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Re-print of “Sputtering of polymers by keV clusters: Microscopic views of the molecular dynamics”☆

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ABSTRACT

This article reviews the results of molecular dynamics simulations of cluster sputtering of hydrocarbon polymers obtained in the last few years and expand them with unpublished data of Ar cluster bombardment. The targets are molecular solids of linear hydrocarbons, polyethylene and polystyrene, including a polyethylene substrate decorated with adsorbed globular macromolecules. The projectiles are (hydro)carbon and Ar_n clusters, from small to massive, as well as Bi_n and Au_{400} clusters. The study focuses on the dynamics of cratering and sputtering, using a coarse-grained representation of the samples, on the study of molecular fragmentation, crosslinking and free H formation, using a fully atomistic model, and on the conditions of desorption of macromolecules by massive clusters. The results explain the similarities and differences between several cluster types and sizes and, to a large extent, the sputtering yields of Ar_n clusters and their ‘universal’ dependence on the scaled cluster energy, as observed in the experiments. They also demonstrate the reduction of sample fragmentation and crosslinking when going to larger clusters and the incidence angle dependence of intact macromolecule emission. Recent experimental validations obtained in our laboratory are also introduced and comparisons with data obtained by other groups are discussed in order to present a more complete picture of the physics of cluster bombardment of organic solids and polymers.

1. Introduction

Sputtering by molecular projectiles, such as SF_6 [1], coronene and phenylalanine [2] or C_{60} [3], was introduced at the end of the 80s for the characterization of organic surfaces. Their ability to produce much larger numbers of characteristic and molecular ions than atomic projectiles was quickly recognized and, later on, depth profiling with retention of the molecular information was reported for molecular and polymeric films under SF_5^+ bombardment [4]. The application of massive clusters for organic surface analysis dates back to the same time period, when Mahoney et al. used massive supersonic water/glycerol clusters to produce secondary ion mass spectra of peptides [5–7]. In parallel, Beuhler and Friedman were conducting pioneering studies of sputtering with smaller water clusters [8] and Yamada was developing Ar cluster ion beams for materials modification and smoothing [9,10]. Gold nanoparticles have also been investigated as primary ions for SIMS [11]. However, it is only after the introduction of commercial cluster ion sources in ToF-SIMS instruments, that molecular and cluster primary beams have definitely replaced atomic ions for SIMS analysis and (molecular) depth-profiling [12–17]. The nano- and microdroplet approach pioneered with massive cluster impact, also developed into several new techniques such as desorption electrospray ionization (DESI) [18,19] and desorption ionization by charge exchange (DICE) [20,21], electrospray droplet impact (EDI) [22,23] or impact desolvation of electrosprayed microdroplets (IDEM) [24], which proved to be outstanding for large organic molecule ionization. The experimental aspects of the cluster secondary ion mass spectrometry of organics and polymers have been reviewed in detail in a review article (upto 2010) [25] and in a book (upto 2013) [26].

Theoretical studies using computer simulations have accompanied the experimental development of molecular and cluster beams aimed at maximizing sputtering/ion yields and minimizing damage in organic depth profiling. Some of these theoretical studies and the fundamentals of organic materials sputtering by clusters have been reviewed in recent articles and book chapters [27–29].

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The principle and concept of the sputtering yield enhancement by molecular clusters such as C_{60} was first explained by the molecular dynamics (MD) simulations of Postawa et al., though the model system was a silver crystal and not an organic material [30]. Generally speaking, clusters transfer their energy to the topmost layers of the target, inducing the formation of a crater and the emission of large numbers of atoms and/or molecules via a collective emission mechanism. This is in sharp contrast with keV atoms such as Ga, which implant deeper in the solid, inducing stochastic collision cascades that are rather inefficient for sputtering. Later on, the same research teams tackled the study of depth profiling by clusters, first for silver [31] and, recently, for an octane crystal, using a combination of MD simulations and a statistical sputtering model [32]. Concerning massive solvent clusters, the fragmentation of fast water nanodroplets on inorganic substrates and the impact desolvation mechanism of IDEM were also explained by MD [33–35].

In this article, we essentially review the results of computer simulations of cluster sputtering of hydrocarbon polymers conducted in our research team, often in collaboration with B.J. Garrison at Penn State University, and expand them with unpublished data of Ar cluster bombardment. The methodology of these studies is classical MD, using either a coarse-grained model (for the study of the dynamics cratering and sputtering) or a full atomistic representation of the target (for the study of crosslinking and free H formation). The results explain the similarities and differences between different cluster types and sizes and, in particular, the experimentally measured sputtering yields and their ‘universal’ dependence on the cluster velocity (or kinetic energy scaled by the cluster mass), the reduction of sample fragmentation and crosslinking when going to larger clusters and the conditions of intact macromolecule emission upon large cluster impact. Some experimental data recently obtained in our laboratory are also introduced and comparisons with results obtained by other groups are discussed when deemed relevant for the purpose.

