



# Sputtering simulations of organic overlayers on metal substrates by monoatomic and clusters projectiles

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## Abstract

This paper reviews our recent work on computer simulations of monoatomic and cluster bombardment of metal and organic surfaces. The investigated surfaces are irradiated with keV monoatomic (C, Ar, Ga) and polyatomic ( $C_{60}$ ) projectiles that are recognized as valuable sources for desorption of high mass particles in secondary ion and neutral mass spectrometry (SIMS/SNMS) experiments. The analysis of the results reveals that the  $C_{60}$  ion beam enables to perform chemical imaging with higher sensitivity, better depth resolution, and lower contamination than monoatomic projectiles with similar kinetic energy. For monoatomic projectiles, the development of a linear collision cascade is the predominant mechanism responsible for the ejection of particles. In contrast, strongly nonlinear, collective processes occur during  $C_{60}$  bombardment. These nonlinear processes lead to the enhanced removal of material and the formation of a macroscopic crater. This paper presents theoretical insight into possible mechanisms responsible for the observed behavior with the emphasis on the phenomena important to the SIMS/SNMS community.

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## 1. Introduction

Cluster ion beams are recognized as valuable sources for desorption of high mass ions in secondary ion mass spectrometry (SIMS) experiments [1–9]. Their use received a boost about 5 years ago when an  $SF_5^+$  ion source was introduced commercially [10]. There have recently been reports of two additional cluster beam sources that overcome lateral resolution and lifetime issues. Both of these sources utilize liquid metal ion gun technology to produce  $Au_3^+$  [11] and  $C_{60}$  ion beams [12,13]. Results from experiments done with these ion sources are quite promising [4,14–20].

For instance, the yield of the peptide gramicidin is enhanced by a factor of 1300 during  $C_{60}$  impact as compared to  $Ga^+$  ion bombardment [12].

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 [9]. For example, 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 [9]. Theoretical calculations are beginning to unravel some of the phenomena responsible for cluster-induced sample erosion [21–28]. Molecular dynamics (MD) simulations of  $C_{60}$  impact with kinetic energies in the range of 10–20 keV on graphite [25,26] and

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diamond [27] show that a crater forms and that the energy is deposited in the near surface region. Calculations of small metal cluster bombardment in the same energy range predict similar crater formation on graphite and metal substrates [21–24]. At lower kinetic energies, it has been shown that the mass of the substrate is important in determining the mechanism of the enhancement effect [28].

In order to understand enhancement of signals in SIMS/SNMS experiments, we have initiated a comprehensive series of MD investigations aimed at understanding the collision cascades due to the keV  $C_{60}$  cluster versus the monoatomic projectile on a number of well-defined substrates and for various beam energies and incident angles [29–32].

## 2. Model details

The bombardment of a clean and benzene covered  $Ag\{111\}$  surface is modeled using molecular dynamics computer simulations. An extensive description of the MD scheme is available elsewhere [33]. In our system the forces among the atoms are described by a blend of empirical pair-wise additive and many-body potential energy functions [30]. Our model approximating the  $Ag\{111\}$  substrate consists of a finite microcrystallite containing 166,530 Ag atoms arranged in 39 layers of 4270 atoms each. The sample size ( $17.5\text{ nm} \times 17.45\text{ nm} \times 8.97\text{ nm}$ ) was chosen to minimize edge effects on the dynamical events leading to the ejection of particles. Organic overlayers were represented by one- and three-layer thick systems of benzene molecules deposited on the surface of the Ag crystal. More information about our model and other details of simulations can be found in [30].

