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Sputtering of thin benzene films by large noble gas clusters

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ABSTRACT

Molecular dynamics computer simulations have been employed to investigate the sputtering process of a benzene (C_6H_6) monolayer deposited on Ag{1 1 1} induced by an impact of slow clusters composed of large number of noble gas atoms. The sputtering yield, surface modifications, and the kinetic energy distributions of ejected species have been analyzed as a function of the cluster size and the binding energy of benzene to the Ag substrate. It is shown that high- and low-energy components can be identified in the kinetic energy distributions of ejected molecules. The mechanistic analysis of calculated trajectories reveals that high-energy molecules are emitted by direct interaction with projectile atoms that are backreflected from the metal substrate. Most of the molecules are ejected by this process. Low-energy molecules are predominantly emitted by a recovering action of the substrate deformed by the impact of a massive cluster. The increase of the binding energy leads to attenuation of both high- and low-energy ejection channels. However, low-energy ejection is particularly sensitive to the variation of this parameter. The area of the molecular overlayer sputtered by the projectile impact is large and increases with the cluster size and the kinetic energy of the projectile. Also the size and the shape of this area are sensitive to the changes of the binding energy. The radius of the sputtered region decreases, and its shape changes from almost circular to a ring-like zone when the binding energy is increased. Some predictions about the perspectives of the application of large clusters in the organic secondary ion mass spectrometry are discussed.

1. Introduction

Cluster projectiles have become important probes in organic and biological secondary ion mass spectrometry (SIMS), since it has been found a few years ago that the sputtering process of certain organic samples can be significantly enhanced when a cluster projectile is used instead of an atomic projectile with the same incident energy [1]. Most of the current SIMS systems that rely on cluster projectiles to probe organic and biological samples concentrate on small clusters due to availability of such ion sources. However, although the advantages of such ion beams have been demonstrated for some thick organic samples, the application of these cluster projectiles in analysis of thin organic overlayers did not result in any improvement of recorded mass spectra [1]. Meanwhile, a novel approach to organic mass spectrometry has been proposed that utilizes large and slow cluster projectiles [2–5]. The results of these works have demonstrated that such cluster ions could be useful in stimulating desorption of intact organic species from both thick [2–4] and thin overlayers [3,6]. A rapid progress in experimental setups was not, however, accompanied by an adequate progress in theoretical understanding of the sputtering process initiated by such massive projectiles [7]. Furthermore, most of theoretical studies of large cluster bombardment have been done on inorganic samples [7]. The investigations of the processes initiated in organic systems are scarce.

Recently, we have modeled the sputtering process of organic monolayers formed from molecules that are strongly (sec-butyl-terminated polystyrene tetramer, PS4) [8] and weakly (benzene) [9] bound to the metal substrate. The emission was stimulated by an impact of large and slow Ar_n clusters. It has been found that molecular ejection is quite strong, and most of the intact molecules are ejected due to direct interactions with backreflected projectile atoms. The role of this process in the ejection of intact molecules is almost negligible during desorption stimulated by atomic projectiles [7,10] or small clusters [7,11]. In this study, molecular dynamics computer simulations are used to probe the effect of the binding energy on the efficiency of ejection, spatial distribution of the ejection sites, and the kinetic energy distributions of benzene molecules emitted by Ar_n ($n = 205–9000$) clusters with a constant kinetic energy per atom.

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2. Model

Details of molecular dynamics (MD) computer simulations used to model the sputtering process are described elsewhere [7]. Briefly, the motion of the particles is determined by integrating Hamilton's equations of motion. The interactions between the atoms in the system 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 [12]. The adaptive intermolecular potential, AIREBO is used to describe the hydrocarbon interactions (C–C, H–H and C–H) [13]. The interaction between Ar atoms as well as the interaction between Ar and Ag atoms is described by a Lennard–Jones potential splined with KrC potential to properly describe high-energy collisions. The interaction of C and H atoms with Ag atoms is described by a Lennard–Jones potential using established parameters [11]. Modification of these parameters allows us to change the binding energy of benzene molecules between 0.4 eV (the experimental value) and 4.0 eV.

