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Polymer-matrix nanocomposites bombarded by large Ar clusters and low energy Cs ions: Sputtering and topography development

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In secondary ion mass spectrometry, hybrid materials such as organic matrices loaded with inorganic nanoparticles (NPs) are notoriously difficult to depth profile with any known ion beam, including large Ar clusters, although they display excellent performance with pure organic materials and polymers. To improve their understanding of the detrimental effects of the hybrid material nature on depth profiling, a precise evaluation of the sputtering and roughness induced upon Cs ion and Ar cluster beam bombardment of a series of composite samples was performed. For this purpose, the authors focused on the sputtering of a selection of extruded, hot-pressed polymer-matrix nanocomposite films by large Ar clusters (20 keV Ar_{1000}^{+} –20 eV/at and 10 keV Ar_{3000}^{+} –3.3 eV/at) and low energy (500 eV) Cs^{+} ions. The selected sample coatings were pure polycarbonate (PC; reference), PC with 5 wt. % graphene nanoplatelets, PC with 5 wt. % Fe_3O_4 magnetic nanoparticles (MNPs), and PC with 10 wt. % graphene oxide decorated with similar MNPs. The original surfaces and crater bottoms obtained after a fixed ion dose were carefully analyzed by stylus profilometry and atomic force microscopy in order to extract crater depth, sputtering yield, and roughness values. The main observation is that the crater roughness strongly increases in all cases when NPs are mixed with the polymer. However, there are specific behaviors depending on the NP inclusion types and the chosen primary beams. The observed effects are tentatively explained on the basis of fundamental studies of atom and cluster-induced sputtering.

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I. INTRODUCTION

Large gas cluster ion beams ($\text{Ar}_{500-5000}^{+}$) have gradually replaced atomic and small cluster ion beams for the depth profiling and 3D imaging of organic or biological specimens and multilayers in SIMS (Refs. 1–5) and XPS.^{6,7} As was noticed in the early reports, their decisive advantage over other primary ion beams is that the molecular integrity of the samples is essentially retained upon etching of organic solids.^{8,9} However, it is now clear that Ar cluster depth profiling of hybrid organic-inorganic multilayer stacks or composite samples is problematic.¹⁰ Blending materials of different atomic mass and cohesive energies at the micro- or nano-scale usually results in preferential sputtering,¹¹ roughening of the sputtered area, and enhanced mixing of heavy atoms in the soft organic matrix.¹² In the particular case of nanocomposites,¹³ the erosion rate and the induced roughness are expected to be affected by the presence of nano-objects in the matrix, while the respective surface concentrations of the involved materials may vary during the sputtering. The particularly strong variation of the sputtering yields for different materials observed upon Ar cluster bombardment^{14,15} is certainly a major cause of problems, but maybe not the only one. Because hybrid materials are being increasingly developed for various applications including protective coatings, organic electronic devices,^{10,16} fuel cells,¹⁷ photocatalysts,¹⁸ biomaterials, or metamaterials,¹⁹ finding solutions for their 3D molecular analysis by SIMS is an important and timely

challenge. As a first step in that direction, this study quantifies the sputtering and crater roughening observed upon depth profiling of a series of organic matrix nanocomposite films using different primary beam conditions, large Ar cluster ions with “low” (3.3 eV) and “high” (20 eV) energy per atom (E/n), as well as 500 eV Cs^{+} atomic projectiles. Different types of nanoparticles are considered, including graphene nanoplatelets (GNPs) and metal oxides, in order to evaluate the effect of the inclusion nature on the sputtering. Polycarbonate (PC) constitutes the composite matrix. The depth profiling of PC is feasible with Ar clusters, but notoriously difficult with other cluster ion beams such as SF_5^{+} or C_{60}^{+} . The obtained organic matrix nanocomposites find applications as frequency selective microwave absorbers.^{13,19,20}

II. EXPERIMENT

A. Samples

The samples consisted of a MakrolonTM PC reference (OD2015 from Bayer), PC mixed with magnetite (Fe_3O_4) nanoparticles (MNPs), PC mixed with GNPs, and PC with 10 wt. % hybrid nanoparticles (NPs) which consist of graphene oxide decorated with magnetite. The details concerning the samples loaded with nanoparticles (MNP, GNP, and NP) are provided in Table I. Transmission electron microscopy (TEM) images of the MNPs and NPs are shown in Figs. 1(a) and 1(c). Preparation of these samples included the melt-mixing of the PC with the nanoparticle inclusions for 10 min at 250 °C using a corotating twin screw extruder DSM micro 15. The collected extrudates were then placed

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TABLE I. Characteristics of the nanocomposite samples.

