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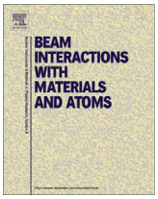

Damage analysis of benzene induced by keV fullerene bombardment

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ABSTRACT

Molecular dynamics computer simulations have been used to investigate the damage of a benzene crystal induced by 5 keV C_{20}, C_{60}, C_{120} and C_{180} fullerene bombardment. The sputtering yield, the mass distributions, and the depth distributions of ejected organic molecules are analyzed as a function of the size of the projectile. The results indicate that all impinging clusters lead to the creation of almost hemispherical craters, and the process of crater formation only slightly depends on the size of the fullerene projectile. The total sputtering yield as well as the efficiency of molecular fragmentation are the largest for 5 keV C_{20}, and decrease with the size of the projectile. Most of the molecules damaged by the projectile impact are ejected into the vacuum during cluster irradiation. Similar behavior does not occur during atomic bombardment where a large portion of fragmented benzene molecules remain inside the crystal after projectile impact. This "cleaning up" effect may explain why secondary ion mass spectrometry (SIMS) analysis of some organic samples with cluster projectiles can produce significantly less accumulated damage compared to analysis performed with atomic ion beams.

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 upon the uplifting of surface constituents by an impact of energetic projectiles followed by a mass analysis of the ionized (secondary ion mass spectrometry – SIMS) and neutral (secondary neutral mass spectrometry – SNMS) surface material. Both these techniques are found to be particularly useful in chemical analysis of organic and biological structures [1]. Cluster projectiles are especially interesting candidates for the surface probes in SIMS/SNMS as it has been found that the sputtering yield can be enhanced when an atomic projectile is replaced by a cluster ion with the same kinetic energy. Furthermore, it has been also observed that in some cases three-dimensional (3D) depth profiling of organic samples could be achieved with cluster ions even in so called dynamic conditions [2–4]. Such phenomenon has never been observed for atomic projectiles. According to these studies a few requirements have to be fulfilled to successfully perform 3D imaging of organic material. Firstly, the impact of the projectile should result in a high sputtering yield. Secondly, the range of the damage generated by the impact of the projectile and the depth of the ejected particles should be as low as possible. Using molecular dynamics (MD) computer simulations, we have investigated impacts of 5 keV C_{20}, C_{60}, C_{120} and C_{180} projectiles on a benzene crystal. The results are utilized to explain why fullerene projectiles can make imaging and depth profiling experiments possible in SIMS and to evaluate which of investigated clusters is the best for such measurements.

2. Model

Details of molecular dynamics computer simulations used to model cluster bombardment are described elsewhere [5]. Briefly, the motion of the particles is determined by integrating Hamilton's equations of motion. The forces among the particles are described by a blend of pair-wise additive and many-body potential energy functions. In this study, we use the coarse-grained approach to model fullerene bombardment of a benzene solid. This technique has proven to significantly decrease simulation time while giving results similar to the data obtained with a full atomistic model [6]. However, the downside of the coarse-grained representation is the inability to consider broad-based chemical reactions. Therefore, any conclusions about the chemistry of irradiated samples must be drawn with caution. In this work, each coarse-grained benzene molecule is represented by six CH particles with a mass of 13 amu. A Lennard–Jones potential is used to describe the C–CH interactions as well as the interactions of the CH–CH particles

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located in different molecules. The CH–CH interaction inside a single benzene molecule is described by a Morse potential. Details of coarse-grained method and appropriate values for the Lennard–Jones and Morse potential parameters can be found in [6]. Finally, the adaptive intermolecular potential, AIREBO, is used to describe the C–C interactions among the projectile atoms [7]. The model approximating the benzene crystal consists of 198720 coarse-grained molecules arranged in 60 layers. The size of the sample is 33.8 × 33.7 × 20.2 nm. The sample was kept at 0 K by a heat bath composed of rigid and stochastic molecules, which is used to prevent pressure waves generated by the cluster projectile impact from reflecting off of the crystal boundaries back into the crystallite [8].

