Organic mass spectrometry with low-energy projectiles

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Abstract

Molecular dynamics computer simulations have been employed to elucidate mechanisms responsible for uplifting of a monolayer of benzene and polystyrene molecules adsorbed on Ag{1 1 1} by low-energy atomic and cluster Ar projectiles. The sputtering yield and mass distributions of ejected particles are analyzed depending on the type and the kinetic energy of a projectile. It is shown that the relative contribution of intact molecules can be greatly enhanced if the kinetic energy of atomic projectile is reduced below 60 eV. At these energies, however, the efficiency of desorption is low and the ejection process is limited only to loosely bound molecules. Much better results can be obtained for cluster projectiles containing hundreds of Ar atoms with the incident energy of a few eV per atom. The impact of such particles leads to a gentle and very efficient removal of intact organic molecules originally adsorbed at the surface.
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1. Introduction

Energetic ion beams have become important processing and characterizing tools for a broad segment of the scientific and technological manufacturing sector. In particular, one of the most sensitive surface analysis techniques relies on uplifting and analysis of the neutral and ionized surface material by an impact of energetic projectiles. Secondary ion mass spectrometry (SIMS) and secondary neutral mass spectrometry (SNMS) were found to be particularly useful in chemical analysis of organic and biological systems. One of the goals of these techniques is to establish experimental conditions which will enable to efficiently collect mass spectra containing only the peaks representing nonfragmented molecules residing at the investigated surfaces.

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. It has been demonstrated recently that cluster ion beams are valuable sources for desorption of high mass ions in time-of-flight SIMS (TOF-SIMS) experiments [1,2]. A particularly interesting group of candidates for projectiles for mass spectrometry are clusters composed of thousands of noble gas atoms. Such clusters can be produced by a supersonic expansion of gas through a nozzle [3]. It has been shown that these projectiles have unique features and can be used in surface smoothing, high-resolution depth analysis or shallow implantation of inorganic samples [4].

In this paper, a monolayer of benzene and polystyrene tetramer molecules irradiated by low-energy Ar atomic and large Ar cluster projectiles is used to investigate mechanism of molecular ejection and to test the most favorable experimental conditions that would lead to the efficient ejection of nonfragmented organic molecules.

2. Model

Molecular dynamics (MD) computer simulations have been used to elucidate the mechanism of molecular

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desorption. The details of simulations can be found elsewhere [5]. 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 MD/Monte Carlo corrected effective medium (MD/MC-CEM) potential for FCC metals [6]. The interactions with the impinging Ar atom are described using the purely repulsive KrC potential [7]. The adaptive intermolecular potential, AIREBO, developed by Stuart and coworkers is used to describe the hydrocarbon interactions [8]. The interaction of C and H atoms with Ag is described by a Lennard-Jones potential [9,10]. The same potential with different parameters, splined at high energy with KrC potential is used to describe interaction between Ar atoms in the cluster projectile [7,11].

Two model crystallites are used to represent investigated systems. A small model approximating the Ag{1 1 1} substrate consisting of 2160 atoms arranged in 9 layers is used for low energy atomic projectiles, while a much larger microcrystallite containing 166,530 atoms arranged in 39 layers is used for cluster projectiles. Organic overlayers are represented by a monolayer of benzene and a monolayer of sec-butyl-terminated polystyrene tetramers (PS4) adsorbed on Ag{1 1 1}. The adsorption scheme and the potential parameters for benzene and PS4 molecules were adopted from Refs. [9] and [10], respectively. 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 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 PS4 which is several times larger that the binding energy of the adsorbed benzene overlayer ($\sim$0.4 eV) [12].

The atoms in the target initially have zero velocity. The Ar_{2953} projectile was created by cutting off a spherical volume from the random Ar solid. The atoms in the cluster projectile initially have no velocity relative to the center of mass motion. The trajectory is terminated when the total energy of the most energetic particle remaining in the solid is less than 0.05 eV. The time of each trajectory ranges between 9 and 59 ps and depends on the type of primary projectile, its impact point and the manner in which the energy distributes within the solid. In all, 85 trajectories were calculated for Ar, while 5 trajectories were probed for A_{2953} projectile. Special care was taken to eliminate the artifacts associated with the pressure waves generated by the cluster impact as described in Ref. [13].