Sample	Nature	Origin and description	Preparation
MNP	Unsupported Fe ₃ O ₄ (magnetite) nanoparticles	Synthesized at UCL using a direct coprecipitation method (details in Ref. 13)	5 wt. % in PC
GNP	Graphene nanoplatelets	TIMREX, BNB 90 from TIMCAL (Ref. 19)	5 wt. % in PC
NP	Graphene oxide decorated by Fe ₃ O ₄ nanoparticles	Synthesized at UCL using a solvothermal method (SOLV-A in Ref. 13)	5.99 wt. % GNP and 4.01 wt. % MNP in PC

into a mold with a thickness of 400 μm and hot pressed for 3 min. The resulting samples were all polymer thin films with the polycarbonate reference being a transparent film, and all others were an opaque black polymer film. A typical scanning electron microscopy (SEM) image of a GNP-containing PC sample prepared by this method is shown in Fig. 1(b). In order to avoid topography on the sample surface, the samples were then hot-pressed again for 1 min with a mirror-polished silicon wafer inserted between the metal mold and the sample.

B. Analysis methods

All ToF-SIMS measurements were carried out using a TOF.SIMS⁵ instrument (IONTOF GmbH) equipped with cesium, bismuth, and argon cluster sources. The sputtering beams consisted of 20 keV Ar₁₀₀₀⁺ (20 eV/at), 10 keV Ar₃₀₀₀⁺ (3.3 eV/at), and 500 eV Cs⁺, all of which were rastered over 600 $\times$ 600 μm^2 surface areas. The sputter beam current for the Ar₁₀₀₀⁺ clusters varied between 1.0 and 1.1 nA, and the Ar₃₀₀₀⁺ sputter beam current was in the range of 0.9–1.0 nA. The areic dose for all Ar cluster sputtering experiments was kept as close as possible to $1.7 \times 10^{15} \text{ cm}^{-2}$. The sputter beam

current for Cs⁺ varied between 37.8 and 40.0 nA. The areic dose for the Cs⁺ sputter beam was kept constant across the sputtering experiments, $1.0 \times 10^{17} \text{ cm}^{-2}$. The analysis sequences were conducted with a primary ion beam of 30 keV Bi₅⁺, using a raster size of 200 $\times$ 200 μm^2 . They were performed in the positive mode when Ar_n⁺ clusters were used for sputtering and in the negative mode for Cs⁺ sputtering since Cs implantation enhances negative molecular ions. For the analyses related to Ar cluster sputtering, the Bi₅⁺ areic dose was $8.71 \times 10^{11} \text{ cm}^{-2}$ for all samples, while under Cs⁺ depth profiling, it was $2.81 \times 10^{11} \text{ cm}^{-2}$.

A Dektak XT contact stylus profilometer (Bruker) with a 0.7 μm tip and a stylus force of 1 mg was used to measure the crater depth after sputtering. Each crater was analyzed by eight profiles (four per direction in two directions rotated by 90°). The profiles were leveled in the software to have the edges of the crater aligned and then analyzed using a cut-off value of 0.08 μm , providing the waviness profile and the R_{q(RMS)} profile.

For the topography measurement before and after surface bombardment, a Bruker Multimode Nanoscope V was used with NanosensorsTM PointProbe[®] Plus noncontact/tapping mode-high resonance frequency-reflex coating atomic force microscopy (AFM) tips in ambient air. The tapping mode measurements were completed in different resolutions in the same spot, starting with an analysis area of 10 $\times$ 10 μm^2 with two subsequent scan sizes of 3 $\times$ 3 and 1 $\times$ 1 μm^2 within the original 10 $\times$ 10 μm^2 scan. All images were scanned with a picture resolution of 512 $\times$ 512 pixels. This was repeated in three areas (on both the polymer surface and the crater bottom) to obtain an average roughness value. The images were corrected for surface tilt, and the three resolutions aligned and overlaid before having R_{q(RMS)} calculated for the image area using the GWYDDION software.

