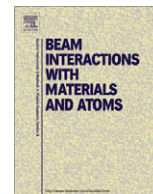




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## Nuclear Instruments and Methods in Physics Research B

journal homepage: [www.elsevier.com/locate/nimb](http://www.elsevier.com/locate/nimb)Sputtering of Langmuir–Blodgett multilayers by keV C<sub>60</sub> projectiles as seen by computer simulationsR. Paruch<sup>a</sup>, L. Rzeznik<sup>a</sup>, B. Czerwinski<sup>a</sup>, B.J. Garrison<sup>b</sup>, N. Winograd<sup>b</sup>, Z. Postawa<sup>a,\*</sup><sup>a</sup>Smoluchowski Institute of Physics, Jagiellonian University, ul. Reymonta 4, 30-059 Kraków, Poland<sup>b</sup>Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

## ARTICLE INFO

## Article history:

Available online 27 May 2009

## PACS:

79.20.Rf

36.40.-c

07.77.Gx

36.20.Eg

## Keywords:

Sputtering

Molecular dynamics

C<sub>60</sub>

Depth profiling

Langmuir–Blodgett overlayers

SIMS

## ABSTRACT

Fundamental processes induced in a thick organic system composed of long, well-organized linear molecules by an impact of 5–20 keV C<sub>60</sub> are investigated. The organic system is represented by Langmuir–Blodgett multilayers formed from bariated molecules of arachidic acid. The thickness of the system varies between 2 and 16 nm. Coarse-grained molecular dynamics computer simulations are applied to investigate the energy transfer pathways and sputtering yields as a function of the kinetic energy of the projectile and the thickness of the organic overlayer.

The results indicate that an impact of keV C<sub>60</sub> projectiles leads to significant ejection of organic material. The efficiency of desorption increases with the kinetic energy of the projectile for a given layer thickness. For a constant primary kinetic energy, the sputtering yield goes through a maximum and finally saturates as the LB layer becomes thicker. Such behaviour is caused by a competition between signal enhancement due to increasing number of organic molecules and signal decrease due to lowering of the amount of the primary energy being backreflected into the organic overlayer by the receding organic/metal interface as the layer is getting thicker. When the sample thickness becomes much larger than the penetration depth of the projectile, the sputtering yield is independent of thickness. The deposited energy is channelled by an open and ordered molecular structure, which leads to abnormally long projectile penetration and ion-induced damage.

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## 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 the 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 chemical surface analysis associated with lateral and vertical probing of material composition has become possible in many organic and biological systems [1]. This success is attributed mainly to the enhanced sputter yields and lower damage accumulation of cluster bombardment, especially for the C<sub>60</sub> projectile [2,3]. All the-

oretical studies performed so far on organic systems have shown that the geometrical structure of irradiated solid does not have any influence on the energy deposition pathways of cluster projectiles, like C<sub>60</sub> [3–13]. In all these studies, the C<sub>60</sub> projectile was quickly decelerated, depositing its kinetic energy close to the surface. Recently several experimental measurements have been published by Zheng et al. in which Langmuir–Blodgett (LB) multilayers of alternating barium arachidate and dimyristoyl phosphatidate (DMPA) deposited on bare silicon and Au-patterned silicon substrates are characterized by SIMS employing the C<sub>60</sub> ion source [14,15]. A dramatic influence of impact angle on the achievable depth resolution was observed in these studies. One possible explanation of these results could be a long penetration depth of C<sub>60</sub> clusters. The goal of this paper is to test this supposition and to supply theoretical foundations for other observations presented in [14,15]. Molecular dynamics computer simulations are used to investigate energy deposition pathways stimulated by an impact of the C<sub>60</sub> projectile in the organic system composed of ordered linear molecules. A similar system has not been investigated so far by computer modelling. In particular, the effect of the incidence energy and the layer thickness on the efficiency of ejection is studied.