The Ag{1 1 1} substrate consists of 611442 atoms, arranged in 39 layers of 15678 atoms each. The crystal size is $33.7 \times 33.4 \times 9.0$ nm. The size of the system was chosen to minimize edge effects which artificially influence the ejection process [14]. A monolayer of 1634 benzene molecules was adsorbed in 3×3 arrangement on the surface. The organic overlayer is irradiated at normal incidence by Ar_n ($n = 205$, 366, 872, 2953 and 9000) projectiles with the kinetic energy of 5 eV per atom. More details about our computational system can be found in Ref. [7–9].

3. Results and discussion

The dependence of the benzene sputtering yield on the projectile kinetic energy has been presented in our previous publication [9]. Briefly, due to a very low binding energy of benzene molecules even an impact of low-energy projectiles results in molecular ejection. For projectiles with kinetic energy below 6 eV/atom only intact benzene molecules are emitted from the surface, and the signal increases with the kinetic energy. As the energy exceeds approximately 6 eV/atom, the ejection of molecular fragments and substrate atoms is initiated. Above 10 eV, the emission of intact benzene molecules starts to saturate while ejection of substrate atoms becomes the dominant emission channel. The ejection process is very efficient. An impact of Ar_{2953} clusters with the kinetic energy of 1, 10 and 30 eV/atom leads to emission of 111, 166 and 232 benzene molecules, respectively.

When the primary kinetic energy per atom is constant, the sputtering yield increases with the size of the irradiating cluster as shown in Fig. 1 for projectiles with kinetic energy of 5 eV/atom. At 5 eV/atom only intact molecules are emitted. Both the dependence on the number of the projectile atoms (see Fig. 1(a)) and on the radius of the projectile (see Fig. 1(b)) are nonlinear. In particular, the dependence on the radius (r) can be fit with a following power formula $r^{1.8}$. This observation differs from the results found previously for more strongly bound monolayer of PS4 molecules, where a linear fit was found [8]. This discrepancy can be attributed most probably to different shapes of sputtered areas. Benzene molecules are emitted from an almost circular region (see Fig. 2(a)), while a ring-like ejection zone is reported for PS4 [8].

There are two factors that differentiate these two molecular systems. One factor is the size of the individual molecule, and the other factor is the binding energy of the molecule to the metal substrate. Benzene molecules are smaller and are more loosely bound to the substrate than PS4 molecules. These observations indicate that a primary beam composed of the largest available clusters should be used to probe organic overlayers. Bombardment by a larger cluster results also in a larger number of Ar atoms having a chance to collectively interact with the organic molecule. The cumulative action of a larger number of projectile atoms should, in turn, allow uplifting larger molecules. As a result, application of such projectiles could potentially allow detection of higher molecular weight molecules. Another potentially positive feature of large cluster ion beams is the ability to collect spectra without fragments. This ability could in some cases simplify the procedure of chemical identification of analyzed material. However, if the presence of specific fragments is necessary to accomplish more elaborate chemical identification, it can be achieved by a simple increase of the kinetic energy of the primary beam [8].

To investigate the role of the binding energy we have artificially modified the parameters of the interaction potential used to describe hydrocarbon–metal interactions. We start with investigation of the effect of the binding energy on the area from where the molecules are emitted. The dependence of the original positions of the ejected benzene molecules on the binding energy is shown in Fig. 2 for 15 keV Ar_{2953} projectile. The molecules are colored according to their final kinetic energy. The most energetic molecules are ejected from the area located just outside the circumference of the projectile. The molecules ejected with the lowest kinetic energy originate from the area located at the outskirts of the ejection region and from the region located directly below the impacting projectile. In our previous studies on PS4