III. RESULTS

The depth profiles were obtained while following the most characteristic peaks for the investigated compounds. With Ar cluster sputtering, the positive mode was selected so that only positive ion fragments were traced. The main ion fragment followed for polycarbonate was C₉H₁₁O⁺ (m/z 135.07), while Fe⁺ (m/z 55.93) was chosen to measure the magnetite level. There were no specific peaks of the GNP as they could not be differentiated from the PC carbon signals. Other remarkable depth profile signals involved surface contamination from sodium (Na⁺ at m/z 22.99), fluorine (CF⁺ at m/z 31.06), and polydimethylsiloxane (SiO₂C₅H₁₅⁺ at m/z 147.08). However, all contaminants were localized in the

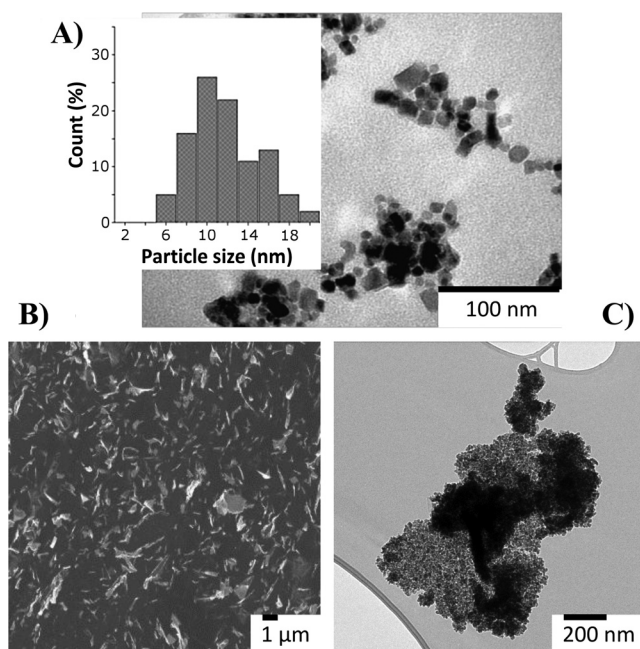


Fig. 1. Micrographs of the samples and nanoparticles. (a) TEM micrograph of the MNPs; Inset: histogram showing the size distribution of the MNPs. (b) SEM micrograph of the GNPs embedded in polycarbonate. (c) TEM micrograph of the MNP-decorated graphene oxide.

topmost layer and were quickly removed in the first stage of the depth profiles. The analysis sequences of the depth profiles performed using Cs as a sputtering beam were carried out in the negative mode, which favors PC but not so much the magnetite. The selected characteristic peak for PC was $\text{C}_8\text{H}_5\text{O}^-$ (m/z 117.03) and for magnetite, FeO^- (m/z 71.93).

As an illustration, Fig. 2 shows the depth profiles of the reference PC (a) and 10 wt. % NP samples (b) under 20 keV Ar_{1000}^+ bombardment and the depth profiles of the 10 wt. % NP sample under 10 keV Ar_{3000}^+ (c) and 500 eV Cs^+ bombardment (d). As was observed elsewhere for similar bombardment conditions, the reference PC profile is stable⁹ and there is no significant intensity for the iron peak. The 10 wt. % NP sample has a distinct iron peak signal which increases up to a maximum value as the depth profile proceeds, but with a different rate for 20 keV Ar_{1000}^+ and 10 keV Ar_{3000}^+ . The PC signal drops upon profiling for the 10 wt. % NP sample, more so when 20 keV Ar_{1000}^+ is used for sputtering (>1 order of magnitude). Obviously, the polymer becomes damaged in the latter bombardment conditions since the PC signal continues to decrease while the magnetite signal remains almost constant [Fig. 2(b)]. In the case of 10 keV Ar_{3000}^+ bombardment [Fig. 2(c)], the slighter decrease of the PC ion signal is compensated by the increase of the iron signal, which is consistent with an enrichment of the surface with inorganic nanoparticles, due to the much slower erosion rate of these particles in comparison with the polymer.