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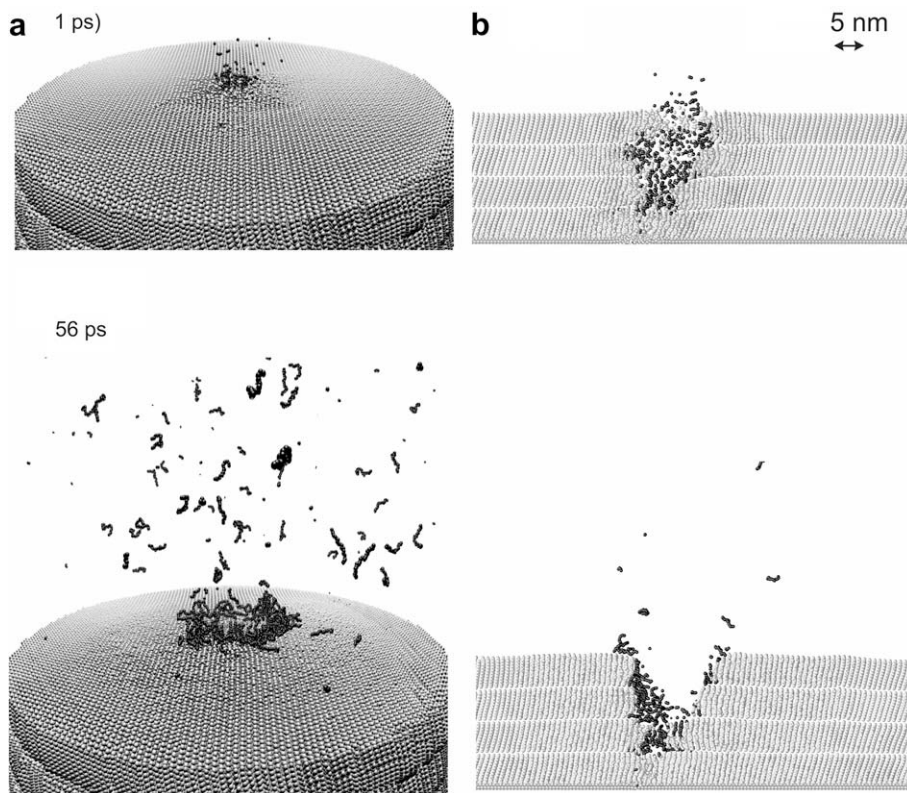
## 2. Computational model

Details of molecular dynamics computer simulations used to model  $C_{60}$  bombardment are described elsewhere [13]. Briefly, the motion of the particles is determined by integrating Hamilton's equations of motion. In this study, we use a coarse-grain approach to model Langmuir–Blodgett films formed from bariated molecules of arachidic acid (AA) deposited on an  $Ag\{1\ 1\ 1\}$ . In this approach groups of atoms are represented as one united particle in order to reduce computational expense. The advantages of this kind of approximation are that there are fewer particles, the potentials are simpler thus quicker to calculate, and the fast H-vibration is eliminated, allowing for a larger time step to be used in the integration [12]. As a result, the large systems required to realistically model keV fullerene interactions with organic solids can be treated within reasonable computational time. The downside of the united atom representation is the inability to consider broad-based chemical reactions. Therefore, any conclusions about the chemistry of irradiated samples must be drawn with caution. Nevertheless, this technique has proven to significantly decrease simulation time while giving results similar to the data obtained with a fully atomistic model [6]. In the coarse-grain approach each AA molecule is represented by a sequence of one COOBa (mass 182 u), 18  $CH_2$  (mass 14 u each) and one  $CH_3$  (mass 15 u) beads.

The forces among the particles are described by a blend of pairwise additive and many-body potential energy functions. The Ag–Ag interactions are described by the MD/MC–CEM potential for metals [16]. The interaction between C atoms in the projectile is described by the adaptive intermolecular potential, AIREBO [17]. The interactions between projectile atoms and the rest of the system are described by a weak Lennard–Jones potential splined at small distances with a purely repulsive Moliere potential to better

describe high-energy collisions. A Lennard–Jones potential is also used to describe the interactions of the particles located in different molecules and the interaction between the components of a given molecule and the rest of the system. A Morse potential has been selected to describe interactions between adjacent particles (nearest neighbours) in the molecule. The same potential with a small well depth is also used to model interactions between particles separated by one particle (next–nearest neighbours). As a result the particles are allowed to interact if the molecule is dissociated, and the molecules adopt the appropriate zigzag shape in an equilibrium configuration [12]. Finally, a Lennard–Jones potential is used to describe interactions between particles of a molecule that are separated by two or more beads to stabilize long-range geometrical configuration of atoms in a molecule. These types of interactions have been preferred to the angle bend term – adopted in studies of lipid film configurations – which does not allow for dissociation and is therefore inappropriate for sputtering simulations [12]. The value of potential parameters used in this study can be found in [18]. They were selected to reproduce the structure and the bond strengths of linear hydrocarbons and polymers [12,19–21] and to reproduce the sublimation energy of arachidic acid, 2.1 eV [22].