3. Results and discussion

3.1. Atomic projectile

The mass distributions of particles ejected from Ar-bombarded C_6H_6 monolayer are shown in Fig. 1. There are two trends visible in the data. The relative contribution of intact C_6H_6 molecules in the total flux of emitted organic material increases as the kinetic energy of Ar projectile is reduced from 100 to 25 eV. For instance, at 25 eV only intact C_6H_6 molecules are ejected from the surface. However, the gain in the mass spectrum quality occurs at the expense of a significant decrease of the sputtered signal. The sputtering yield at 25 eV is almost twice smaller than the yield at 100 eV and more than an order of magnitude smaller than the yield collected at 4 keV Ar bombardment [14].

Visual inspection of sputtering animations leads to the conclusion that two distinct mechanisms are responsible for removal of C_6H_6 molecules by low-energy projectiles as shown in Fig. 2. First, the primary projectile can hit the adsorbed molecule directly. At very low kinetic energy the energy transfer is not sufficient to fragment the molecule but can be large enough to stimulate ejection. However, as the kinetic energy of the projectile increases, the energy transfer between the projectile and the part of the molecule becomes too large to be accommodated by internal motions, and the molecular fragmentation becomes important. Benzene molecules can be also removed when hit from behind by Ar projectile that bounced from the surface. As shown in Fig. 1, almost all Ar atoms are back-reflected into the vacuum. Some of these atoms bounce at oblique angles and can collide with the adsorbed molecule located in the vicinity of the primary point of impact.

Molecular ejection by collisions with projectiles can be efficient only for organic molecules that are loosely bound with the substrate. As the binding energy increases, more and more energy is required to uplift the molecule. As the collision process is spatially and temporally localized, the energy imparted to the fragment of the molecule cannot be efficiently accommodated and converted into the center of mass motion of an intact molecule, but rather leads to fragmentation. For this reason the total sputtering yield calculated for a more strongly bound PS4/Ag{1 1 1} system was 0.18 PS molecules for 100 eV Ar. At this energy we have observed ejection of barely 8 intact PS4 molecules (partial sputtering yield $\approx$0.1) within the investigated 85 trajectories. All these molecules were ejected after being repeatedly hit by a projectile that bounced from the substrate than hit the molecule at one location, bounce again and hit the molecule at least one more time at a different location. Bombardment with 50 eV Ar yielded a single ejection of PS4 molecule, while no intact molecules were ejected by 25 eV projectiles.