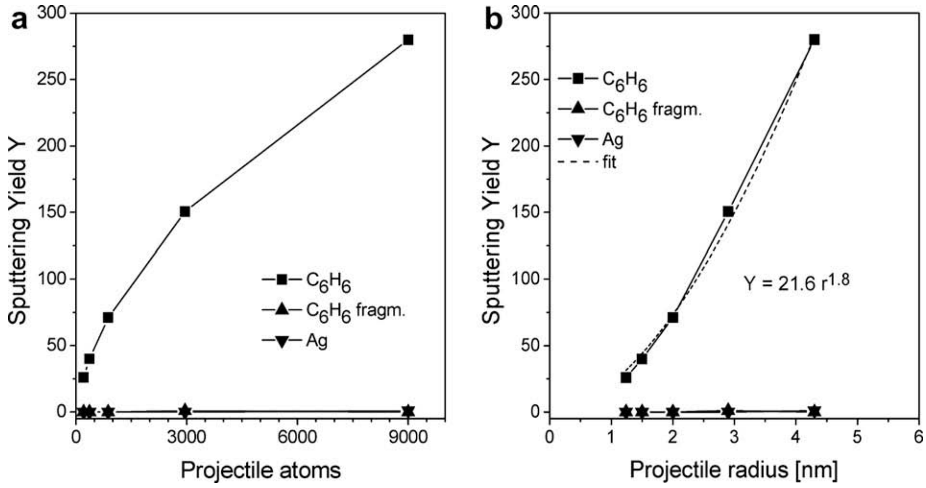

Fig. 1. Dependence of the sputtering yield of silver atoms, fragmented and intact C_6H_6 molecules on: (a) the number of atoms in the projectile, and (b) the projectile radius for projectiles with kinetic energy of 5 eV/atom. The broken line depicts a fit of the power function to the calculated data.

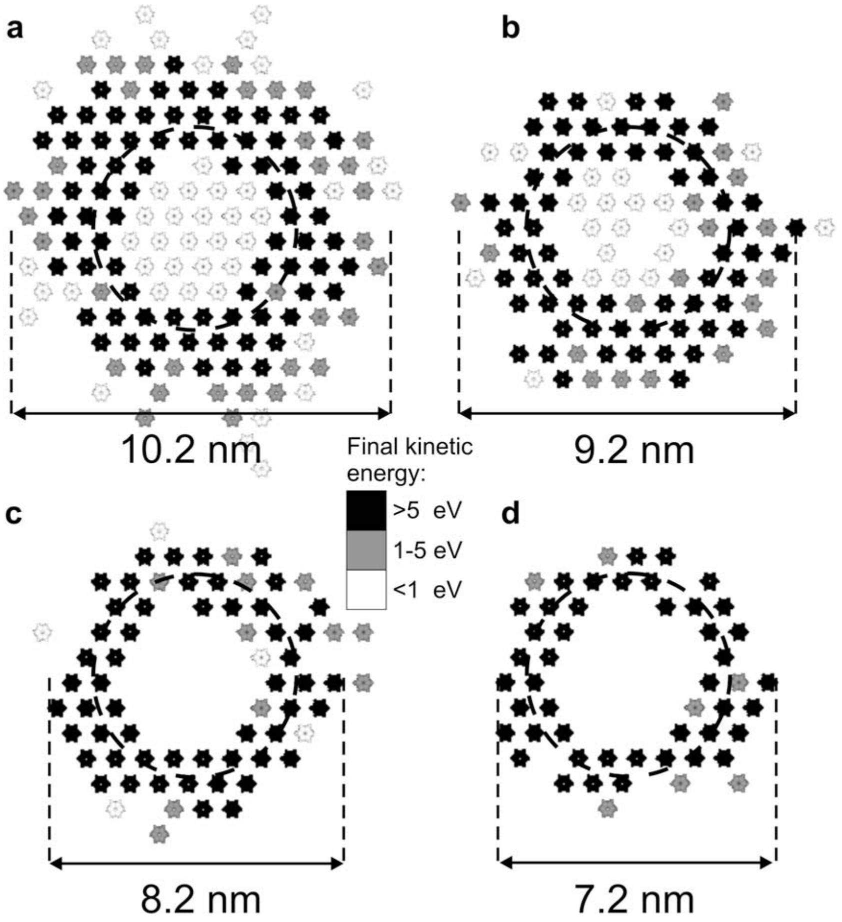

Fig. 2. Initial locations of emitted benzene molecules on the binding energy: 0.4 eV (a); 0.8 eV (b); 1.2 eV (c) and 2.1 eV (d). The molecules ejected by 15 keV Ar_{2953} are colored by their final kinetic energy (0–1 eV: white; 1–5 eV: gray; over 5 eV: black). The projectile circumference is drawn as a dashed line.

molecules we have found that two different mechanisms are responsible for the ejection of molecules from these two areas [8]. The molecules originally located outside the impacting cluster are emitted by direct interaction with backreflected projectile atoms, while low-energy molecules located below the cluster are casted into the vacuum by a recovering action of the substrate deformed by the impact of a massive cluster [8]. The same scenario is also present for benzene. It is evident from Fig. 2 that the variation of the binding energy influences both these processes. As the binding energy increases, the ejection area becomes smaller and transforms from a circular to a ring-like shape [8]. This observation proves that the ring-like shape of the sputtered area observed for PS4 molecules can be entirely attributed to the larger binding energy of these molecules. It is interesting to note that at 1.2 eV, the ejection of benzene molecules stimulated by surface recovery is not present, while some molecular ejection is still observed at analogous conditions for PS4 molecules [8]. It seems that a difference in size of these two molecules is now important. A small molecule has its binding area more localized, and its ejection will be more prone to be blocked by a stronger binding.