Under 500 eV Cs^+ sputtering, the PC and magnetite negative signals first increase quickly, due to the change in ionization probability accompanying the gradual inclusion of Cs in the surface. Then, the PC signal stabilizes, while the magnetite signal continues to increase at a much slower rate. Polymer damage does not seem to accumulate in this case.

The profilometry scans give an idea of not only the crater depth but also the topography across the length of the crater in a small profile. They are exemplified in Fig. 3 for the same samples and conditions as in Fig. 2. In general, NP loaded samples give much shallower profiles and larger roughness than the reference PC for the same sputtering dose, as will be summarized in Table II.

Figure 4 shows the 3D AFM images obtained from the bottom of the craters for the same samples and conditions as in Figs. 2 and 3. The scales for the images are locked to the highest and lowest points of the images. The reference PC sample has a much lower scale and roughness value than all the polymers that contain nanoparticles, illustrated here by the sample with 10 wt. % NP. Another feature common to all the nanoparticle-containing samples is that the topography created by 20 keV Ar_{1000}^+ bombardment reveals much broader peaks than that obtained with 10 keV Ar_{3000}^+ and 500 eV Cs^+ ions.

Table II summarizes the profilometry and AFM results, providing an overview of the crater depths and topographies for the full set of tested samples and bombardment conditions. The values concerning the Ar clusters all correspond to the same ion dose and can therefore be directly compared on that basis.

Several observations can be drawn from Table II. First, the crater depth values obtained with the reference PC correspond to sputter volumes of $74 \text{ nm}^3/\text{ion}$ for 20 keV Ar_{1000}^+ (20 eV/atom) and $18 \text{ nm}^3/\text{ion}$ for 10 keV Ar_{3000}^+ (3.3 eV/atom) bombardment. These numbers are consistent with the sputter volumes reported in the literature and fit well in the “universal curve” established for polycarbonate.¹⁴ Second, the nanoparticle-containing samples generally have smaller crater depths than the reference, especially for 20 keV

