projectile generates a pressure wave that propagates in the organic overlayer pushing the molecules away from the point of impact. As a result, these molecules avoid collisions with ejecting substrate particles and are unable to eject. The same phenomenon is not observed for more strongly bound PS₄. In this case, however, the fragmentation of large molecules plays a significant role in reducing the efficiency of molecular ejection. We find that almost half of all removed PS₄ molecules are fragmented.

Acknowledgments

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