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MD-Based Transport and Reaction Model for the Simulation of SIMS Depth Profiles of Molecular Targets

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Supporting Information

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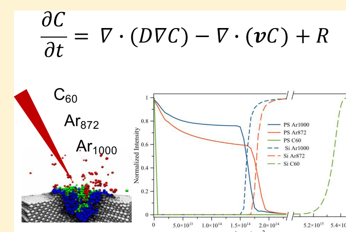
ABSTRACT: We present a novel theoretical approach allowing us to model erosion and chemical alteration of organic samples during depth profiling analysis by secondary-ion mass spectrometry with cluster projectile ion beams. This approach is able to take into account all of the cumulative phenomena occurring during such analysis, including ion-beam-induced reactions and atomic/molecular mixing by means of the numerical solution of an advection−diffusion−reaction (ADR) differential equation. The results from the single-impact molecular dynamics computer simulations are used as a source for the input parameters into the ADR model. Such an approach is fast and allows turning the phenomenological model into a more quantitative tool capable of calculating molecular secondary-ion mass spectrometry depth profiles. The model is used to describe phenomena taking place during depth profiling of polystyrene samples by 20 keV C_{60}, Ar_{872}, and Ar_{1000} projectiles. It is shown that theoretical findings are in good agreement with the experimental results. The model is also used to determine the overall efficiency of nitrogen monoxide molecules in eliminating the radicals responsible for polystyrene cross-linking induced by analyzing ion beams.



INTRODUCTION

In recent years, secondary-ion mass spectrometry (SIMS), a well-established technique for the characterization of solid surfaces and thin films of both inorganic and organic materials,[1,2] has undergone a drastic evolution, related to the introduction of polyatomic primary ion beams,[3] which boosted new perspectives in the analysis of organic materials and polymers. A big effort has been made to model the impact of primary cluster ions on the organic target by means of molecular dynamics (MD) simulations.[4−9] These simulations are used to model the phenomena involved in an individual cluster-target impact that typically occurs over a time scale of the order of a few tens of picoseconds.[10] In some aspects, MD simulations can be considered as the theoretical counterpart of static-SIMS experiments. In contrast, the theoretical modeling of the physicochemical phenomena occurring during dynamic-SIMS (D-SIMS) depth profiling of organic and polymer targets under cluster ion beams is less developed.

In modeling D-SIMS experiments, time scales much larger than those involved in MD simulations must be considered to take into account slower and cumulative phenomena. Such phenomena, including ion-beam-induced reactions and atomic/molecular mixing, can substantially modify the nature of the target. Wucher et al.[11,12] were the first to develop a model (statistical sputtering model, SSM) aimed to correlate the information obtained from molecular dynamics simulations to depth profiles. Additional models based on the SSM concept appeared later.[4,5] However, all of these approaches were computationally intensive. Recently, we simulated D-SIMS experiments by means of the numerical solution of an advection−diffusion−reaction differential equation.[13] Such a transport−reaction (TR) model takes into account the effects of ion-beam-induced mixing and reactivity, which occur during the depth profiling experiments. This model is able to simulate a complete D-SIMS experiment without requiring large computational capabilities. The values for the model input parameters can be estimated either from experimental data, as in our previous work, or from the output of computational simulations. Recently, it has been shown that the results of MD simulations can be used successfully for determining these parameters in the case of nonreactive inorganic samples.[14] In this paper, we present the integration of MD simulations results into the transport−reaction model for depth profiling of polymer films, also in the case when ion-beam-induced chemical damage cannot be neglected. The MD simulation outputs are used as input parameters into the model. This allowed us to turn the previously reported phenomenological transport−reaction (TR) model into a quantitative model for the prediction of molecular D-SIMS depth profiles by the MD results. Henceforth, we call this model MD-TR.

