Vacuum 83 (2009) S95–S98

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Molecular dynamics computer simulations of 5 keV C_{60} bombardment of benzene crystal

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ARTICLE INFO

Article history:
Received 16 June 2008
Received in revised form
26 January 2009
Accepted 30 January 2009

Keywords:
Sputtering
SIMS/SNMS
Depth profiling
Cluster projectiles
Organic material
Molecular dynamics computer simulations

ABSTRACT

Coarse-grained molecular dynamics computer simulations have been used to investigate the damage of a benzene crystal induced by 5 keV C_{60} projectile bombardment. The sputtering yield, mass distributions and the depth distributions of ejected organic molecules are analyzed. The temporal evolution of the system reveals that impinging C_{60} cluster leads to creation of almost hemispherical crater. Most of the molecules damaged by the projectile impact are ejected into the vacuum during cluster irradiation. 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 on 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 [1,2]. 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 3-dimensional (3D) depth profiling of organic samples could be achieved with cluster ions even in so called dynamic conditions [1,3]. Such phenomenon has never been observed for atomic projectiles. According to Wucher [4] and Winograd et al. [5] few requirements have to be fulfilled to successfully perform 3D imaging of organic material. First, the impact of the projectile should result in a high sputtering yield. Then, the depth of the projectile penetration and the range of the damage generated by the impact of the projectile should be as low as possible. In this paper the molecular dynamics (MD) computer simulations are used to investigate an impact of 5 keV C_{60} projectiles on a benzene crystal. The results are utilized to explain why projectiles like C_{60} clusters make imaging and depth profiling experiments possible in SIMS.

2. Model

Details of molecular dynamics computer simulations used to model C_{60} bombardment are described elsewhere [3]. 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 C_{60} bombardment of a benzene solid. This technique has proven to significantly decrease simulation time giving the results similar to the data obtained with a full atomistic model [6]. In the coarse-grained approximation each 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 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

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doi:10.1016/j.vacuum.2009.01.034

parameters can be found in the work of Smiley et al. [6]. Finally, the adaptive intermolecular potential, AIREBO, is used to describe the C–C interactions among the atoms of the C_{60} projectile [7]. The model approximating the benzene crystal consists of 198 720 coarse-grained molecules arranged in 60 layers. The size of the sample is $33.8 \times 33.7 \times 20.2$ nm. The micro crystallite is surrounded by a heat bath composed of rigid molecules and several layers of molecules kept at 0 K by a frictional force, which is used to prevent energy induced by pressure waves generated by the cluster projectile impact being reflected from the boundary walls back into the crystallite [8]. Due to a long time required to complete the simulation only a single trajectory was run. However as it has already been proven for C_{60} bombardment of thin organic overlayers [9], the removal of organic material is almost independent of the impact point of this projectile. This means that each C_{60} impact gives statistically reliable results.

As shown above coarse-grained benzene molecules interact by a combination of pair-wise potentials. This means that although the bonding strength between two beads can be described properly and they can recombine, the phenomena like bounding orders or bond saturations are not taken into account. This is a big deficit of the current approach. Unfortunately, at least for the time being, it is not feasible to apply a proper many-body AIREBO potential which properly describes chemical reactions into the organic system of the size necessary to contain the primary energy of the projectile used in the current study. Such calculations would last too long to be practical. However, the test calculations performed with the AIREBO and coarse-grain potentials on a smaller benzene system irradiated with 0.5 keV C_{60} projectile have shown that parameters such as the geometrical damage and the total sputtering yield are similar in these two approaches [6].

3. Results and discussion

Snapshots of the temporal evolution of collision events leading to the ejection of particles during 5 keV C_{60} bombardment of the benzene crystal are shown in Fig. 1. It is visible that due to its large size C_{60} projectile strongly interacts with the organic sample breaking apart during first picosecond of the 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 [9,10]. One of the consequences of this movement is generation of pressure waves that propagate in the sample. Furthermore, a large number of benzene molecules is relocated during bombardment which leads to the formation of a roughly hemispherical crater surrounded by a huge rim built up mostly from molecules originating from first few layers of the crystal. The evolution of the topography of the benzene crystal is similar to the behavior of clean silver irradiated with the same projectile [8]. However, certain differences are still observed. First, due to a larger binding energy, atomic density, and mass of the individual atoms composing silver crystal, the metal sample more effectively stops the C_{60} and confines the energy closer to the surface. Then, in the case of clean Ag{111} the ejection process terminates much sooner