The model approximating LB films consists of 1, 2, 3, 4 and 6 Y-type layers [22] of coarse-grained bariated arachidic acid molecules deposited on the surface of the Ag crystal. The thickness of the formed overlayers is: 2.6, 5.2, 7.8, 10.4 and 16.1 nm for 1, 2, 3, 4, and 6 layer systems, respectively. The monolayer thickness for AA is 2.7 nm as measured by ellipsometry [14]. Usually LB films are not prepared on metal, but on semiconductor substrates [14,15,22]. In this current study, however, a metal substrate was selected on account of a simpler form of the potential, which results in much faster calculations. Silver was selected as a substrate



**Fig. 1.** Side view of the temporal evolution of typical collision events leading to ejection of particles due to 15 keV  $C_{60}$  impact at a 4 layer system at normal incidence (a). A slice 1.5 nm wide centred at the projectile impact along the azimuth of the largest molecular inclinations is shown (b). Particles relocated by more than 0.8 nm their original positions are shown in black.

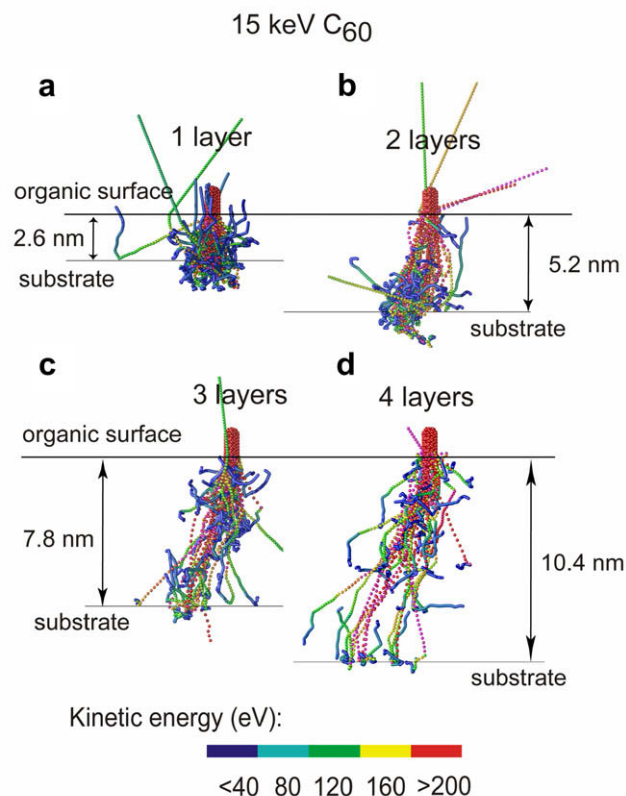
because adsorption sites of AA on the Ag(1 1 1) surface could be arranged very close to the sites measured for AA/Si(1 0 0) system [23,24], for which the experimental data of C<sub>60</sub> irradiation of AA system have been published recently [14,15]. It should be also noted that, although the substrate used was not a proper substrate, the geometrical arrangement of the molecules, the adsorption sites, organic film density, and the value of the molecular-surface binding energy were all selected to reproduce the experimental data obtained for cationized arachidic acid adsorbed on Si(1 0 0) [19,23,24]. Finally, special care was taken to eliminate artifacts associated with possible backreflection of a pressure wave from the boundaries of the system generated by an impact of cluster ions, as described in [2,18].

The atoms in the target initially have zero velocity. The atoms in the C<sub>60</sub> projectile initially have no velocity relative to the centre of mass motion. It is known that the motion induced by C<sub>60</sub> bombardment is mostly independent of the initial aiming point [2,13]. Consequently, only three trajectories were sampled for a given layer thickness and kinetic energy. Each trajectory was initiated with a fresh sample with all atoms in their equilibrium minimum energy positions. Each trajectory is terminated at 66 ps for 30 keV and 40 keV impacts, and at 46 ps in all other cases. It has been verified that these times are sufficient to properly describe the ejection process. More details about the simulation model can be found in [18].

### 3. Results and discussion

Snapshots of the temporal evolution of typical collision events leading to ejection of particles due to 15 keV C<sub>60</sub> impact at a 4 layer system are shown in Fig. 1. An impact of a cluster projectile leads to the formation of a crater. Many particles are ejected, and the intact molecules compose a significant portion of the ejected flux. Two particularly interesting phenomena were observed: firstly, the shape of the crater created in the LB film by C<sub>60</sub> impact differs from the shapes of craters formed in other organic systems investigated so far by computer modelling [5,7–13]. Secondly, the damage extends deep into the overlayer. While almost hemispherical craters surrounded by rims composed of relocated particles were observed in the previous studies, the crater formed in the LB overlayer is elongated and asymmetric. The snapshot representing the 1.5 nm cut through the sample centred at the cluster impact point collected at 1 ps suggests that the energy deposition pathways can be channelled by the geometrical structure of the overlayer. This observation is also unique among simulations of C<sub>60</sub> bombardment. Although a similar process is well known from the sputtering of single crystals by atomic projectiles [25], it has not been anticipated to occur during C<sub>60</sub> bombardment given the large size of the projectile.