EXPERIMENTAL METHODS

The molecular dynamics (MD) computer simulations are used to model cluster bombardment of polystyrene, silicon, and diamond surfaces by 20 keV C_{60} at a 45° impact angle. Briefly, the motion of the particles is determined by integrating Hamilton's equations of motion. The forces among carbon atoms in the system are described by the ReaxFF-lg force

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field,[15] which allows for the creation and breaking of covalent bonds. This potential is splined at short distances with a ZBL potential[16] to describe high-energy collisions accurately. The forces among Si−Si are described by the Tersoff-3 potential.[17] The interactions between Ar atoms in the projectile and between the projectile atoms and all other atoms in the systems are represented by the Lennard-Jones potential splined at short distances with the KrC potential,[18] which is better than ZBL to describe energetic collisions of noble gas atoms. Energetics of bond breaking, essential for our studies (C−H or C−C bond cleavage), was calculated with the ReaxFF potential. The values were compared with the reference data to verify whether this potential gives correct predictions. The results are presented in the Supporting Information. We observe some deviations between the bond energies predicted by ReaxFF and the reference data. However, the differences always remained below 10% of the reference data.

A detailed description of the MD method can be found elsewhere.[19] The shape and size of the samples are chosen based on visual observations of energy transfer pathways stimulated by impacts of C_{60} projectiles. As a result, hemispherical samples with diameters of 40, 32, and 26 nm for polystyrene, silicon, and diamond, respectively, are used. These samples contain 1 621 182, 432 449, and 823 719 atoms. The calculated densities of these samples are 1.097, 2.334, 3.54 g/cm^3 and agree well with the experimental values of 0.96−1.04, 2.33, and 3.5−3.53 g/cm^3 for polystyrene, silicon, and diamond, respectively. Rigid and stochastic regions near the external boundaries of the sample with thicknesses of 0.7 and 2.0 nm, respectively, were used to simulate the thermal bath that keeps the sample at the required temperature to prevent reflection of pressure waves from the boundaries of the system and to maintain the shape of the sample.[20,21] The simulations are run at the 0 K target temperature in an NVE ensemble and extend up to 50, 20, and 20 ps for polystyrene, silicon, and diamond, respectively, which is long enough to achieve saturation in the ejection yield vs time dependence. Impacts of 20 keV C_{60}, Ar_{872}, and Ar_{1000} were modeled at a 45° incidence angle relative to the surface normal to comply with the experimental conditions used in ref 22. The two different Ar clusters, differing about 10% in size, were chosen to get an idea on the possible effects of non-monodisperse size distribution of the clusters since in real experiments clusters exhibit a distribution around the nominal size. Simulations are performed with the Large-scale Atomic/Molecular Massively Parallel Simulator code,[21] which was modified to describe sputtering conditions better. Numerical solution of the equation involved in the proposed model was performed by means of a Python-based script, developed on purpose. We simulated the D-SIMS depth profiles of 100 nm-thick PS thin films deposited onto a Si substrate. The primary ion beam current was 1 nA, rastered over 500 × 500 μm^2. Experimental results have been replicated as in ref 22.

RESULTS AND DISCUSSION

In the MD-TR model, the position of the bombarded surface is kept invariant so that the erosion process is represented as a "travel" of the underlying material toward the surface. The sputtering rate is represented by the travel velocity (**v**) of the inner target layers toward the surface. When the material moving toward the surface enters the layer altered by the ion beam, it is redistributed by ion-beam mixing and, also, ion-beam-induced chemistry is triggered. The partial differential equation describing the evolution of the concentration profile, **C**(z,t), of a certain species during a sputter-profile experiment can be written as

$$\frac{\partial C}{\partial t} = \nabla\cdot(D\nabla C) - \nabla\cdot(vC) + R \tag{1}$$

where **C** is the volumetric atomic concentration of the species composing the target material, expressed in atoms/nm^3. If the sputtering area is kept constant during the simulations, only the traveling direction **z** (normal to the surface plane) must be considered; thus, the unit of **C** is atoms/nm. For the reconstruction of the depth profile, the model is using the so-called sampling depth, which takes into account the fact that atoms ejected by a single projectile impact can be initially located also below the surface. SIMS intensities ($I(t)$) are calculated by the following equation

$$I(t) \propto \int_0^\infty C(z,\ t)\cdot e^{-z/(\lambda)}dz \tag{2}$$

where λ is the extent of the sampling depth distribution, which is known to be of the order of interatomic distances.

