Molecular dynamics simulations of sputtering of organic overlayers by slow, large clusters

L. Rzeznik [a], B. Czerwinski [a], B.J. Garrison [b], N. Winograd [b], Z. Postawa [a,*]

[a] Jagiellonian University, Smoluchowski Institute of Physics, ul. Reymonta 4, 30-059 Kraków, Poland
[b] 104 Chemistry Building, Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

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The ion-stimulated desorption of organic molecules by impact of large and slow clusters is examined using molecular dynamics (MDs) computer simulations. The investigated system, represented by a monolayer of benzene deposited on Ag{1 1 1}, is irradiated with projectiles composed of thousands of noble gas atoms having a kinetic energy of 0.1–20 eV/atom. The sputtering yield of molecular species and the kinetic energy distributions are analyzed and compared to the results obtain for PS4 overlayer. The simulations demonstrate quite clearly that the physics of ejection by large and slow clusters is distinct from the ejection events stimulated by the popular SIMS clusters, like C_{60}, Au_3 and SF_5 at tens of keV energies.

1. Introduction

Desorption stimulated 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 [2–7]. Much less is known about processes initiated in organic systems by large cluster impact. In pioneering experiments with massive glycerol clusters Mahoney et al. have shown that desorption of large peptide and protein ions is possible [8].

Almost all atomistic modeling of large cluster bombardment have been done on inorganic samples [9,10]. In our recent study, we have investigated the mechanism of molecular desorption from a monolayer of sec-butyl-terminated polystyrene tetramer (PS4) molecules by impact of large and slow Ar clusters [11]. It has been found that the physics of ejection by these projectiles is distinct from the ejection events stimulated by small cluster. The ejection of majority of intact molecules is initiated by direct interactions between the molecules and backreflected projectile atoms,

provided that these atoms have sufficient lateral component of momentum [11].

The PS4 overlayer is formed of large molecules that are strongly bound to the metal substrate. In this study, we would like to investigate the effect of the projectile's kinetic energy on the molecular ejection efficiency and the kinetic energy distributions of molecules ejected from overlayer that is weakly bound to the substrate. A monolayer of benzene molecules is used and bombarded by the Ar_{2953} projectile with a kinetic energy from 0.1 eV/atom up to 20 eV/atom.

2. Model

Molecular dynamics computer simulations used to model particle bombardment are described elsewhere [12]. 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 pair-wise additive and many-body potential energy functions. The Ag–Ag interactions are described by the MD/MC-CEM potential for fcc metals [13]. The adaptive intermolecular potential, AIREBO is used to describe the hydrocarbon interactions (C–C and C–H) [14]. The interaction between Ar atoms as well as interactions between Ar and Ag atoms is described by a Lennard–Jones potential splined with KrC potential to properly describe high-energy collisions [15]. Finally, the interaction of C and H atoms with Ag atoms is described by a Lennard–Jones potential using established parameters [4].

The model approximating the Ag{1 1 1} substrate consists of 611,442 atoms arranged in 39 layers of 15,678 atoms each. The

* Corresponding author.
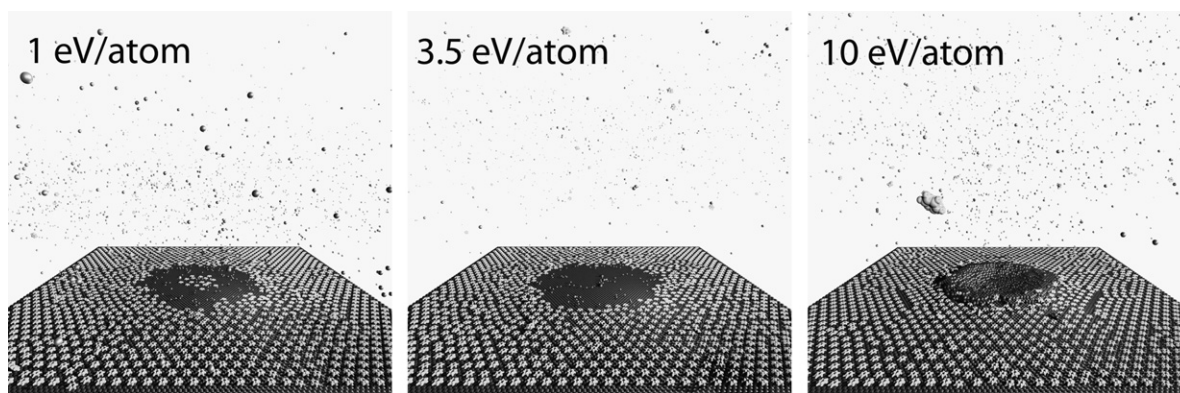 E-mail address: zp@castor.if.uj.edu.pl (Z. Postawa).