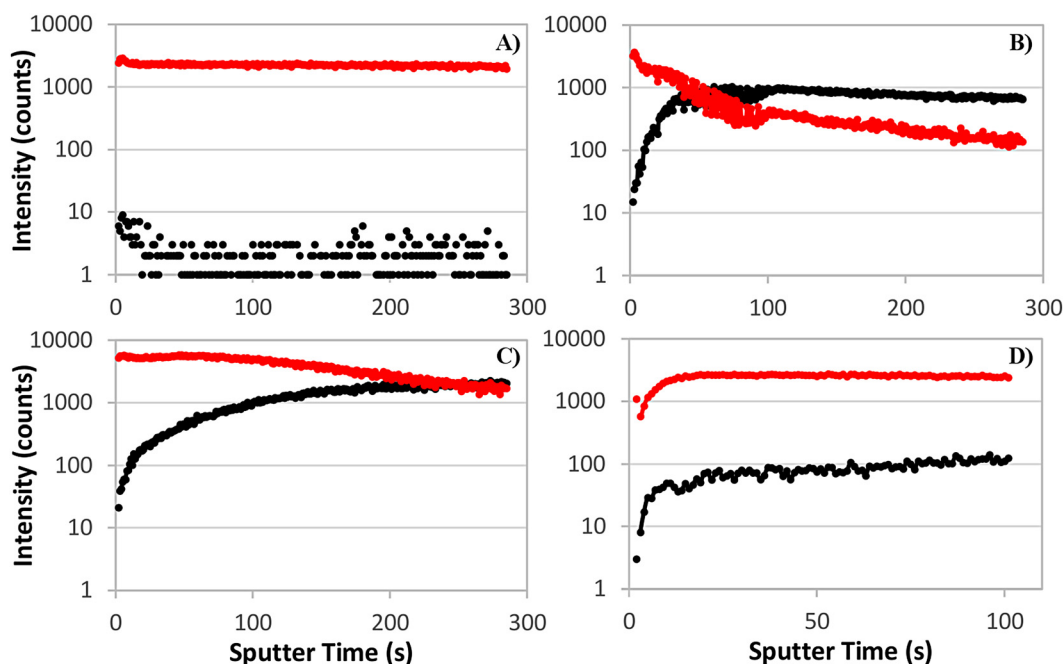


FIG. 2. (Color online) Depth profiles of pure PC (a) and PC with 10 wt. % NP [(b)–(d)]. The ion beams are 20 keV Ar_{1000}^+ [(a) and (b)], 10 keV Ar_{3000}^+ (c), and 500 eV Cs^+ (d). Gray (red online) indicates the polymer signal [$\text{C}_8\text{H}_5\text{O}^+$ in (a)–(c) and $\text{C}_8\text{H}_5\text{O}^-$ in (d)] and black the magnetite signal [Fe^+ in (a)–(c) and FeO^- in (d)].

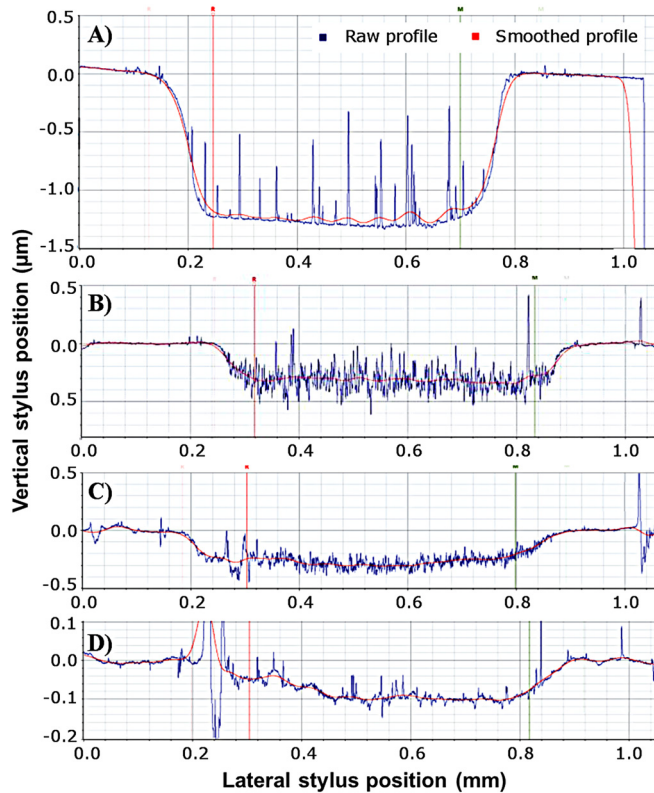


FIG. 3. (Color online) Profilometer linescans showing the sputtering crater cross-section in pure PC (a) and PC with 10 wt. % NP [(b)–(d)]. The ion beams are 20 keV Ar_{1000}^+ [(a) and (b)], 10 keV Ar_{3000}^+ (c) with a total areic dose of $1.7 \times 10^{15} \text{ cm}^{-2}$, and 500 eV Cs^+ (d) with a total areic dose of $1.0 \times 10^{17} \text{ cm}^{-2}$.

Ar_{1000}^+ bombardment and especially for samples where the nanoparticles contain graphene. The variation is less pronounced in the case of 10 keV Ar_{3000}^+ bombardment. Third, while the roughness remains similar to the original polymer surface after Ar cluster bombardment for the pure PC (around 1% of the crater depth), it is equal to or larger than $\sim 15\%$ of the crater depth for all the samples containing nanoparticles and for all the depth profiles obtained with 500 eV Cs^+ . In terms of samples, the 5 wt. % GNP surfaces behave worse, with a roughness exceeding 30% of the crater depth.

IV. DISCUSSION

The results indicate that Ar clusters degrade the polycarbonate when it is loaded with nanoparticles, at least in our experiments with the highest energy per atom of 20 eV