To investigate this phenomenon more closely, a temporal evolution of the positions of projectile atoms forming 15 keV C<sub>60</sub> clusters bombarding LB films of various thickness at the early stages of sputtering is shown in Fig. 2. Indeed, it is evident from Fig. 2(c) and (d) that the trajectories of many carbon atoms are collimated and influenced by the initial orientation of organic molecules. Many of the carbon atoms penetrate deep into the overlayer. For 15 keV bombardment projectile atoms can penetrate up to 14 nm into the organic film, a depth 4–5 times larger than for keV C<sub>60</sub> in materials like graphite [4,10], fullerite [10], molecular benzene [7,8], water ice [9], or polymer samples [11,12]. All previous theoretical studies with C<sub>60</sub> projectiles have shown that the projectile atoms are almost immediately decelerated, and the primary energy is deposited close to the surface [3–5,7–12]. These studies have also shown that the sample material is relocated by a concerted action of atoms composing the projectile. The formation of almost



**Fig. 2.** The temporal evolution of the positions of projectile atoms forming 15 keV C<sub>60</sub> cluster bombarding a 1, 2, 3 and 4 layer-thick AA film at normal incidence at the early stages of sputtering (up to 400 fs). The colour scheme represents the kinetic energy of individual atoms. The scale goes from red (most energetic atoms) to dark blue (the least energetic atoms). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

hemispherical craters was a consequence of such collective action. As it is visible in Fig. 2, the integrity of the projectile bombarding LB films along the surface normal is quickly compromised. This effect hampers the ability of these atoms to work in a collective manner. The lack of collective interaction as well as the collimating action of the organic film is responsible for the formation of an elongated crater.

The question arises, therefore, as to the cause(s) for such different behaviour of the C<sub>60</sub> projectile in LB films as compared to all other organic samples investigated so far by computer modelling. The main difference is in the geometrical structure of the overlayer. The LB overlayers are made of long, linear molecules that form an open and ordered network. In fact, each AA molecule occupies an area of almost 0.2 nm<sup>2</sup> [15,23]. Thus, the distance between the molecules (~0.47 nm) is comparable to the C<sub>60</sub> diameter. The samples irradiated in the previous studies were less open and more disorganized. As a result, in those systems, atoms composing the C<sub>60</sub> cluster begin to interact simultaneously with many sample atoms immediately after the impact. The cluster projectile impacting on the LB sample at directions close to the surface normal sees the organic layer as a low-density stockade with ends directed toward the cluster. As a result the interaction between the projectile and the LB film is spatially localized around small areas, and consequently, C<sub>60</sub> breaks into smaller pieces. The trajectories of these pieces can be subsequently collimated by the presence of open channels for as long as the impact angle does not differ too much from the channel axis.

As shown in Fig. 1, the sputtered flux is composed of intact and fragmented molecules. The ejection is quite efficient. The total



sputtering yield for 20 keV fullerene at normal incidence is  $\sim 200$  molecules from a 6 layer system. The experimental measurements made on an LB film of bariated arachidic acid at liquid nitrogen temperature show that approximately 230 molecules are ejected by a single 20 keV  $C_{60}$  at  $5^\circ$  impact [26]. This number is in very good agreement with the calculated value taking into account approximations of the computer model. The ejection efficiency depends on the overlayer thickness. As shown in Fig. 3, at the beginning the total sputtering yield increases to a maximum with the increase of the thickness, then decreases and finally saturates. A similar behaviour of the sputtering yield on the organic overlayer thickness has been observed experimentally for Ar bombardment of adenine overlayers [27], or, recently, in experiments on cluster depth profiling of cholesterol film in which the erosion rate of organic material increases as the profiling beam gets near the silicon/organic interface [28]. Two factors are responsible for this kind of behaviour. The first factor is the increase of the amount of the material available for sputtering from a thicker layer, for as long as the layer thickness does not exceed the depth of the active volume contributing to sputtering [29]. However, this factor could account only for an initial increase and finally leads to the signal saturation. The second important factor is the influence of the organic/inorganic interface. The metal substrate used in this study is dense and is composed of atoms heavier than the atoms composing the projectile. As a result, it can reflect the projectile atoms that arrive at the organic/metal interface back into the organic overlayer. The presence of such a process is clearly visible in Fig. 2. The organic/substrate interface can also reflect a part of already deposited energy that propagates vertically within the organic film. Both these phenomena will increase the density of the energy in the near-surface region which, in turn, will enhance ejection. As shown in Fig. 2, the role of the organic/substrate interface will decrease with the increase of the layer thickness. This is happening because both a larger number of projectile atoms will be stopped in the organic film before reaching the organic/substrate interface, and less of the backreflected energy will be stored in the volume that actually can contribute to sputtering. The maximum visible in Fig. 3 is, therefore, a result of interplay between these counter-acting phenomena. This interpretation is additionally supported by the observation that the position of the maximum depends on the

