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Effect of substrate thickness on ejection of phenylalanine molecules adsorbed on free-standing graphene bombarded by 10 keV C_{60}

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ABSTRACT

Molecular dynamics computer simulations have been employed to investigate the effect of substrate thickness on the ejection mechanism of phenylalanine molecules deposited on free-standing graphene. The system is bombarded from the graphene side by 10 keV C_{60} projectiles at normal incidence and the ejected particles are collected both in transmission and reflection directions. It has been found that the ejection mechanism depends on the substrate thickness. At thin substrates mostly organic fragments are ejected by direct collisions between projectile atoms and adsorbed molecules. At thicker substrates interaction between deforming topmost graphene sheet and adsorbed molecules becomes more important. As this process is gentle and directionally correlated, it leads predominantly to ejection of intact molecules. The implications of the results to a novel analytical approach in Secondary Ion Mass Spectrometry based on ultrathin free-standing graphene substrates and a transmission geometry are discussed.

1. Introduction

In recent years, cluster ion beams have attracted increasing experimental and theoretical attention due to their capacity to enhance ejection of large intact organic molecules in Secondary Ion Mass Spectrometry (SIMS) [1,2]. One of the most successful clusters used in organic SIMS is C_{60} fullerene [3]. In a typical SIMS geometry the detector is located on the same side of the target as the ion gun. Usually metal or semiconductor supports are used to deposit the investigated material. A novel SIMS configuration, using transmission orientation, has been proposed recently [4,5]. In this orientation, the analysed organic material is deposited on one side of the ultrathin substrate, while another side is bombarded by cluster projectiles. It is argued that such geometry can be particularly attractive for analysis of small amounts of organic material, molecular nano-objects and supramolecular assemblies [5].

There are several simulations performed on C_{60} bombardment of graphene and graphite [4,6–13]. However, most of these studies concentrate on defect creation in the bombarded system rather than on material ejection. Theoretical studies of sputtering of graphite by keV C_{60} projectiles show that the sputtering yield is low [11,13]. Krantzman et al. have attributed this fact to a low atomic density of graphite [11], while the effect of the layered structure of graphite was emphasised by Tian et al. [13]. It also has been shown that the membrane-like structure of graphite can be made to vibrate as a result of a cluster impact [4,8,9]. The mesoscopic motion of created circular acoustic waves can stimulate ejection of small weakly bound molecules [8,9]. Although this mechanism may not be efficient for uplifting heavier molecules as it may not provide enough energy, it has been postulated that vibrational energy can be utilized to stimulate ionization [4]. Computer simulations of bombardment of organic molecules deposited on metal substrates show that intact molecules are emitted by low-energy collisions with ejecting substrate or projectile atoms [14], and/or by surface deformations occurring during crater formation [15]. As sputtering of graphite is different from sputtering of metals [13,16] we would like to check if similar phenomena are present for the ultrathin graphite. Furthermore, the only theoretical study performed so far with C_{60} impacts in transmission geometry was done on a system of a constant thickness [4]. The goal of this paper is, therefore, to investigate processes that lead to ejection of organic molecules deposited on ultrathin free-standing graphene of various thickness bombarded by 10 keV C_{60} projectiles in a transmission orientation.

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2. Computer model

A detailed description of the molecular dynamics computer simulations used to model cluster bombardment can be found elsewhere [1]. Briefly, the motion of particles is determined by integrating Hamilton's equations of motion. The forces among atoms in the system are described by a Reax-FF force field [17] splined at short distances with a ZBL potential to properly describe high energy collisions. The shape and size of the samples are chosen based on a visual observation of energy transfer pathways stimulated by impact of C_{60} projectiles. As a result, cylindrical samples with a diameter of 400 Å are used. Substrates with a thickness ranging from 2 to 16 graphene layers with a HOPG structure are bombarded by 10 keV C_{60} projectiles that are directed at the bottom of the sample. Ten phenylalanine molecules are deposited on the top of the graphene substrate, as shown in Fig. 1. Molecules are placed away from each other to mimic submonolayer coverage. They are also located at different distance from the impact zone to probe the influence of this parameter on the mechanism of ejection. Phenylalanine molecules are selected as they are important amino acids, they are simple, yet consist of most elements that are present in biomaterials. Particles ejected both in direction of the primary beam (transmission direction) and in the opposite direction (reflection direction) are collected. Rigid and stochastic regions are used to simulate the thermal bath and to prevent reflection of pressure waves from the boundaries of the system [1,18]. The simulations are run at 0 K target temperature in an NVE ensemble and extend up to 10 ps, which is long enough to achieve saturation in the ejection yield vs time dependence. Eight impact points within the linear impact zone represented by white line in Fig. 1 are chosen to achieve statistically more reliable data.