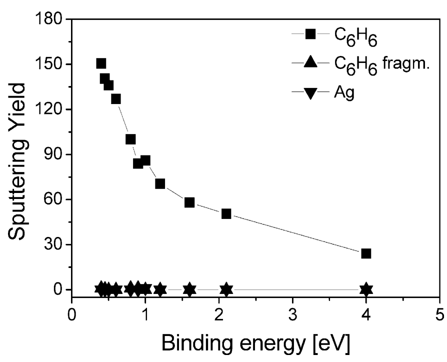

Fig. 3. The dependence of the sputtering yield of intact and fragmented C_6H_6 molecules, and silver atoms on the binding energy of benzene molecules for 15 keV Ar_{2953} cluster.

The reduction of the area of the ejection region indicates that the sputtering yield will also be influenced by the molecular binding energy. Indeed, as shown in Fig. 3, the sputtering yield of intact molecules decreases with the binding energy. In fact, two separate regimes can be identified. At low binding energy, the decrease is fast while only modest changes occur at binding energies above 1.2 eV. As shown in Fig. 2, the same binding energy terminates the ejection of low-energy molecules initially located below the impinging cluster. It is justifiable, therefore, to assume that a steep decrease of molecular emission observed at low binding energy is caused predominantly by the attenuation of the ejection of these molecules. To further test this hypothesis, the kinetic energy distributions are calculated for several binding energies. The results are presented in Fig. 4. As the binding energy increases, the intensity of both low- and high-energy peaks is reduced. However, it is evident that the low-energy peak is much more sensitive to the binding energy. While the modification of the binding energy from 0.4 eV to 2.1 eV results in a reduction of the high-energy peak intensity by

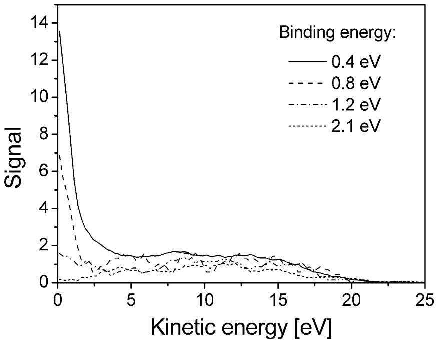

Fig. 4. The dependence of the kinetic energy distributions of benzene molecules sputtered by 15 keV Ar$_{2953}$ on the binding energy.

only 50%, the low-energy peak is entirely eliminated from the spectrum. This observation, indeed, supports the hypothesis that a fast decay observed in Fig. 3 occurs due to modification of a low-energy ejection channel.

4. Conclusions

The role of the binding energy and the projectile size in the sputtering of benzene molecules adsorbed on Ag{1 1 1} substrate stimulated by Ar$_n$ cluster impact with kinetic energy of 5 eV/atom is investigated. It is found that the ejection is efficient and increases with the projectile size having a constant value of kinetic energy per atom. As strong signal is always beneficiary factor for SIMS applications, this indicates that the largest projectiles should be used in chemical analysis. The yield decreases with the binding energy of the sample, and two separate regimes can be identified. In the first regime, the decrease is strong, while in the second regime the yield decreases only moderately with the increase of the binding energy. Each of these regimes can be correlated with the attenuation of ejection of low- and high-energy molecules, respectively. The area sputtered by the projectile impact is large and increases with the cluster size and the kinetic energy of the projectile. The size and shape of the sputtered zone is sensitive to the change of the binding energy. The radius of this area decreases, and its shape changes from almost circular to a ring-like region when the binding is increased. The kinetic energies of ejected molecules are also influenced by the binding energy. However, the ejection of the low-energy molecules is altered the most. When the binding energy reaches 1.2 eV, a low-energy component disappears from the kinetic energy spectrum, as the concerted action of recovering substrate is not sufficient to eject benzene molecules.

Acknowledgments

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