kinetic energy of the projectile. As apparent in Fig. 3, the position of the maximum shifts to thicker overlayers as the kinetic energy increases. This is a consequence of the increasing penetration depth of energetic projectile fragments, and a larger active volume available to contribute to sputtering [29]. The sputtering yield is also sensitive to the kinetic energy of the  $C_{60}$  cluster (not shown here). At the beginning the yield increases non-linearly with the kinetic energy. However, at the energy above 6.1 keV the yield scales linearly with the impact energy. Similar behaviour was observed in the experiment on LB films [15] and is theoretically predicted for cluster bombardment [29,30].

#### 4. Conclusions

Coarse-grained molecular dynamics computer simulations have been employed to investigate the sputtering process of a Langmuir–Blodgett multilayer of bariated arachidic acid composed of long, well-organized linear molecules induced by an impact of energetic  $C_{60}$  projectiles at normal incidence. The simulations indicate that the energy deposition pathways can be channelled by the geometrical structure of the overlayer. Although, a similar process is well known from sputtering of single crystals by atomic projectiles [25], it has not been anticipated to occur during  $C_{60}$  bombardment due to the large size of the projectile. An open and ordered molecular structure of LB films is responsible for such behaviour. Both the kinetic energy of the projectile and the layer thickness have a pronounced influence on the efficiency of the molecular ejection. Above a certain threshold of the kinetic energy, the sputtering yield increases linearly with the primary kinetic energy within the investigated energy range (up to 40 keV). For a constant primary kinetic energy the sputtering yield first increases with the increase of the film thickness, reaches the maximum and finally saturates. The position of the maximum shifts to thicker overlayers with the increase of the projectile kinetic energy. The presence of the maximum is a result of a competition between signal enhancement due to increasing number of organic molecules that can contribute to sputtering, and signal decrease due to lowering of the amount of the primary energy being backreflected into the organic overlayer by the receding organic/metal interface as the organic overlayer thickens. When the sample thickness becomes much larger than the penetration depth of the projectile, the sputtering yield is independent of thickness. The simulations indicate that the projectiles can penetrate deep into the Langmuir–Blodgett film. This unusually long penetration is a result of a channelling of projectile atoms by an ordered and open molecular structure. Large projectile penetration leads to a significant depth of ion-induced damage. This observation can explain the inability to depth profile Langmuir–Blodgett multilayers by  $C_{60}$  projectiles at normal incidence reported in [14,15].

#### Acknowledgments

The financial support from the Polish Ministry of Science and Higher Education programs No. PB 4097/H03/2007/33 and NN204 093535, and the National Science Foundation grant #CHE-0456514 are gratefully acknowledged.

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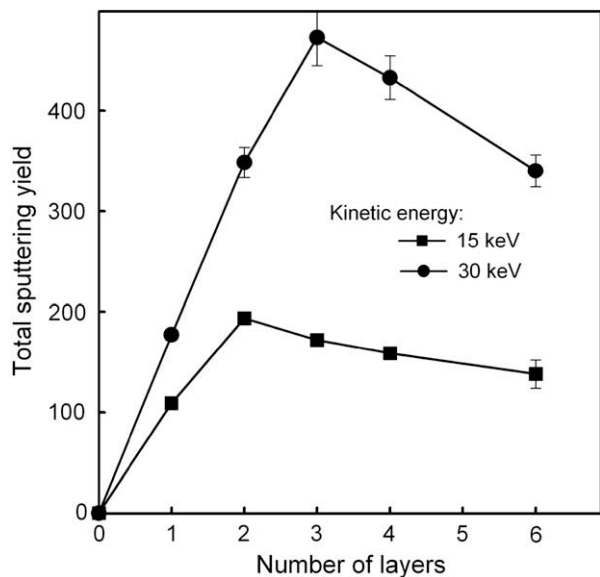


Fig. 3. The dependence of the total sputtering yield of organic material on the AA film thickness for 15 keV (circles) and 30 keV (squares)  $C_{60}$  projectile at normal incidence.

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