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

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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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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

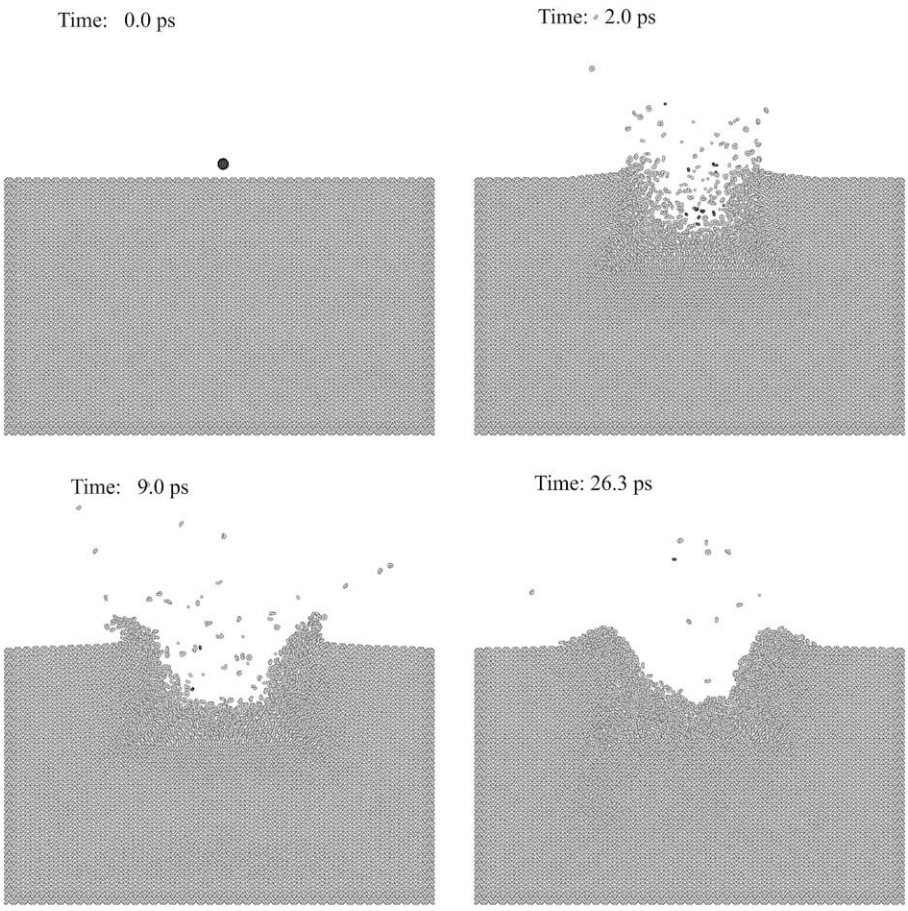

Fig. 1. A cross-sectional view of the temporal evolution of collision event leading to ejection of particles due to 5 keV C_{60} bombardment of thick benzene crystal at normal incidence. A slice 1.5 nm-wide, centered at the projectile impact point is shown.