## 3. Results and discussion

### 3.1. Elemental analysis

Cross sectional views of the temporal evolution of typical collision events leading to ejection of atoms due to 15 keV Ga and  $C_{60}$  bombardment are shown in Fig. 1. It is obvious that the nature of the energy deposition process is very different for these two

projectiles. The high-energy Ga projectile penetrates deeper into the crystal creating a damaged area that is cylindrical in shape whereas the  $C_{60}$  projectile creates a crater. As described also by Yamada and co-workers for  $C_{60}$  bombardment on diamond [27], the  $C_{60}$  projectile dissociates upon impact and most of the carbon atoms are backscattered into the vacuum. The impact leads to formation of numerous superimposing cascades that highly disorder a relatively shallow volume of the crystal below the surface in a very short time. This dense, liquid-like region closes off open channels so that individual carbon atoms cannot penetrate deep into the sample. As a consequence, a significant amount of the projectile's energy is deposited close to the surface, leading to the emission of many particles. In addition, immediately after the impact, pressure waves are generated in the bulk [30]. Both the ejection of atoms and the propagation of the pressure pulse are driving forces for a crater formation. The process of crater formation is almost macroscopic in nature and only weakly depends upon the initial impact point of the  $C_{60}$  molecule on the surface. As shown in Fig. 1 only a thin perimeter around each crater exhibit an appreciable amount of atomic rearrangement or mixing. The thickness of this region increases with the kinetic energy of the projectile [31]. Outside this region, the structure of the crystal is almost unaltered. The crater size increases with the kinetic energy of the  $C_{60}$  projectile [31]. However, the increase is greater in the lateral dimension, i.e. diameter, rather than the depth of the crater. For instance, for 5 and 15 keV  $C_{60}$  irradiation the diameter of the crater more than doubles while the depth increases barely by 30%. This phenomenon is fortunate for depth profiling because the increase of the  $C_{60}$  kinetic energy will result in substantial signal enhancement and only a minor decrease of the depth resolution.

A different type of movement is visible for 15 keV Ga. The monomer projectile penetrates much deeper into the crystal as compared to  $C_{60}$  bombardment and the damaged area has more cylindrical rather than hemispherical geometry. There is a significant amount of movement but it occurs deep under the surface. The movement leads to a creation of a large void in the crystal and a substantial volume where atoms are relocated and mixed [31]. As shown in Fig. 1, the extent of this volume is much larger for Ga than for  $C_{60}$  bombardment.