The quantity (**v**) is equivalent to the erosion rate expressed in nm/s. If we express the flux (φ) of projectiles in ions nm^{-2} s^{-1} and the volumetric sputtering yield (**Y**) in nm^3/projectile, we can write

$$v\left[\frac{\text{nm}}{\text{s}}\right] = Y\left[\frac{\text{nm}^3}{\text{projectile}}\right]\cdot\varphi\left[\frac{\text{projectile}}{\text{nm}^2\text{s}}\right] \tag{3}$$

The dominant quality of the transport and reaction model is the capability to simulate depth profiles of reactive target layers, such as those constituted by organics or polymers. For example, during depth profiling of the organic target by monatomic beams or during the bombardment of polystyrene-like polymers by means of C_{60} primary beams, the intensity of fragments characteristic of the original polymer is readily lost.[23] Even in the case of sputtering of thick samples by means of large argon clusters, damaging is not negligible so far.[24]

Focusing on the specific case of the depth profiling of a polystyrene layer deposited onto a silicon substrate, based on the simplified assumption that the instantaneous erosion rate is equal to the weighted mean between the erosion rates of the intact and fully damaged material, we can write

$$v = v_{PS}C_{PS} + v_c C_{damage} + v_{Si}C_{Si} \tag{4}$$

where v_{PS}, v_c, and v_{Si} are the erosion velocities of the pristine polystyrene, damaged material, and silicon substrate, respectively. C_{PS}, C_{damage}, and C_{Si} are the normalized relative concentrations of target atoms that, inside the altered layer, pertain to undamaged polystyrene repeating units, to the damaged material, and to the silicon substrate, respectively. In the present application of the MD-TR model, the volumetric sputtering yields of Y_{PS}, Y_c, and Y_{Si} are obtained by MD simulations performed on polystyrene, diamond (chosen as a representative of the fully damaged, carbonlike material formed upon beam irradiation), and silicon, bombarded with C_{60}, Ar_{872}, or Ar_{1000} projectiles. It should be noted that the choice of diamond as a representative of a fully damaged polymer is probably too extreme, while an amorphous carbon or a:C−H cross-linked network would be more realistic. However, the generation of a truly amorphous system for MD simulation is very difficult and, on the other hand, the good agreement of

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our MD-TR simulations with experimental results (see infra) indicates that the choice of diamond is acceptable.

The volumetric sputtering yield values, calculated by MD simulations, are reported in Table 1.

Table 1. Volumetric Sputtering Yield (nm^3/ion) from MD Simulations

	C_{60}	Ar_{872}	Ar_{1000}
PS	84	99	93
Si	6	2	0.8
diamond	1.9	0.011	0.011

The quantity **D** in eq 1 is a function that takes into account the ion-beam-induced mixing in the altered layer region. In the present simulation, surface roughening is neglected. The mixing term **D** in eq 1 is related to the ion-beam-induced motion of particles in the collision cascade, which can be described by analogy with the self-diffusivity process. Strictly speaking, we should also consider the lateral component to the diffusion. In simulating a depth profile of a laterally homogeneous system, however, we can neglect the lateral component and, consequently, the model is reduced to a unidimensional one along the traveling direction **z** (normal to the surface plane). By analogy with the unidimensional random walk model for diffusion, the units of **D** is nm^2/s. To extract the per impact ion-beam-induced diffusion (D') from the MD simulations, we divide each simulated sample into the equally spaced slices along the z-axis. For each slice, we calculated a sum of the total square displacements along the z-axis of all atoms located initially in a given slice multiplied by the volume occupied by the displaced atom. For a slice i of a width dz at depth z_i, this can be expressed by the following equation

$$D'[z_i] = \sum_{j=1}^{N_i} \mathrm{d}z_j^2 V_j/\mathrm{d}z \tag{5}$$

where N_i is the total number of atoms in the given slice, dz_j is the total displacement of the jth atom along the z-axis, and V_j is the atomistic volume occupied by this atom calculated from a modeled sample density. Final diffusion can be obtained with a simple multiplication by the flux

$$D = D'\varphi \tag{6}$$

Figure 1 shows such distribution, obtained from simulations, after the impact of each primary ion (Ar_{1000}, Ar_{872}, and C_{60}) on the three target materials (PS, Si, and diamond, respectively). Note that, in the case of Ar clusters, a mass spread of ±10% does not have a significant impact on the D' distribution.