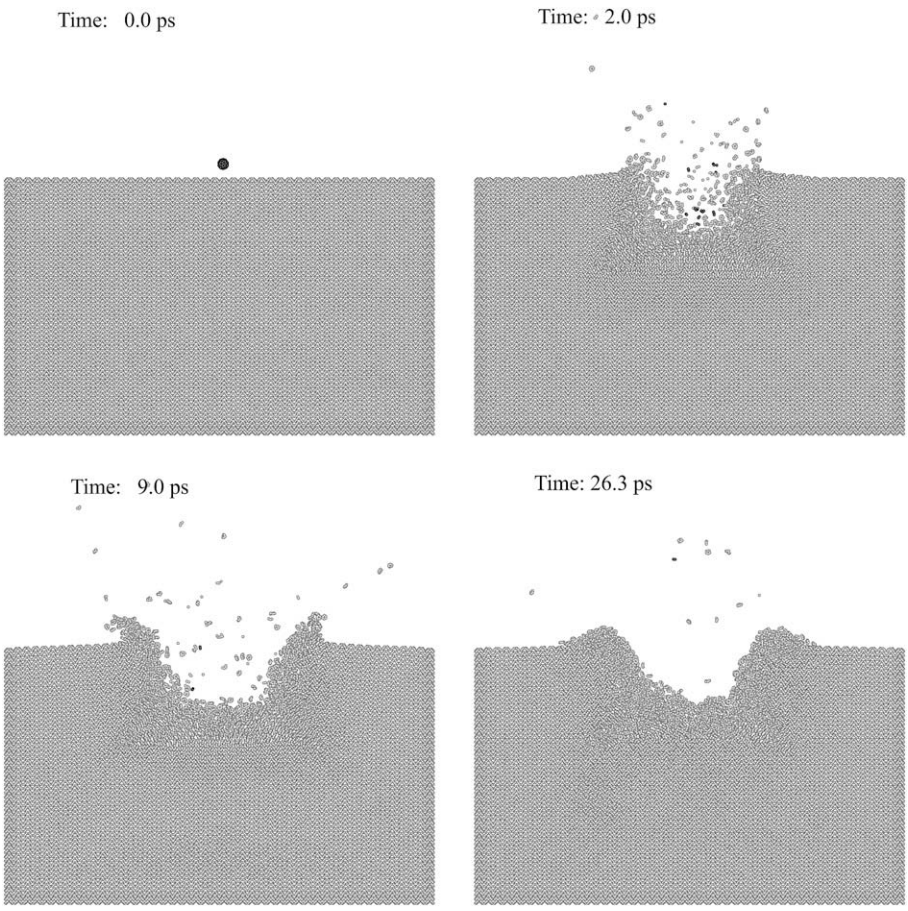

Fig. 1. A cross-sectional view of the temporal evolution of collision event leading to ejection of particles due to 5 keV C_{60} bombardment of thick benzene crystal at normal incidence. A slice 1.5 nm-wide, centered at the projectile impact point is shown.

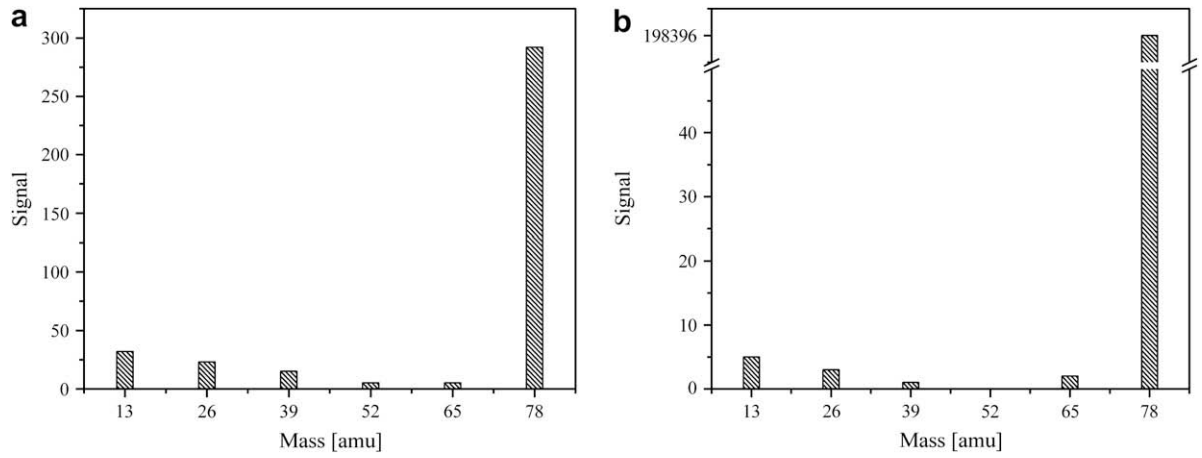

Fig. 2. Mass spectra of: a) ejected particles and b) particles left in the benzene crystal after 5 keV C_{60} bombardment at normal incidence.

(~4 ps) as compared to the emission stimulated from solid benzene (~20 ps), which is a consequence of almost 6 times larger cohesive energy of a metal sample. The analysis of the projectile movement reveals that the ejection process can be divided into two main stages. In the first stage (from 0 ps to ~2 ps), 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 (starting from ~9 ps), which occurs much later, the ejection is dominated by particles which are emitted from the surface with very low kinetic energy. The impact of 5 keV C_{60} cluster on the benzene crystal leads to emission of ~320 of benzene molecule equivalents. Such sputtering yield is sufficiently high to fulfill first requirement of a successful depth profiling given by Wucher [4] and Winograd et al. [5]. However, a strong ejection is only one of several conditions needed to successfully perform depth profiling. Another very important issue is 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.