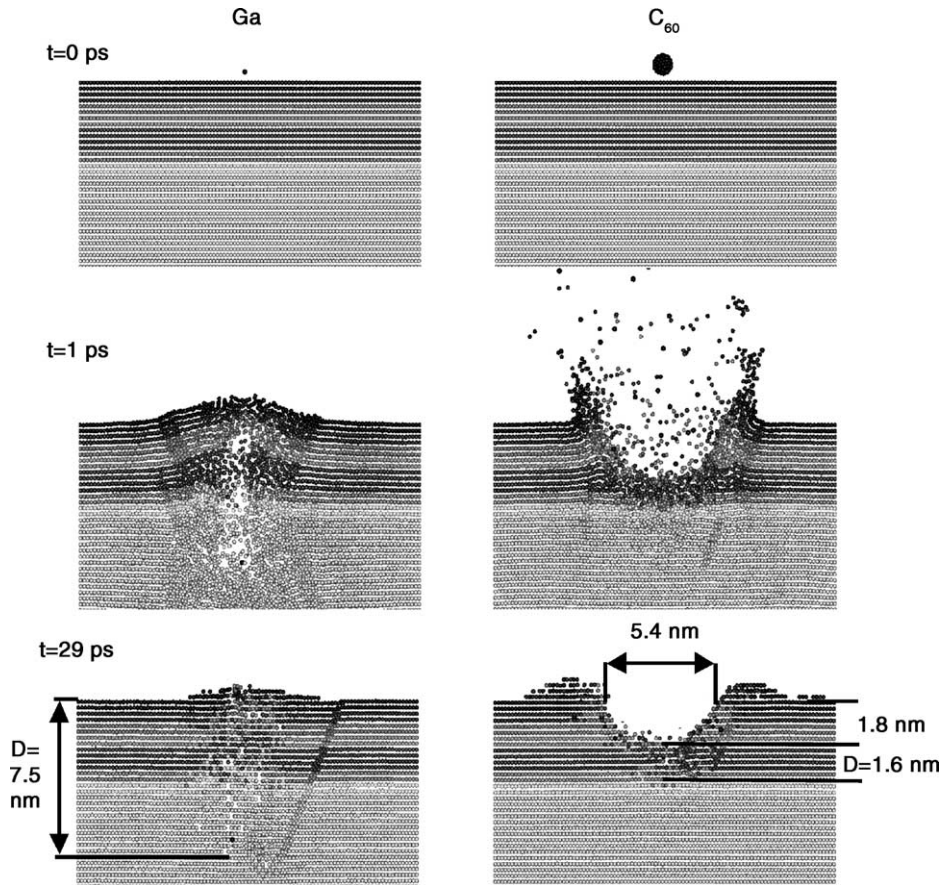


Fig. 1. A cross sectional view of the temporal evolution of a typical collision event leading to the ejection of atoms from Ag(111) surface due to 15 keV Ga and  $C_{60}$  bombardment at normal incidence. D denotes maximum, at which mixed volume is observed.

The  $C_{60}$  projectile has several advantages over Ga that should allow for better depth resolution in the SIMS/SNMS analysis in experiments where spatial imaging is also required. First, the  $C_{60}$  ion beam can be focused to a small spot [13]. Second, to obtain the same amount of material removal as with one  $C_{60}$  projectile, numerous Ga atoms must strike the same region of the target. As shown in Fig. 1, the mixing of layers due to the Ga atom bombardment extends to 20 or more layers so that by the time the particles are being ejected from, for example, the 12th layer, the chemical identity is significantly scrambled. Third, since the damage induced by  $C_{60}$  is limited to a region that appears to be smaller than the amount of material removed, it is conceivable that the next  $C_{60}$  impact will remove the entire damaged region below the crater as well as pristine material. Hence, the computer simula-

tions strongly suggest that yields from the bombarded surface will not appear much different from those of the pristine surface and that the degree of interlayer mixing will be dramatically reduced.

Calculations show that the total sputtering yield is approximately 16 times larger for 15 keV  $C_{60}$  as compared to 15 keV Ga bombardment [31]. The enhancement is different for various ejectees, and the processes initiated by  $C_{60}$  impacts favor more abundant ejection of larger clusters. A comparison with an accumulated sputtering yield of 60 separate C impacts having the same kinetic energy per atom as in 15 keV  $C_{60}$  cluster shows that the yield is non-additive and a strong nonlinearity occurs in the bombarded system. The amount of nonlinear enhancement increases with the kinetic energy of the projectile within investigated energy range (up to 20 keV).

It is a customary approach in the SIMS/SNMS analysis to increase the impact angle to enhance the sputtering yield and the depth resolution. We found that this approach is not suitable for  $C_{60}$  bombardment of heavy and dense samples. Calculations performed for 15 keV  $C_{60}$  bombardment of Ag{1 1 1} show that sputtering yield decreases as the incident angle becomes more off-normal, except for possibly  $15^\circ$  incidence. This observation differs from the data reported for monoatomic projectiles [34], where the sputtering yield increases up to a certain critical angle, usually around  $60^\circ$ , and then starts to decrease. Such behavior for atomic bombardment has been attributed to the increase of the amount of projectile's kinetic energy deposited in the subsurface region with the increase of the impact angle [34]. For sputtering initiated by  $C_{60}$  bombardment on Ag{1 1 1} at normal incidence most of the primary energy is deposited at the depth at which it can efficiently contribute to ejection. As a result, the ejection efficiency does not benefit from the increase of the impact angle. On the other hand, as the impact angle increases, more energy is reflected into the vacuum [31]. It seems that such unusual behavior will be characteristic to experiments in which a heavy and dense sample is bombarded by a cluster composed of light atoms. If the mass of the atoms composing a cluster is comparable or larger than the mass of the atoms composing the sample or the sample structure is more open, one can expect that the energy will be deposited at a larger depth and a cluster-induced sputtering yield versus incident angle should follow the trend observed for monoatomic projectiles.