The function **R** in eq 1 incorporates beam-induced reactions occurring in the region involved in the interaction with the beam. Since the aim of the model is that of simulating the molecular depth profile, we are interested in estimating the evolution, with projectile fluence, of the surface concentration of the undamaged material. In view of this, **R** can be interpreted as a numeric function representing the sink of the reacted portion (C_{react}) of the original material in the simulated volume at each simulation step Δt. It is worth noting that at each iteration step of the simulation (involving the solution of the transport and reaction differential equation) the concentration of the unreacted material changes due to the formation of damaged material so that **R** will change with ion fluence.

We assume that the ion-beam-induced reactions occur in the same region where the beam-induced mixing is active. Thus, we write

$$R(z) = -\frac{D(z)}{\int_0^\infty D(z)\mathrm{d}z}\frac{\Delta C_{react}}{\Delta t} \tag{7}$$

where $\frac{D(z)}{\int_0^\infty D(z)\mathrm{d}z}$ is a factor representing the normalized numeric function D, obtained from MD simulations as described above. The negative sign accounts for the fact that **R** is a sink term, which decreases the amount of pristine material. To estimate the atomic fraction of material that underwent some modification, we count, at the end of the MD simulation, (i) the number of C−H bonds that were turned into C−C bonds (indicating the formation of cross-links during the time scale of the simulation) and (ii) the number of atoms that exhibit a number of bonds lower than those they had in the original polymer. The latter quantity provides an indication about the concentration of reactive species (such as radicals) that, in turn, can evolve in damaged material on a time scale longer than that considered in the MD simulation. Table 2 reports the atomic portion of the reacted material per single ion beam impact, in the case of C_{60}, Ar_{872}, and Ar_{1000} projectiles. Results indicate, in agreement with experimental results,[25−27] that C_{60} induces much greater damage into polystyrene compared to Ar clusters. We observe that the amount of atoms participating to newly formed C−C bonds or that remain reactive (carbon

Table 2. Atomic Portion of the Reacted Material per Single Ion Beam Impact

	C_{60}	Ar_{872}	Ar_{1000}
free H atoms	24	3	0
reactive carbon atoms[a]	675	180	104
C−H bonds converted to C−C	2	0	0
C_{react}	701	183	104

[a] C atoms that at the end of MD simulations display less bonds than the pristine material.

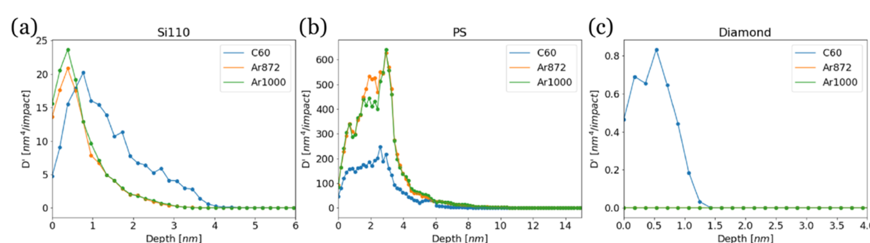

Figure 1. Distribution along the depth of ion-beam-induced diffusion stimulated by the impact of each primary ion (C_{60}, Ar_{872}, and Ar_{1000}) in (a) silicon, (b) polystyrene, and (c) diamond targets. Note that, according to MD results, the considered Ar clusters do not modify the diamond target.