3. Results and discussion

The temporal evolution of collision events leading to the ejection of particles during 5 keV C_{60} bombardment of the benzene crystal can be found in our previous publications [9,10]. It has been shown that, due to its large size, the C_{60} projectile strongly interacts with the organic sample breaking apart during first picosecond of movement. A large fraction of the carbon atoms originating from the projectile is backscattered into the vacuum. The impinging projectile deposits its energy close to the surface stimulating a mesoscopic process in which carbon atoms are working cooperatively to relocate target particles [5,11]. The analysis of the projectile movement reveals that the ejection process can be divided into two main stages. In the first stage, the ejection of molecules and fragments occurs mainly due to energetic processes initiated by direct interactions between the impinging projectile and the sample molecules. In the second stage of emission, which occurs much later, the sputtering is stimulated by intermolecular collisions, and the ejection is dominated by particles which are emitted from the surface with very low kinetic energy. The general evolution of the benzene system during bombardment with all other projectiles used in this study is quite similar. The final effect of the bombardment by all investigated projectiles is shown in Fig. 1. It is visible that all projectiles deposit their energy close to the surface. As a consequence large number of benzene molecules is relocated during bombardment which leads to the formation of a roughly hemispherical crater surrounded by a rim built up mostly from molecules originating from first few layers of the crystal. The coloring scheme depicts the distance by which the molecules are relocated from their original positions. For all investigated projectiles the diameter and the depth of the crater, as well as the extent of the mixed volume are relatively small, which implicates a possibility to obtain a good spatial resolution in depth profiling experiments using fullerene ion clusters. Furthermore, the range of the mixing created by impinging projectiles is well localized and limited to the nearest proximity of the formed crater. Because the crater depth is much greater than the mixed region, the next fullerene impact at the modified surface has the potential to remove a majority of the mixed volume and to sample a considerable amount of unaltered volume, which is a desired condition for 3D molecular depth profiling. Both the size of the crater and the thickness of the mixed volume only slightly depend on the size of the projectile.

The impact of 5 keV fullerene clusters on the benzene crystal leads to the emission of ~332, 320, 309 and 268 benzene molecule equivalents for C_{20}, C_{60}, C_{120} and C_{180} projectiles, respectively [6]. As can be seen, the obtained sputtering yield is the highest for 5 keV C_{20} and decreases with the increase of the size of the projectile [6]. Such sputtering yield is sufficiently high to fulfill the first requirement of a successful depth profiling experiments given by Wucher et al. [2,3]. However, a strong ejection is only one of several conditions needed to successfully perform depth profiling. Another very important issues are: the erosion dynamics of the surface, the amount of the chemical damage created by the impinging projectile and the spatial extent of the projectile-induced mixing.

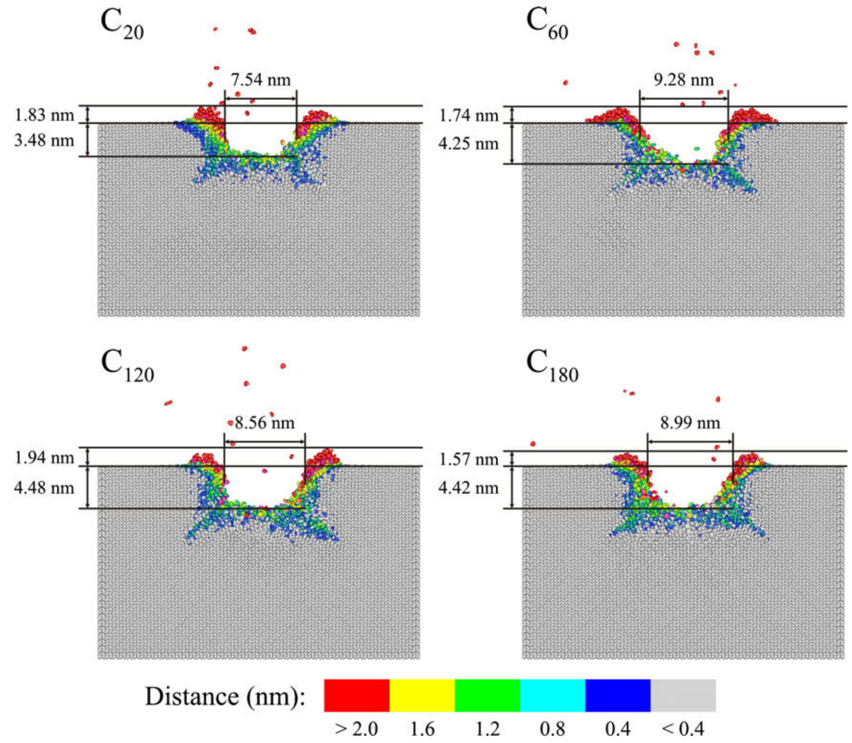

Fig. 1. A cross-sectional view of the crater formed after ~26 ps by an impact of 5 keV C_{20}, C_{60}, C_{120} and C_{180} projectile on solid benzene at normal incidence. Coloring depicts the distance the molecules are relocated from their original positions. A slice 1.5 nm-wide, centered at the projectile impact point is shown.