Another aspect important for chemical analysis is the contamination induced by the primary beam in the analyzed sample. Also in this case computer simulations suggest that the analysis will benefit from application of  $C_{60}$  projectiles. Calculations show that on average five carbon atoms are implanted into Ag{1 1 1} sample by a single impact of 15 keV  $C_{60}$ . At the same time one Ga atom is buried into the sample. Comparison of these two numbers seems to favor Ga projectiles. However, one should keep in mind that the sputtering yield induced by  $C_{60}$  bombardment is 16 times larger than for Ga. This means that the effective contamination is almost two times lower for  $C_{60}$  because of the 16-fold lower dose is required to complete analysis.

### 3.2. Analysis of organic overlayers

Snapshots of the model system consisting of Ag{1 1 1} covered with three monolayers of benzene taken 13 ps after 15 keV Ga and 15 keV  $C_{60}$  impacts are shown in Fig. 2. As in the bare metal studies, a crater is formed in the metallic substrate by  $C_{60}$  impact because the organic layer is too thin to contain the energy of penetrating projectile. The size of the crater is, however, smaller than the one shown in Fig. 1. On average,  $C_{60}$  penetrates intact through the organic overlayer and does not fragment until it hits the metal substrate, imparting only a minor fraction of the primary energy directly into the overlayer. However, this energy is sufficient to stimulate a small amount of ejection of benzene molecules and fragments [29] and more importantly it leads to the formation of an almost planar pressure wave that propagates in the organic overlayer forcing the molecules to move away from point of impact. As a result, a secondary circular rim is formed from piled-up benzene molecules. A weaker pressure wave is also observed for Ga, but due to its much smaller size, the extend of layer modifications is less significant for this ion.

MD studies of processes leading to ejection of molecules from thin organic overlayers induced by monoatomic impacts show that molecules are ejected mainly due to collisions with departing substrate atoms [35,36]. As discussed in the previous section,  $C_{60}$  bombardment leads to a significant enhancement of silver particle emission. In addition, when compared to results obtained for Ga bombardment, the average kinetic energy of departing substrate atoms sputtered with  $C_{60}$  is lower [20,31], leading to gentler collisions with the molecules in the overlayer and, consequently, to the emission of cooler, more stable molecules [29]. Both these factors should promote more efficient emission of intact molecules. Surprisingly, we see only a modest enhancement of the benzene ejection yield. For 15 keV projectiles the yield of benzene is barely two times larger with  $C_{60}$  as compared to Ga. Moreover, a flux of  $C_{60}$ -sputtered particles contains more low-mass fragments. Both these observations are supported by results of experiments on cluster irradiation of monolayer organic systems [9,19].

A detailed analysis reveals that two processes are responsible for such behavior [32]. First, there is only