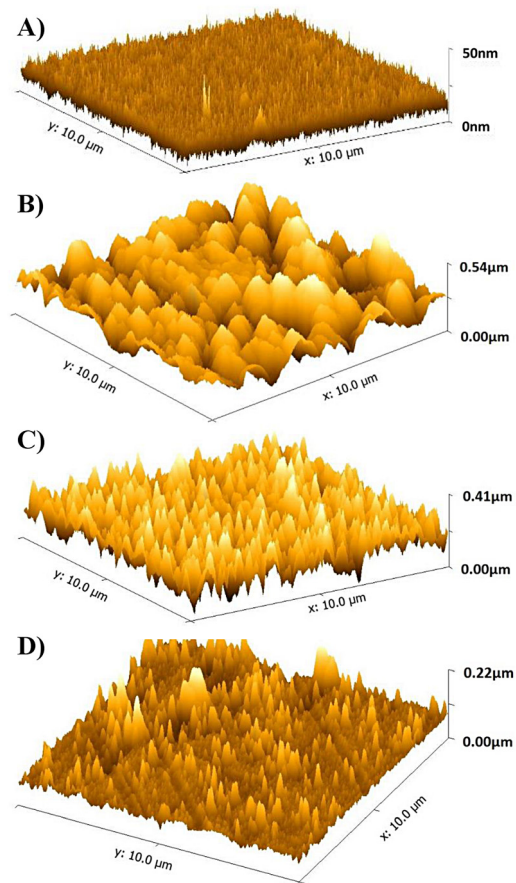


FIG. 4. (Color online) 3D AFM images taken in the sputtered area for pure PC (a) and PC with 10 wt. % NP [(b)–(d)]. The ion beams are 20 keV Ar_{1000}^+ [(a) and (b)], 10 keV Ar_{3000}^+ (c) with a total areic dose of $1.7 \times 10^{15} \text{ cm}^{-2}$, and 500 eV Cs^+ (d) with a total areic dose of $1.0 \times 10^{17} \text{ cm}^{-2}$.

[Fig. 2(b)], which is consistent with the expectation that higher energies per atom lead to higher degradation rates. The comparison of the profiles obtained for 10 wt. % NP [Fig. 2(b)], 5 wt. % GNP [Fig. 5(a)], and 5 wt. % MNP [Fig. 5(b)] also shows that degradation is more important for samples containing carbon-based particles. For instance, the intensities of the polymer signals obtained with 20 keV Ar_{1000}^+ from the 5 wt. % MNP sample decrease by a factor of 2–3 over the whole profile, suggesting limited damage [Fig. 5(b)], while those obtained for the GNP-containing sample decrease by a factor of 20–30 [Fig. 5(a)]. In the same conditions, the samples containing carbon-based particles exhibit the smallest sputter depth for a given primary ion

TABLE II. Depth and roughness of the sputtering craters.

	Depth (μm)				RMS roughness (nm) (% depth)		
	20 keV Ar_{1000}^+	10 keV Ar_{3000}^+	500 eV Cs^+		20 keV Ar_{1000}^+	10 keV Ar_{3000}^+	500 eV Cs^+
Reference PC	1.25 ± 0.03	0.31 ± 0.02^a	0.05 ± 0.01^a	4.2 ± 5.2	5.8 ± 4.8 (0.5%)	5.2 ± 2.4^a (2%)	19.1 ± 4.1 (38%)
10 wt. % NP	0.32 ± 0.02	0.25 ± 0.04^a	0.11 ± 0.02^a	3.4 ± 1.0	89.1 ± 19.5 (15%)	52.3 ± 6.1 (14%)	16.4 ± 4.2 (15%)
5 wt. % MNP	0.95 ± 0.06	0.37 ± 0.04	0.13 ± 0.05^a	4.3 ± 1.8	137.9 ± 45.5 (14%)	59.6 ± 12.2 (15%)	28.3 ± 4.2 (22%)
5 wt. % GNP	0.28 ± 0.03	0.23 ± 0.03	^b	3.1 ± 3.7	86.8 ± 18.4 (31%)	84.9 ± 29.7 (37%)	^b

^aNot all scan directions possible.

^bNo crater scans completed.