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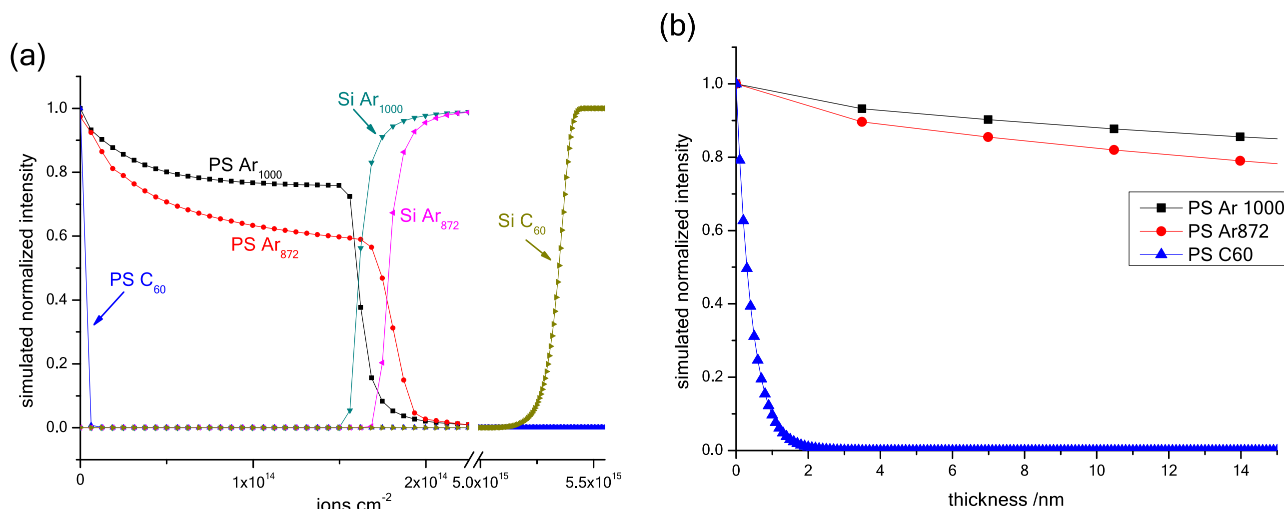


Figure 2. Simulated depth profiles of polystyrene on silicon obtained by Ar_{872}, Ar_{1000}, and C_{60} primary ions as a function of ion fluence (a) and depth (b).

atoms with "missing" bonds or free H atoms) represents a small fraction (0.512% for C_{60}, 0.057% for Ar_{872}, and 0.036% for Ar_{1000}) of the atoms that experienced the primary ion impact (please refer to Figure 1) and remained in the target at the end of the MD simulation (i.e., that were not sputtered away).

However, as we will see in the following (Figure 2), the 1 order of magnitude difference between C_{60} and argon clusters can account for the different behavior of the two kinds of a projectile in terms of damage since the reactive species (most of them, presumably, radicals) can produce cross-linking in polystyrene. This is consistent also with previous findings, obtained in a different experimental context, showing that a few ion-beam-induced cross-links can induce an irreversible sol−gel transition in polystyrene.[28−30]

As it is evident from the simulated profiles reported in Figure 2, the model is able to reproduce the essential characteristics of the experimental profiles,[25] namely, the initial drop of molecular signal intensity, which is very pronounced in the case of C_{60} and much lighter in the case of the largest argon cluster, as well as the strong differences in the primary ion dose needed for reaching the interface.

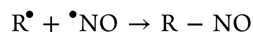
Table 3 reports the average volumetric sputtering yields for a 100 nm-thick PS film, obtained by means of the MD-TR model using the rise of the substrate signal. Considering that the single-impact sputtering yields (as obtained from MD simulations, see Table 1) are rather similar for C_{60} and the two considered Ar clusters, it is clear that the much smaller average sputtering yield obtained in the case of C_{60} is due to the damage produced in the target by C_{60} ions. The value of 2 nm^3/ion obtained by the MD-TR model for polystyrene sputtering with C_{60} primary ions is in reasonable agreement with the experimental finding of 0.5 nm^3/ion for PS[25] and <0.2 nm^3/ion for a similar system.[26] In other words, the MD-TR model is able to fill the gap between the experimentally determined yields and those calculated by MD simulations, thanks to the introduction of the reactivity term. Interestingly, also in the case of Ar clusters, the MD-TR model gives rise to lower average sputtering yields (ca. 30 and 7% lower than those reported in Table 1 for Ar_{872} and Ar_{1000}, respectively), but in reasonable agreement with the figures (107 nm^3/ion for Ar_{872} and 94 nm^3/ion for Ar_{1000}) obtained by extrapolation, according to the equation proposed by Seah,[32] of experimental data obtained by Rading et al. in slightly different conditions.[25] Also, the predicted trend of reduction of sputtering yield (larger for the smaller cluster) is in agreement with the expected increase of damage at higher energy per component atom of the cluster. Moreover, we observe that a deterioration of the depth resolution at the interface accompanies the case (C_{60} projectile) where large damage accumulation occurs, as observed in systems with PS-like behavior.[26]

Table 3. Volumetric Sputtering Yields (Average) and Depth Resolution Calculated by the MD-TR Model for a 100 nm-Thick PS Film

	C_{60}	Ar_{872}	Ar_{1000}
Y (nm^3/ion)	2	77	87
depth resolution (nm)[a]	118	16	19

[a]Depth resolution was calculated by the usual[31] 16−84% intensity method.