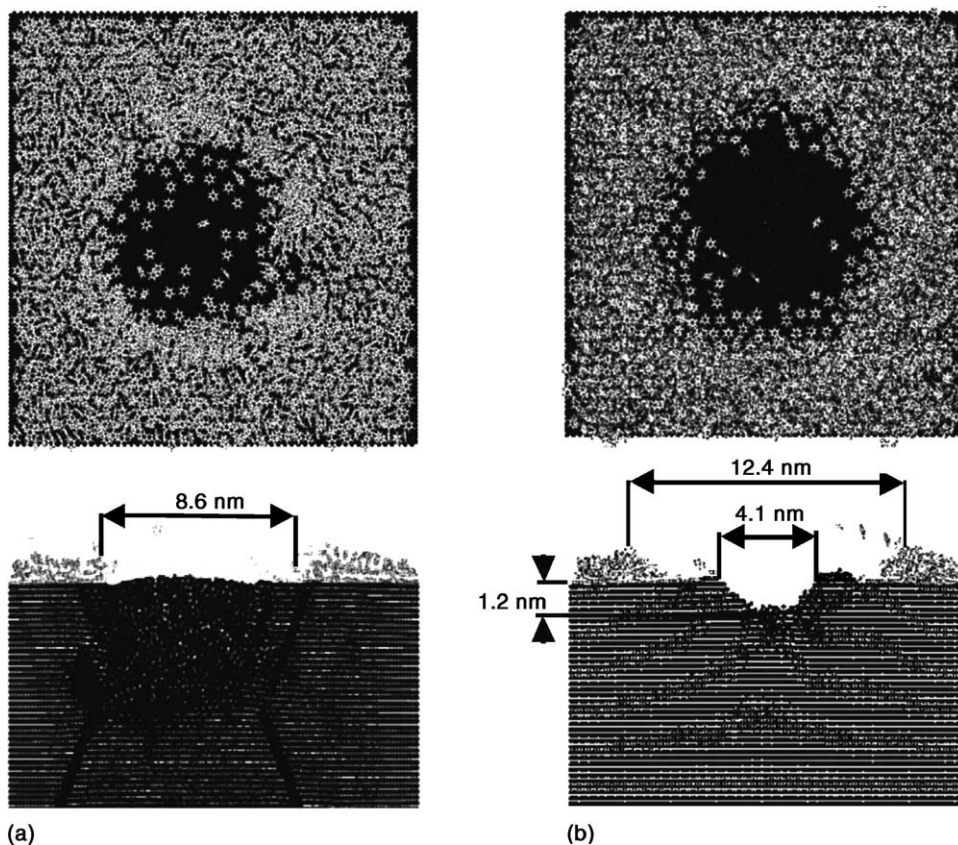


Fig. 2. Snapshots of the model system consisting of Ag[1 1 1] covered with three layers of benzene taken 13 ps after 15 keV (a) Ga and (b)  $C_{60}$  impact at normal incidence.

a limited number of molecules in the monolayer. As seen from Fig. 2 even impact of monoatomic projectile ejects benzene molecules from significant area. Furthermore, the impact of the large  $C_{60}$  projectile generates a pressure wave that propagates in the organic overlayer pushing molecules away from the point of impact. As a result, most of the ejecting substrate particles have nothing to collide with, and a much more abundant ejection of substrate atoms results in only a slightly more efficient molecular emission.

As shown in Fig. 3, intact molecules originate from a well-defined ring-like region close to the inside of the crater rim. Molecules located originally in this region are ejected by a catapult-like action of the unfolding crater [32]. Molecular fragments are ejected from the area closer to the impact point. Collisions with the large projectile and with the energetic back-

reflected carbons are mainly responsible for the formation of fragments. Most of these fragments are immediately ejected, however, some of them propagate in the organic layer leading to additional damage [29]. Direct interaction between the organic overlayer and the small Ga ion is less probable, which, consequently, results in the lower lateral damage to the thin organic overlayer and lower emission of molecular fragments.

Simultaneous interactions with numerous substrate atoms are required to stimulate uplifting of large organic molecules having multiple contact points with the surface [36]. The probability that monoatomic projectiles can generate a temporally and spatially correlated ejection of enough atoms to dislodge a large organic molecule decreases steeply as the number of these contact points increases. On the other hand, the concerted motion associated with