2. Computer simulations

The molecular dynamics simulation program used in this study is the SPUT code especially developed by the group of B.J. Garrison at Penn State University for sputtering applications [27]. In the classical MD method, Hamilton’s equations of motion are numerically integrated over some time interval, providing us with the position and velocity of each particle at each time step. Forces among the atoms or particles in the system are derived from empirical interaction potentials.

The characteristics of the model targets used in this study are summarized in Table 1. For the investigation of impact dynamics, cratering and sputtering, the polymeric targets were coarse-grained, made of united atoms of CH_2 (14 amu) and CH_3 (15 amu), in order to reduce computational expense (samples 1 and 2). Sample 1 was an amorphous polyethylene (PE) solid containing $\sim 4 \times 10^5$ united atoms, where each molecule was a string of $97CH_2$ particles of 14 amu and capped with $2CH_3$ particles of 15 amu (1.4 kDa) [36]. The crystalline PE sample (2) consisted of a box with either 4.8×10^5 united atoms or 9.6×10^5 united atoms (used to compute ranges) forming aligned chains of PE arranged horizontally in the linear zig-zag configuration [37]. Each chain was formed of 200 individual CH_2 elements, with the particles at each end being held rigid. Sample 3 was hybrid, using a substrate made of sample 1 (coarse-grained) but carrying 5 polystyrene (PS61: 61 styrene repeat units) macromolecules described at the atomistic level [38]. For the study of free H formation, chemical reactions and crosslinking, a series of trajectories were also calculated using samples fully described at the atomistic level. These simulations were restricted to the beginning of the interaction and, therefore, smaller samples could be used. Sample 4 contained 400 short PE molecules (icosane) in an amorphous arrangement [39]. Sample 5 was an amorphous molecular sample made of 464 *sec*-butyl-terminated PS tetramers (PS4 [40]). The computations using samples 4 and 5 were restricted to the first picosecond and open boundary conditions were used in these simulations. Finally, sample 6 was a much larger molecular sample of PS4 containing 1.9×10^6 atoms. In the presented data, trajectories were run for 3 ps with this sample in order to investigate the crosslinking induced by irradiation [41]. For the targets, the interaction potentials were Lennard Jones potential functions for PE–PE intermolecular interactions, the AIREBO potential for the C—C and C—H interactions [42] and Morse potential functions for the intramolecular interactions in coarse-grained PE. Additional details about the sample potential parameters can be found in [43].

The (hydro)carbon molecular projectiles used in this study included coronene, C_{60}, polystyrene oligomers (PSX with $X = 4,16,61$ repeat units) [39] and a molecular nanodrop containing 4 PS16 and 104 trimethylbenzene molecules [44]. Among the hydrocarbon projectiles, there was a series of $(PS4)_y$ oligomer molecular clusters ($y = 4$, 16, 34, 66, 197), such as $(PS4)_{66}$ illustrated in Fig. 1. Other projectiles include Bi_n [45], $^*C_{60}$ with artificial atomic mass [46], Au_{400} [37] and Ar_n [47]. All the projectiles were modeled at the atomistic level, with hydrogen ^1H replaced by tritium ^3H for computational efficiency. The interaction potentials including the different projectiles were described in the corresponding references. They were aimed at the surface with normal incidence except when the effect of incidence angle was studied (Section 3.3). In the set of simulations involving $^*C_{60}$ bombarding sample 2, the atomic mass of the projectile was artificially varied (hence the “*” before the atomic symbol) to specifically investigate the influence of this physical parameter [46]. The chosen atomic mass values were 1, 12, 69, 98, 138 and 197 amu.

The simulations were run for 20 or 25 ps total time, up to saturation of the sputtered flux. Except for samples 4–5, the targets were surrounded by a zone of rigid atoms and a Langevin heat bath region to prevent pressure waves generated by the cluster projectile impacts from reflecting off the system boundaries and to keep the sample at the required temperature of 0 K [27].

Table 1
List of the model samples used in the simulations and their main characteristics.

Sample number	Description	Level of approximation[a]	Number of molecules	Formula	MW (amu)	Sample size (Å^3)
1	PE amorphous	Coarse-grained	4050	$C_{99}H_{200}$	1388	$301 \times 264 \times 153$
2	PE crystalline	Coarse-grained	2400/4800	$C_{200}H_{400}$	2800	$300 \times 250 \times 150/300 \times 250 \times 300$
3	PE amorphous + 5 PS oligomers	Coarse-grained + atomistic	4050 + 5	$C_{99}H_{200} + H(C_8H_8)_{61}C_4H_9$	1388 + 7402	$301 \times 264 \times 153 + 30 \times 30 \times 25$[a]
4	PE amorphous (icosane)	Atomistic	400	$C_{20}H_{42}$	366	$60 \times 60 \times 60$
5	PS amorphous	Atomistic	464	$H(C_8H_8)_4C_4H_9$	559	$75 \times 72 \times 80$
6	PS amorphous	Atomistic	24,500	$H(C_8H_8)_4C_4H_9$	559	$317 \times 317 \times 236$

[a] The PS molecules are globular but fit in a cube of these dimensions.