According to Table 2, the main contribution to the ion-beam-induced damage is the production of reactive species such as H atoms or C species with "dangling bonds" that may undergo successive reactions. In the case of polystyrene, these reactions produce an increasingly cross-linked material. Many of these reactive species can be regarded as radicals. Recently, some of us demonstrated that nitrogen monoxide (NO), a well-known radical scavenger, is able to reduce strongly the damage of PS-like polymers in C_{60}-SIMS depth profiling experiments.[22,26] Since the MD-TR model can include any chemical reaction occurring inside the altered layer, we included NO radical scavenging. We assumed that the reactive radical species $R^{\bullet}$ produced during a cluster impact, whose amount is estimated from the MD simulation (see Table 2), are quenched by the reaction with NO molecules with the formation of stable, unreactive species



$$R^{\bullet} + {}^{\bullet}NO \rightarrow R - NO$$

accordingly to a 1:1 stoichiometry. Thus, eq 5 becomes

$$R(z) = -\frac{D(z)}{\int_0^{\infty} D(z)\mathrm{d}z}\frac{\Delta(C_{react} - C_{NO})}{\Delta t} \quad (8)$$

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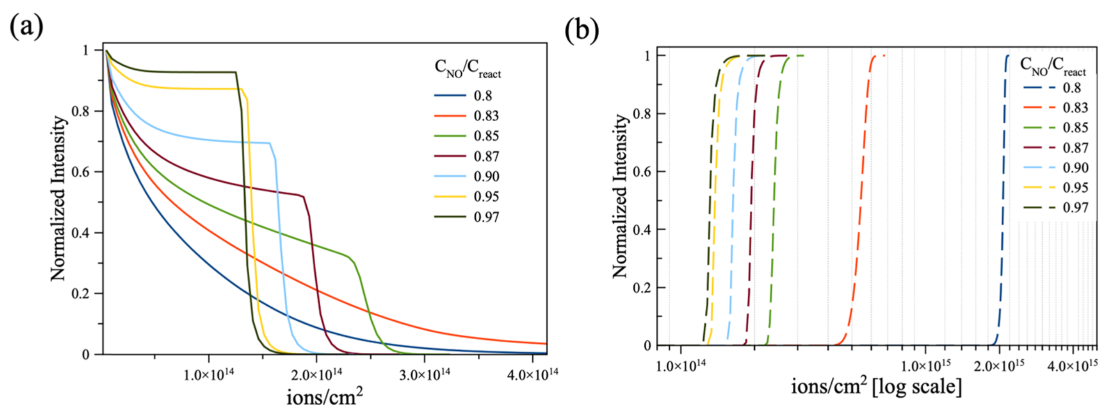

Figure 3. Simulated C_{60}-SIMS depth profiles of a 100 nm-thick film of polystyrene on silicon. Polystyrene (a) and silicon (b) intensities were calculated at different levels of C_{NO}/C_{react} ratios.