It is interesting to note that a relative contribution of nonfragmented C_6H_6 molecules as well as the total signal is much better for 4 keV Ar projectiles. From previous studies on monolayer C_6H_6/Ag{1 1 1} [9,14] and PS4/Ag{1 1 1} systems [10] it is known that at this kinetic energy molecules that are directly struck by the impinging projectile do fragment. Collisions between ejecting substrate atoms and the adsorbed molecules is a dominant process leading to emission of intact molecules.
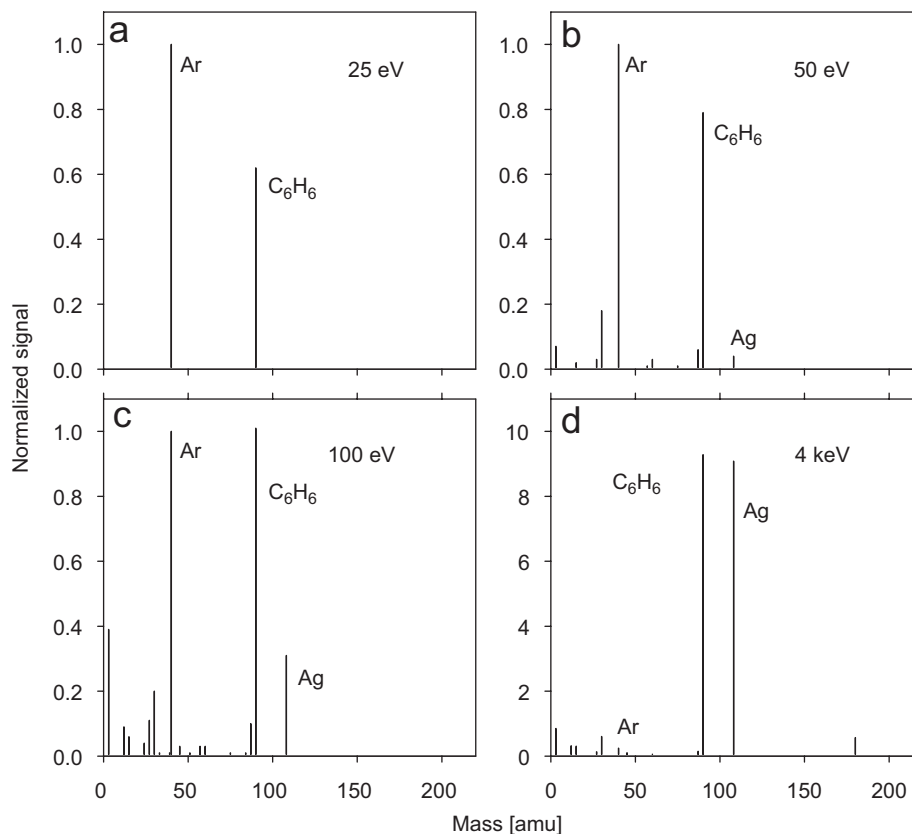
Fig 1. Mass distributions of particles ejected by bombardment of a benzene monolayer deposited at Ag{1 1 1} in 3 × 3 arrangement with Ar projectiles having primary kinetic energy: (a) 25, (b) 50, (c) 100 eV, and (d) 4 keV. The data were collected ~12 ps after the projectile impact.
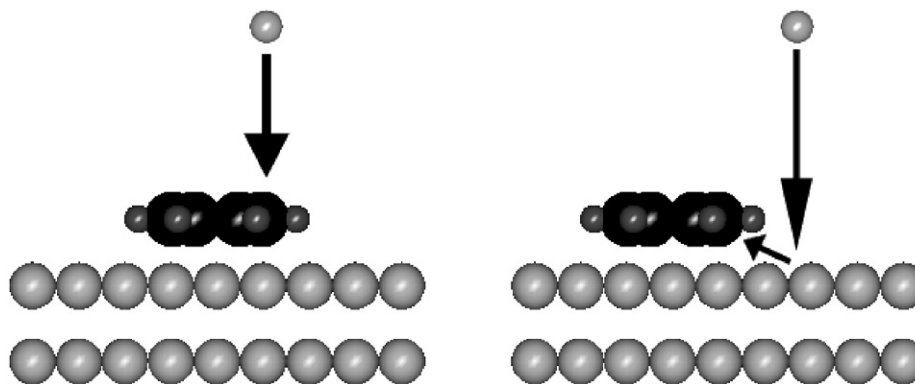

Fig. 2. A graphic representation of mechanisms leading to molecular ejection from thin organic overlayers adsorbed on metal substrates bombarded with low energy atomic projectiles.

3.2. Cluster projectiles

Snapshots of the temporal evolution of typical collision events leading to ejection of particles due to ~3 keV Ar_{2953} bombardment of PS4/Ag{1 1 1} system are shown in Fig. 3. Although the total kinetic energy of the projectile is relatively large, the energy carried by a single Ar atom composing a cluster is very low (1 eV/atom). As shown in Fig. 3 the cluster projectile decomposes immediately upon the impact and most of the Ar atoms bounce from the surface. Mechanism of molecular ejection by large Ar