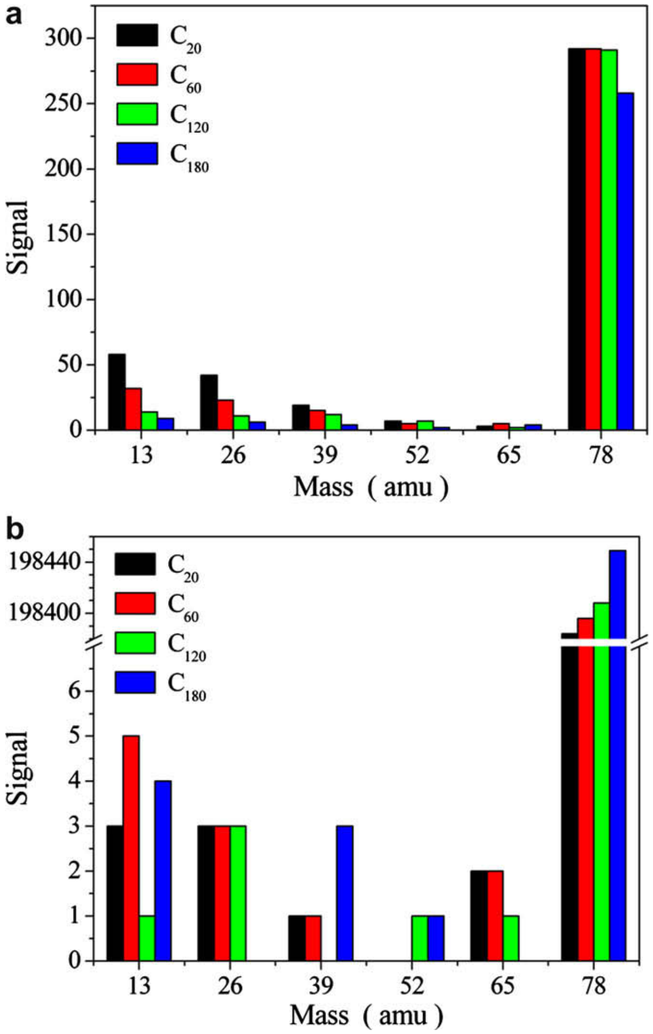

Fig. 2. Mass spectra of: (a) ejected neutral particles, and (b) neutral particles left in the benzene crystal after 5 keV C_{20}, C_{60}, C_{120} and C_{180} bombardment at normal incidence.

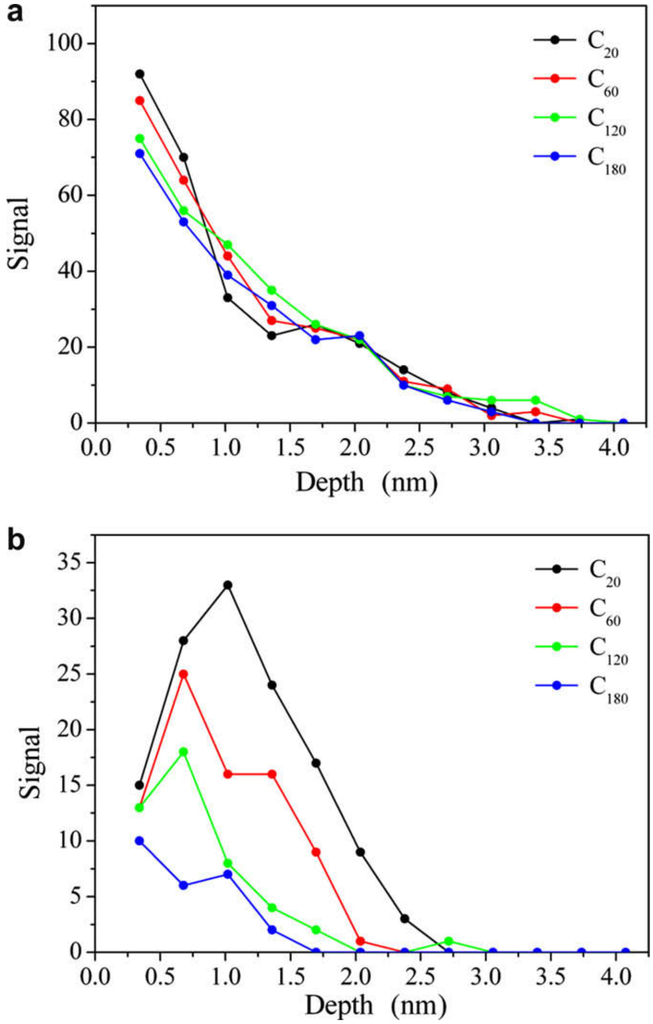

Fig. 3. Molecular depth profiles of ejected: (a) benzene molecules, and (b) organic fragments after 5 keV C_{20}, C_{60}, C_{120} and C_{180} bombardment at normal incidence.