Fig. 1. Snapshots of the $C_6H_6/Ag\{1\,1\,1\}$ system at 36 ps after Ar_{2953} impact.

sample size 337 Å × 334 Å × 90 Å was chosen to minimize edge effects associated with the dynamical events leading to ejection of particles. Organic overlayers were represented by a monolayer of benzene molecules deposited on the surface of the Ag crystal. The system contains 1634 benzene molecules adsorbed in 3 × 3 arrangement. The Ar_{2953} projectile was directed normal to the surface with the kinetic energy between 0.1 and 20 eV/atom. A special care was taken to eliminate artifacts associated with a possible backreflection of a pressure wave generated by impact of such massive clusters and to take into account the process of molecular fragmentation on the way to detector, as described in Refs. [16] and [4,11], respectively. Since it is known that statistical accuracy increases with cluster size [4,16], three trajectories were calculated for most impacts. A total of 26 trajectories were calculated in cases where kinetic energy spectra were evaluated. More details about our computational system can be found in Refs. [4,11].

3. Results and discussion

Snapshots of the $C_6H_6/Ag\{1\,1\,1\}$ system taken at 36 ps after impact of Ar_{2953} projectiles with kinetic energy of 1, 3.5 and 10 eV/atom are shown in Fig. 1. A significant portion of the benzene overlayer is altered upon the impact of each projectile. At 10 eV/atom, most of the primary energy is deposited in a shallow volume of the metal substrate leading to a massive damage and ejection of many particles. A large hemispherical crater is formed in the substrate. The physics of the crater formation and molecular ejection is the same as for energetic small cluster bombardment [4,9]. In this paper, we focus on processes leading to molecular ejection initiated by projectiles with kinetic energy not sufficient to eject substrate atoms. Ejection of substrate particles strongly decreases when the kinetic energy of the projectile is reduced. Surprisingly, emission of benzene molecules is much less influenced by a decrease of the primary kinetic energy. A shown in Fig. 1, at 3.5 eV/atom, Ag atoms are not emitted and the substrate is virtually intact. At the same time, many benzene molecules are still visible in the flux of ejected particles. These molecules are removed from a circular surface area. As the energy goes down further, emission of molecules decreases. It is interesting to note that at 1 eV/atom C_6H_6 molecules are not ejected from the area where the density of deposited energy is the largest, and that the ejection zone changes from a circular into a ring-like area.

The dependence of the sputtering yield on the initial kinetic energy is shown in Fig. 2. As the kinetic energy exceeds a threshold of 0.15 eV/atom, the ejection of intact C_6H_6 molecules is initiated and the yield steeply increases with the kinetic energy. At higher

kinetic energy, the yield saturates while the ejection of molecular fragments and substrate atoms initiates. While the ejection of molecular fragments also saturates around 15 eV/atom, the sputtering yield of substrate atoms increases almost linearly with the primary kinetic energy above the energy threshold of approximately 10 eV/atom.

The ejection process is very efficient. As shown in Fig. 2, 15 keV Ar2953 (∼5eV/atom) cluster leads to emission of 157 C_6H_6 molecules. By comparison, 46 molecules are uplifted by a 15-keV C_{60} and there is a significant molecular fragmentation [5]. 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, provided that a low-energy ionization mechanism can be secured. In particular, analysis of thin organic overlayers could benefit from large cluster projectiles, since application of small clusters is not effective at enhancing the yield when compared to atomic projectiles [1].

Angle-integrated kinetic energy distributions of C_6H_6 molecules ejected by 2.95 and 15 keV Ar_{2953} projectiles are shown in Fig. 3. The spectrum for 15 keV Ar_{2953} is quite different from the distribution obtained for 15 keV C_{60} bombardment [5]. Several peaks (marked by arrows) can be identified in the spectrum induced by Ar cluster and the spectrum extends to much larger kinetic energies [5]. The shape of the spectrum depends on the projectile kinetic energy. When the kinetic energy is decreased from 5 to 1 eV/atom, the high-energy peaks shift towards lower kinetic energy and the intensity of the low-energy peak around 0.15 eV is drastically reduced. Such unusual behavior occurs
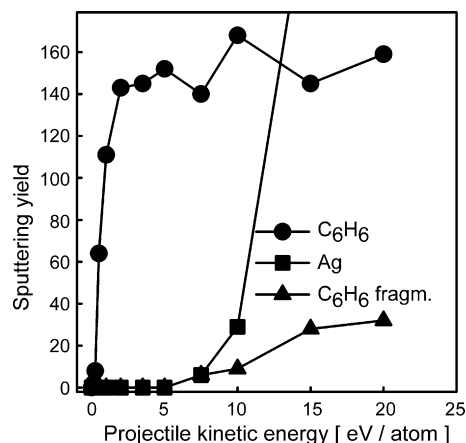