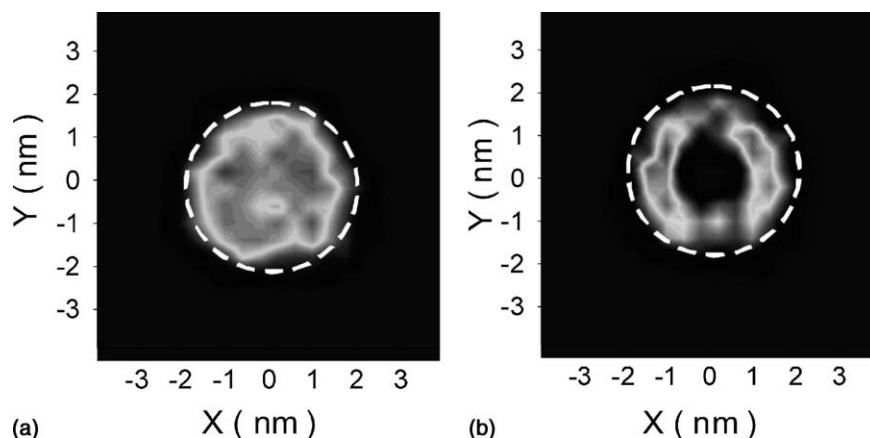


Fig. 3. Dependence of the desorption signal of (a) small molecular fragments ( $\text{CH}_2$  and below) and (b) benzene on the initial location of the benzene molecules on the  $\text{Ag}\{111\}$  surface relative to the point of impact of the 15 keV  $\text{C}_{60}$  projectile at normal incidence. The broken line depicts internal perimeter of the crater formed in the substrate.

the unfolding of the crater rim will accompany every cluster impact. This catapult-like action will eject even very large organic molecules that reside at the appropriate distance from the point of impact. One may expect, therefore, that an enhancement factor associated with the application of  $\text{C}_{60}$  versus a monoatomic projectile should be more spectacular for large organic molecules than for small ones.

Up to this point, the ejection of molecules from thin organic layers was discussed. Preliminary calculations on a thick benzene crystal indicate that the  $\text{C}_{60}$  projectiles penetrate deeper into the organic solid than into metal. As a result, a small volume of excited molecules and fragments is formed at a certain depth beneath that surface. This volume expands by the formation of an outgoing energetic pressure pulse which has a vertical component and leads to the ejection of a large amount of loosely bound organic material. As in the case of metal bombardment, the Ga projectile deposits its kinetic energy at a much larger depth than  $\text{C}_{60}$  on the benzene crystal. In fact, the difference in penetration depth between Ga and  $\text{C}_{60}$  is even larger in the  $\text{C}_6\text{H}_6$  crystal than in Ag. As a result, a larger difference in sputtering yield induced by  $\text{C}_{60}$  and Ga is expected. These simulations show additionally that the ratio of the removed to mixed material is again much better for  $\text{C}_{60}$ . Therefore, this projectile should enable to achieve a better depth resolution, which is indeed observed in experiments [17–19].

The data presented in this paper relate to the sputtering of thin organic overlayers composed of weakly interacting molecules. As the binding strength increases between the molecules and the substrate, one may expect to see a decrease of the ejection efficiency and an increase in the molecular fragmentation, as it is more difficult to eject the whole molecule. Finally a few comments should be made on the feasibility of the application of our results to SIMS data. Predictions such as: emission enhancement, creation of the crater, possibility to achieve better depth resolution, or lower effective sample contamination using keV primary ions of  $\text{C}_{60}$  rather than Ga are applicable to the study of both ions and neutrals. However, by no means should quantitative comparisons between emission enhancements of ions be inferred from this study. For this analysis, ionization and neutralization processes should be included into the model calculations. This is still an unresolved problem, although, some promising attempts are already being made [37].

#### 4. Conclusions

We have investigated sputtering of metal and organic substrates irradiated with keV monoatomic (C, Ar, Ga) and  $\text{C}_{60}$  projectiles. The results show that keV  $\text{C}_{60}$  projectiles have several advantages over monoatomic ions of similar kinetic energy. These projectiles enable us to achieve higher sensitivity,

better depth resolution, and lower contamination in SIMS/SNMS measurements as compared to monoatomic ions of similar kinetic energy. It has been shown that the modest enhancement observed in experiments with cluster bombardment of thin organic samples is limited by a small number of molecules available for ejection and by the generation of a pressure wave that pushes these molecules away from the area where they could be desorbed by collisions with departing substrate particles. There are some initial predictions that difference in the deposition depth of C<sub>60</sub> versus Ga and the generation of an intense pressure pulse from beneath the surface by the C<sub>60</sub> impact will result in a substantial increase of molecular ejection from a thick organic film. However, additional studies have to be made to confirm this supposition.

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