The mass spectrum of sputtered particles is presented in Fig. 2a. It is clearly visible that the ejected flux is dominated by intact molecules. Only a small number of fragments is present in the distribution. Because a coarse-grain approach is used in this study, only five possible fragments CH_n, $n = 1, \ldots, 5$ can be created by fragmentation of benzene molecules. It is interesting to note that the number of sputtered fragments is so low. Taking into consideration that dissociation threshold of benzene molecules is only ~5 eV [11] as compared to the 5 keV of initial energy of C_{60} projectile, one could expect that numerous benzene molecules would be broken during cluster bombardment. This supposition is not supported by the calculated mass spectrum where the total number of emitted fragments is equivalent to ~28 benzene molecules, which is less than 9% of the total sputtering yield. 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. To evaluate this hypothesis the mass spectrum of the benzene crystal after C_{60} impact is calculated and shown in Fig. 2b. As it can be seen, the mass distribution of the sample particles also contains few fragments. The total number of fragmented particles is only 11, which corresponds to barely 4 complete benzene molecules equivalents. The presented mass spectra show, therefore, that the total number of fragmented molecules is indeed small and most of created fragments are immediately ejected. Similar "Cleaning up" effect does not occur during atomic bombardment where many molecular fragments are left inside the sample after bombardment [3]. Both these observations are again very fortunate from the point of view of 3D depth profiling.

Additional observation is the fact that particles larger than one benzene molecule are not presented in mass spectra. The lack of ejected benzene complexes may be an artifact of the model. It is possible, however, that 5 keV C_{60} projectiles do not have sufficient energy to compress two molecules so they form a dimer. Unfortunately, there are no experimental results on C_{60} irradiation of benzene, so, at least for the time being, we are not able to determine which explanation is correct. The calculations performed with a full AIREBO potential for 15 keV C_{60} irradiation of a thin layer of benzene deposited on Ag{111} show that such complexes are formed. However, their number is very small (<2% of all ejected particles) [12] and, consequently, this dilemma should not influence the main conclusions from the current work.

Although the C_{60} projectile indeed has the unique ability to remove most of the chemical damage 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 projectile-induced mixing of the sampled material. The spatial distribution of the damage created by 5 keV C_{60} projectile is shown in Fig. 3. The grayscale scheme depicts the distance the molecules are moved from their original positions. It is visible that an impact of the C_{60} projectile creates almost

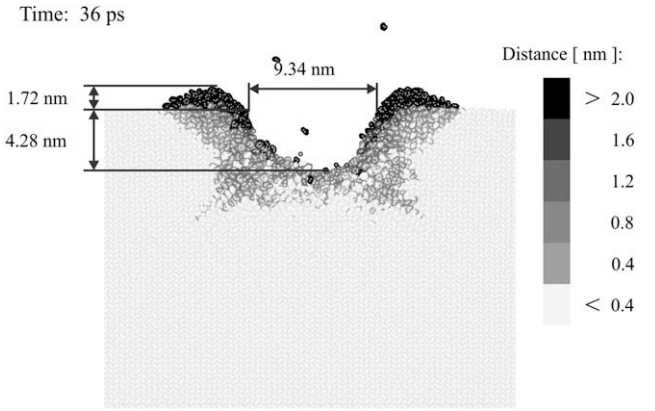

Fig. 3. A cross-sectional view of the crater formed by an impact of 5 keV C_{60} projectile on solid benzene at normal incidence. Grayscale depicts the distance the molecules are relocated from their original positions.

hemispherical crater with a ~9.3 nm diameter on the surface. The crater is surrounded by the narrow volume in which the molecules are relocated from their original positions. The depth of the crater (~4.3 nm) and the extent of the mixed volume are relatively small which implicates a possibility to obtain a good spatial resolution in depth profiling experiments using C_{60} ion clusters. Furthermore, the range of the mixing created by the impinging C_{60} projectile 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 C_{60} hit has the potential to remove a majority of the relocated molecules and sample a considerable amount of unaltered volume which is an ideal condition for 3D molecular depth profiling.

4. Conclusions

The simulations presented here provide a graphic and clear understanding of why cluster beams composed of C_{60} projectiles make imaging and depth profiling experiments possible in SIMS. First, the impact of these projectiles results in a strong signal and the ejected flux is composed mostly from intact molecules. The alteration of the chemical composition of the probed surface is small because 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. Finally, the depth of the projectile-induced mixing region is much smaller than the depth of the ejected material, which means that each C_{60} projectile will mostly probe pristine, unaltered sample. 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 between molecules. Thus, any conclusion about the chemistry of the irradiated sample must be done with caution and with caveats regarding the limitation of the potential.

Acknowledgments

The financial support from the Polish Ministry of Science and Higher Education programs no. PB 4097/H03/2007/33 and PB 0935/B/H03/2008/35, and the National Science Foundation grant #CHE-0456514 are gratefully acknowledged.

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