Fig. 2. Dependence of the total sputtering yield of silver atoms, fragmented and intact C_6H_6 molecules on the kinetic energy of Ar_{2953}.
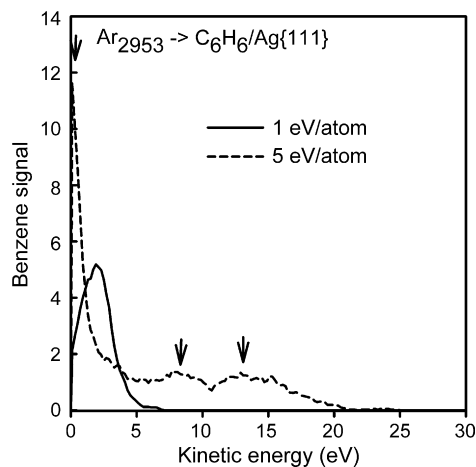
Fig. 3. Angle-integrated kinetic energy distribution of C_6H_6 molecules ejected by Ar_{2953} projectiles with kinetic energy 1 and 5 eV/atom.

because two different mechanisms are responsible for ejection of low- and high-energy molecules [11]. The high-energy molecules are ejected by direct interaction with backreflected Ar atoms and the velocity of ejected molecules is proportional to the velocity of backreflected Ar atoms [11]. It is not surprising; therefore, that the kinetic energy of emitted molecules shifts towards lower values when the energy of projectile atoms decreases.

The disappearance of the low-energy peak is a consequence of the fact that ejection of these molecules is stimulated by a recovery of the substrate deformed during large projectile impact [11]. Recovering substrate plays a role of a trampoline gently uplifting the molecules into the vacuum [11]. Ejection of benzene molecules by collective surface deformations was also predicted by Webb et al. for low-energy C_{60} projectiles [3]. In this case, however, deformation of the metal substrate is very small and benzene molecules were ejected by interaction with surface acoustic waves. In our case, this process is overshadowed by ejection initiated by a surface recovery. The amount of the substrate deformation will decrease when the primary energy is reduced. As a result, the ejection of low-energy molecules will also diminish.

Finally, we would like to relate current results to the data obtained on PS4 system to shed some light on the effect of the mass and the binding energy of the molecule [11]. PS4 molecules are larger than C_6H_6 molecules and are more strongly bound to the surface (binding energy ~0.4 eV for benzene and ~2.1 eV for PS4). In general, the calculated characteristics of molecular ejection are similar in both systems. However, the ejection of benzene molecules is more efficient. Especially, the low-energy ejection channel is stronger for benzene, which can be attributed to a lower binding energy of this system. Benzene molecules are also ejected with lower average kinetic energy than PS4. Both lower binding energy and a smaller mass of benzene is responsible for this difference.

4. Conclusions

The processes of molecular ejection from a monolayer of benzene adsorbed on Ag{1 1 1} substrate stimulated by Ar_{2953} with kinetic energies from 0.1 to 20 eV/atom were investigated. It is found that below a critical primary kinetic energy, the emission characteristics are distinctly different from these stimulated by atomic and small cluster impacts. The emission of intact, organic molecules is very efficient even if no substrate atoms are ejected. A significant number of molecules is ejected with unexpectedly high kinetic energy. The yield increases strongly with the primary kinetic energy above certain threshold energy and then saturates. The kinetic energy distributions of benzene shift towards larger kinetic energy as the energy of a projectile increases. The results can be interpreted by a desorption model in which the ejection of high-energy intact molecules is initiated by direct interactions between organic molecules and projectile atoms, provided that these atoms have sufficient lateral component of momentum [11]. Low-energy molecules are ejected by a concerted trampoline-like action of recovering substrate [11]. Both these processes are sensitive to projectile kinetic energy and surface binding energy.

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