cluster projectiles is quite different from the mechanisms occurring during atomic [9,10] or small-cluster bombardment [13]. The molecules are not removed by separate collisions but are entrained in a dense flux of low-energy backreflected Ar atoms. Due to a very low impact energy of an individual Ar atom, only organic molecules are removed and the metallic substrate is not altered by the projectile. The sputtering yields of intact, fragmented PS4 molecules and the substrate atoms are shown in Fig. 4 as a function of the projectile's kinetic energy. It is visible that the most favorable sputtering conditions are achieved at 5 eV/atom
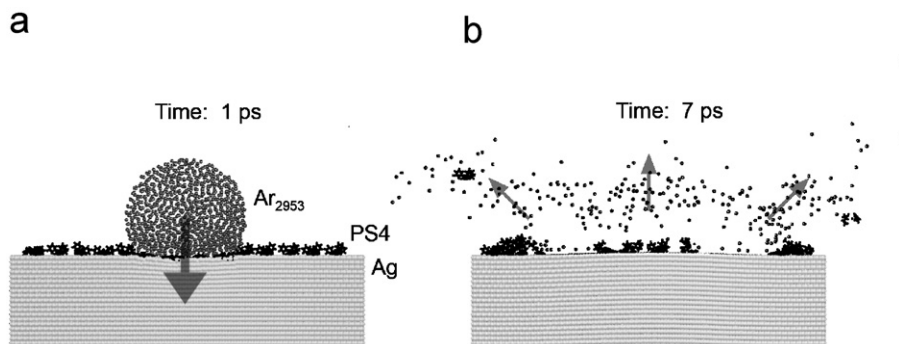
Fig. 3. A cross-sectional view of the temporal evolution of collisions stimulated by an impact of 3 keV Ar_{2953} cluster at PS4/Ag{1 1 1} system at normal incidence. A slice 0.7 nm wide of the system centered at the impact point is shown. Arrows depict the most preferred directions of Ar movement 7 ps after Ar_{2953} impact on the Ag{1 1 1} surface.
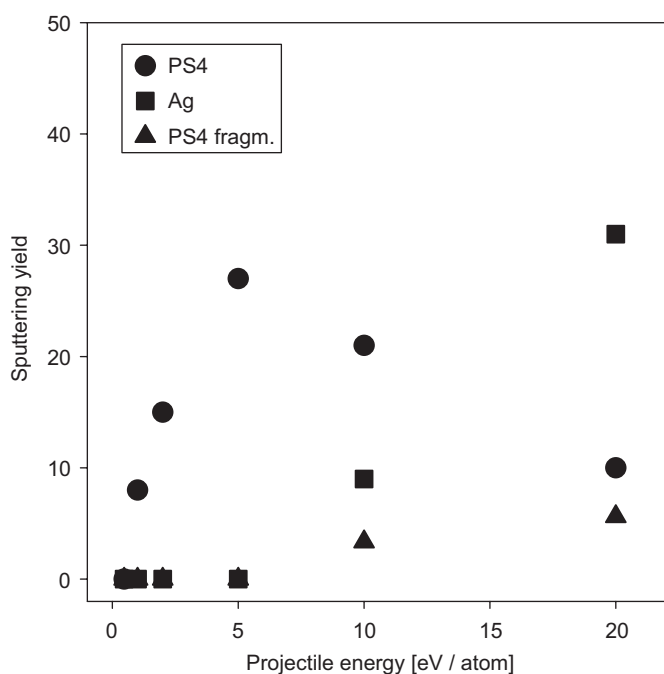

Fig. 4. Dependence of the sputtering yield of intact (circles), fragmented (squares) PS4 molecules and substrate atoms (triangle) on the kinetic energy of the Ar_{2953} projectile. To calculate the sputtering yield of fragmented molecules the mass of all fragments has been added and divided by a mass of a complete PS4 molecule.

($\sim$15 keV). At this energy the sputtering yield of intact molecules is the largest, while the molecular fragmentation and the substrate erosion are still not present. Molecular fragmentation and surface erosion begins to occur at the energy of 10 eV/atom. However, even at this energy the surface damage is very limited.

4. Conclusions

Our calculations indicate that low-energy projectiles can, in principle, be used in the mass analysis of organic samples. The molecules are removed by direct collisions with impinging or backreflected projectiles. However, the analysis has to be limited to loosely bound organic systems

and the flux of projectiles has to be significant to compensate for a low sputtering yield. In addition, one should keep in mind that lowering of the primary energy will lead to a more severe decrease in the yield of secondary ions than neutrals. Therefore, an additional ionization technique or some alternative detection schemes may be necessary which will complicate the experimental arrangement. For these reasons, bombardment with more energetic keV Ar projectiles seems to be a better choice.

Much better results can be obtained with large noble-gas cluster projectiles having a low kinetic energy per atom. With an appropriate selection of this parameter one is able to obtain efficient ejection of intact organic molecules, which are entrained in a flux of backreflected Ar atoms and gently removed from the surface. In this case, the analysis does not have to be limited to the molecules that are loosely bound to the surface.

Acknowledgments

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