3. Results and discussion

Numbers of particles ejected from systems of various thickness by 10 keV C_{60} impacts are given in Table 1. While it is evident that the yields depend on substrate thickness, the actual dependence is different for different particles. The number of projectile atoms penetrating the sample decreases with a thickness of the substrate. Interestingly, almost no projectile atoms are backscattered even from the thickest system, which means that non-ejected atoms are implanted into the sample. The ejection yield of substrate atoms in the transmission direction depends non-monotonically on the substrate thickness. At first, the signal increases as more carbon atoms become available for ejection when the sample is getting thicker. However, with the increase of the substrate thickness more primary kinetic energy is sacrificed to penetrate through a thicker solid. As a result, less energy is available near the surface from where the ejection occurs, and, ultimately, the signal decreases. Atoms originally located in all layers are recorded in the ejected flux, although ejection from the topmost layer is dominant. A similar dependence on the substrate thickness occurs for atoms originating from phenylalanine molecules, however, the reason of such behavior has to be different than for substrate atoms as the number of molecules available for ejection is constant. For substrates composed of up to 6 graphene layers predominantly molecular fragments are ejected. For thick substrates ($\geqslant$12L) the ejected flux is composed entirely from intact molecules.

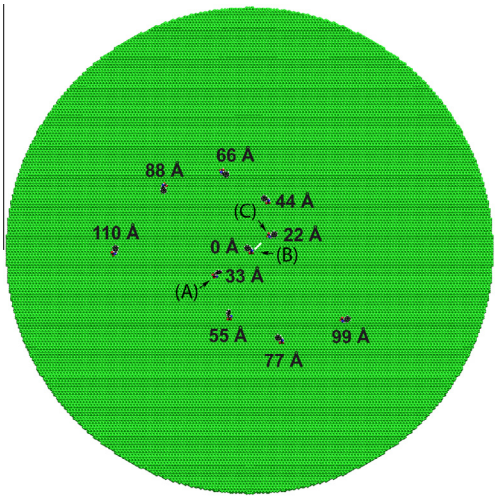

Fig. 1. The model system used to study ejection processes of phenylalanine molecules deposited on free-standing graphene. Numbers indicate distance from the centre of the system. The white line depicts impact points.

Cross sectional views of the temporal evolution of 2, 8 and 16-layer systems are shown in Fig. 2 to identify processes responsible for molecular ejection. In all systems C_{60} projectiles decompose into smaller pieces almost immediately after the impact. As indicated in Table 1 at the 2-layer (2L) sample almost all projectile atoms penetrate through the substrate. Nevertheless, even in this system a projectile-graphene interaction is surprisingly strong, as already a half of the primary kinetic energy is transferred to the substrate. Most of this energy is carried away by ejected substrate particles. Ejection of both projectile and substrate atoms is forward directed. Ejecting atoms can collide with organic molecules causing their ejection. However, the average kinetic energy of ejected projectile and substrate atoms is high. As a result, such collisions lead to molecular fragmentation, as seen for molecule B in Fig. 2a. The projectile impact also leads to a creation of cylindrical acoustic waves that propagate in the graphene outward from the point of impact with a maximum amplitude of 1 Å. It was reported that these waves are capable to uplift benzene and cumene molecules [8,9]. However, no similar phenomenon has been observed in our study.

A dramatic alteration of a substrate structure caused by C_{60} impact is observed at thicker systems, as shown in Fig. 2b for the 8L graphene. The projectile is more efficiently decelerated, depositing almost all of its primary kinetic energy into the substrate. Part of this energy is used to eject substrate atoms in the forward direction. The remaining part is used to deform the substrate. Soon after the projectile impact substrate integrity is compromised. Near the point of impact graphene sheets become separated from each other and bend up in a direction parallel to the movement of incoming projectile. Finally, a cylindrical opening is formed surrounded by elevated rim at the top surface of the sample.

While the average kinetic energy of ejected projectile and substrate atoms is smaller than in the 2L system, it is still high enough to fragment molecule B. However, the unfolding of graphene sheets, which works like a catapult can also eject other molecules, as visible for molecule C. As the process is gentle and occurs in a coordinated fashion, the ejected molecules are not fragmented. This process supplements molecular ejection by collisions leading to an increase of the organic signal and to the appearance of intact molecules in the sputtered flux. A similar mechanism was observed during crater formation at the metal surfaces bombarded by cluster projectiles [15]. However, surface deformation observed in graphene extends to a much larger lateral distance making this process much more efficient than in metals. It is also worth mentioning that catapult-like sheets movement is almost absent at the surface directly hit by a projectile. This observation indicates that a transmission geometry is a better choice for efficient ejection of adsorbed molecules, at least, for ultra-small coverages.

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