The mass spectrum of sputtered neutral particles is presented in Fig. 2(a). It is clearly visible that for all used projectiles the ejected flux is dominated by intact molecules. Only a small number of fragments is present in the distribution. Because a coarse-grained approach is used in this study, only five possible fragments CH_n, $n = 1, \ldots, 5$ can be created. It is interesting to note that the number of sputtered fragments is so low, taking into consideration that the dissociation threshold of benzene molecules is only ~5 eV [12] as compared to the 5 keV of initial energy of fullerene projectiles. One could expect, therefore, that numerous benzene molecules should be broken during cluster impact. This supposition is not supported by the calculated mass spectra, where the total number of emitted fragments is equivalent to ~40, 28, 18 and 10 benzene molecules for C_{20}, C_{60}, C_{120} and C_{180}, respectively. This value composes about 12%, 9%, 6% and 4% of the total sputtering yield in each case. The total number of fragmented molecules as well as the ratio of fragmented to intact molecules is decreasing as the size of the projectile increases. This trend can be attributed to lowering of the kinetic energy of individual carbon atom in larger cluster projectile. However, lack of the fragments in the ejected flux does not necessarily mean that they are not formed. It is possible that the molecules are still fragmented but fragments are left inside the crystal. This phenomenon may potentially alter chemical composition of the irradiated material. The comparison of the mass spectra of the benzene crystal after fullerene impact is shown in Fig. 2(b). As it can be seen, indeed all mass distributions contain fragments, however, the total number of these fragments is very low. It does not exceed the number of four complete benzene molecules equivalents for all investigated projectiles. The presented mass spectra show, therefore, that the total number of fragmented molecules is indeed small, and most of the created fragments are immediately ejected. The efficiency of molecular fragmentation and the observed "cleaning up" effect are the most effective for the smallest fullerene cluster (C_{20}). A similar effect does not occur during atomic bombardment where many molecular fragments remain inside the sample after bombardment [5]. Both these observations are very fortunate from the point of view of 3D depth profiling.

Although the fullerene projectiles indeed have the unique ability to remove most of the chemical damage in the benzene crystal almost as fast as it is created, the projectile-induced chemical modification is only one of the processes that can influence ultimate resolution in depth profiling. Another important factor is the depth of ejected molecules. Fig. 3(a) shows the depth distribution of intact benzene molecules ejected from the benzene crystal bombarded by 5 keV C_{20}, C_{60}, C_{120} and C_{180} projectiles. It is clearly visible that despite the different size of these projectiles, all of presented distributions are very similar. In all of these spectra benzene molecules are preferably emitted from first few layers. Quite interesting behavior is observed for emission of fragmented benzene molecules. As shown in Fig. 3(b), the fragments are not preferentially ejected from the topmost layer. The most probable ejection depth is located deeper inside the crystal, and it depends on the size of the projectile moving closer to the surface of the benzene crystal as the size of the fullerene cluster increases. This unexpected behavior is not yet fully understood, but most probably, it is connected with the spatial profile of the energy deposited by the projectile. However, additional analysis still has to be made to verify this hypothesis or to find another explanation of such behavior.

4. Conclusions

The simulations presented here provide an understanding of why cluster beams composed of C_{20}, C_{60}, C_{120} or C_{180} projectiles make imaging and depth profiling experiments possible in SIMS for certain organic molecules, and which of these projectiles is the best choice for such experiments. First, the impact of all investigated projectiles results in a strong signal, and the ejected flux is composed mostly from intact molecules. The highest signal is observed for the 5 keV C_{20} and decreases while the size of the projectile increases. However, as it has been shown, the ejection efficiency depends not only on the size of the projectile, but also on its kinetic energy [13,14]. As a consequence, C_{20} is the best choice at 5 keV impact but the most efficient ejection will shift to larger clusters with the increase of the kinetic energy. For all of the presented projectiles, the alteration of the chemical composition of the probed surface is small and most of the damage is removed almost as fast as it is created. This “cleaning up” effect may explain why secondary ion mass spectrometry (SIMS) analysis of some organic samples with cluster projectiles can produce significantly less accumulated damage compared to analysis performed with atomic ion beams. For all of the investigated projectiles, the depth of the projectile-induced mixing region is much smaller than the depth of the ejected material. This observation means that each fullerene projectile will mostly probe pristine, unaltered sample. The depth distribution of ejected molecules show that most of intact molecules as well as molecular fragments is ejected from first few layers of the substrate, which is very fortunate from a point of view of depth profiling experiments. Finally, some statements should be made about limitations of the current study. The calculations have been made on a system of small loosely bound molecules. The behavior of the system composed from longer, entangled molecules may be different. In particular, the “cleaning up” effect may be much more difficult in this case. Next, the coarse-grained approach does not allow reactions to occur between molecules. Thus, any conclusion about the chemistry of the irradiated sample must be drawn with caution and with caveats regarding the limitation of the potential.

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