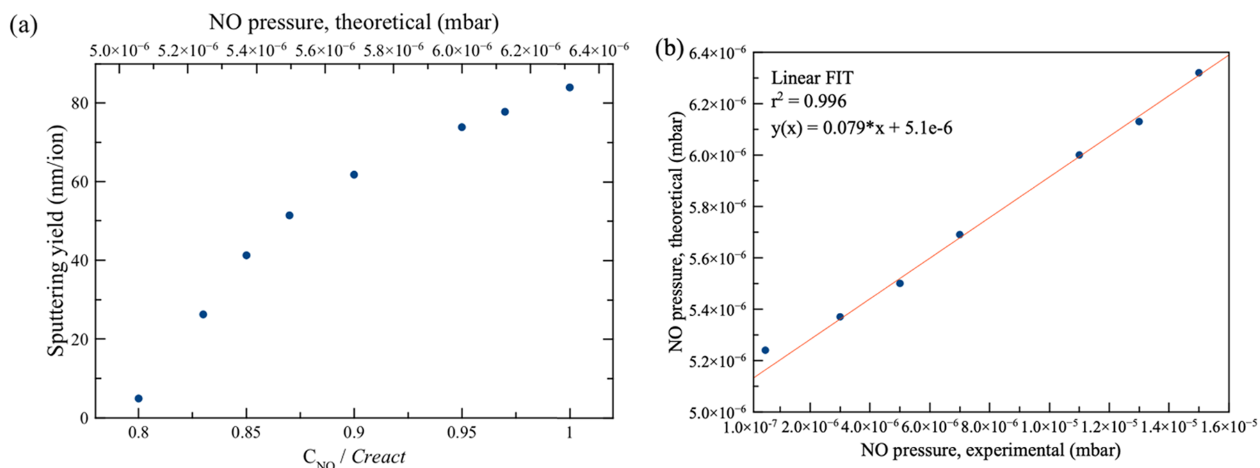

Figure 4. (a) PS sputtering yield (20 keV C_{60} projectile) as a function of C_{NO}/C_{react}. The top X-axis shows the NO partial pressure computed as described in the main text. (b) Linear regression of the theoretical to experimental NO partial pressure.

where C_{NO} represents the number of nitric oxide molecules reaching the surface during the simulation step Δt.

Figure 3 reports the simulated depth profiles of silicon and polystyrene in the case of C_{60} projectiles at various C_{NO}/C_{react} ratios. For the sake of simplicity, we assumed that (i) the probability that a NO molecule reacts with a beam-produced radical is unitary and (ii) such probability is independent of the location of the radical inside the (remaining) modified material. Also, we assume (iii) that the quenched macromolecular radicals will continue to behave, under ion impacts, in the same way as the original polymer.[13]

In agreement with the data obtained in NO-assisted C_{60} depth profiling of PS and PS-like polymers,[22,26] simulation shows that the higher the NO amount, the faster the erosion process and the better the shape of the molecular depth profile of PS.

To correlate theoretical findings with experimental results, we estimated the number of NO molecules hitting the surface per time unit by means of impingement rate at several NO pressures

$$\frac{\text{molecules}}{\text{cm}^2\text{s}} = \frac{N_A P}{\sqrt{2\pi MRT}} \tag{9}$$

where N_A is Avogadro's number, P is the NO partial pressure in the analysis chamber, M is the NO molar mass, R is the ideal gas constant, and T is the temperature.

Figure 4a shows the trend of PS sputtering yield as a function of the NO/radical ratio as obtained from the simulation. In the same figure, the top X-axis shows the corresponding NO partial pressures, computed according to eq 9. In Figure 4b, we report the correlation between theoretical and experimental pressures needed for obtaining the same sputtering yield volume. In the range of NO pressures considered, correlation is linear, with a slope of about 0.1. This means that to obtain a certain effect on the sputtering yield the experimental NO pressure must be increased about 10 times more than expected from the simulation. We believe that this discrepancy is related to the approximation that NO molecules can access quantitatively all of the radicals produced in the altered layer so that the predicted overall efficiency of NO in "killing" the radicals is overestimated (unity instead of ca. 0.1). Also, we must note that the linear correlation between calculated and experimental NO pressures is verified when significant amounts of NO ($C_{NO}/C_{react} > 0.8$) are considered. Indeed, the nonzero value of intercept in Figure 4b has no physical meaning and it indicates that the linear behavior cannot be extrapolated at very low NO pressures. Clearly, although the qualitative agreement between the previsions and the experiment is promising, additional elaboration and refinements are needed on this point.

In conclusion, the integration of the results of molecular dynamics simulations in a transport/reaction model was used

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for the prediction of the SIMS depth profile. In particular, the model allows the simulation of the SIMS depth profiles of organic samples under cluster primary beam irradiation and is able to take into account ion-beam-induced reactions and the effect of reactive gas dosing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b01653.

List and energetics of the selected chemical reactions essential for our studies leading to C−H or C−C bond cleavage calculated with the ReaxFF potential (PDF)

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Notes

The authors declare no competing financial interest.

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