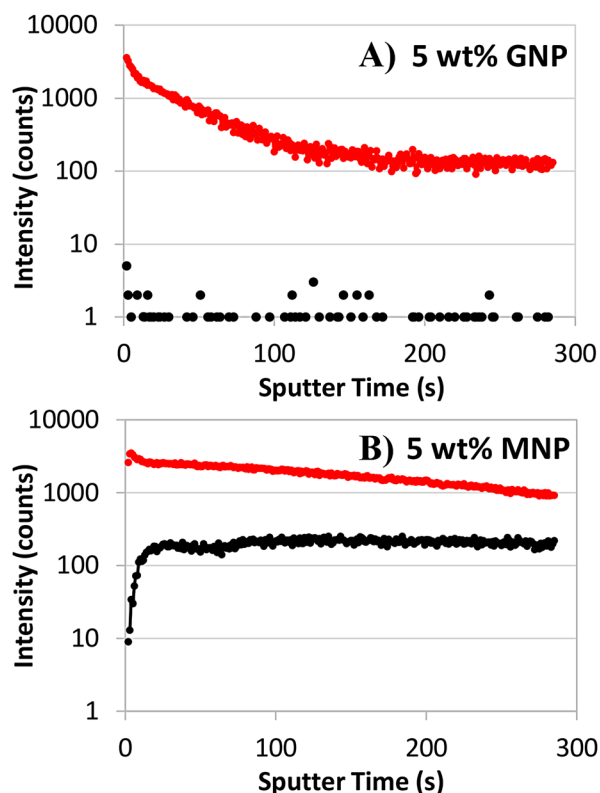


FIG. 5. (Color online) Depth profiles of PC with 5 wt. % GNP (a) and with 5 wt. % MNP (b) under 20 keV Ar_{1000}^+ bombardment. Gray (red online) indicates the polymer signal ($\text{C}_6\text{H}_{11}\text{O}^+$) and black, the magnetite signal (Fe^+).

dose as well as pronounced roughness, especially the 5 wt. % GNP sample. The concomitant reduction of the sputter yield and of the characteristic signals of the polymer leads us to speculate that the main damage mechanism might be crosslinking of the polymer triggered by the presence of the graphitic inclusions. Indeed, previous measurements^{21,22} and molecular dynamics simulations^{23,24} involving carbonaceous solids such as fullerenes demonstrated a strong tendency to crosslinking under cluster irradiation and, for Ar cluster bombardment, an increase in the crosslinking rate with the energy per atom in the cluster. In this hypothesis, it is plausible that the regions surrounding the carbon particles act as crosslinking centers and become more resistant to the beam, while other regions continue to sputter easily, leading to strong topography in the irradiated region. The effect of the magnetite nanoparticles in terms of damage to the polymer (Fig. 5) and reduction of the sputter yield (Table II) is much less pronounced. However, the presence of the MNPs also leads to topography, probably because of differential sputtering and possible aggregation of the metal preferentially left on the surface.

An alternative explanation for the polymer ion yield and the sputter yield decrease based on the accumulation of the carbon-based nanoparticles at the surface resulting from the differential sputtering between organic and inorganic materials cannot be excluded (preferential sputtering). However, it seems that this effect should be more pronounced under 10 keV Ar_{3000}^+ than 20 keV Ar_{1000}^+ because the difference between the sputter yields of organic and inorganic materials

is the largest at low energy per atom, while we observe the opposite trend (Table II).¹⁴ In addition, a comparable effect should be observed with iron oxide nanoparticles, and it is not.

In the case of Cs^+ bombardment, interestingly, the polymer and the metal-related signals remain constant for all samples beyond the initial transient corresponding to Cs implantation in the surface. This indicates that the initial damage caused by the energetic atomic ions quickly reaches a stabilization. In the aforementioned hypothesis of ion beam-induced crosslinking, the activity of Cs as a radical-scavenger, advocated in other works,²⁵ could explain this stabilization of the damage. In the hypothesis that crosslinking is negligible and preferential sputtering prevails, it would just reflect the smaller difference of sputter yields between organic and inorganic materials upon low-energy Cs bombardment. The beam-induced roughness, however, is also significant in these conditions, especially in relative terms (percentage of the sputtered depth in *italic* in Table II).

V. CONCLUSIONS

This investigation of polymer matrix nanocomposite depth profiling by SIMS shows that the sputtering of such sample results in significant topography development irrespective of the selected ion beam (Ar clusters, low energy Cs) and the type of inclusion (metal oxide, nanocarbons). However, carbonaceous nanoparticles, especially at high energy per atom (20 eV), seem to induce the additional problem of chemical damage that is reflected by the decrease of the polymeric matrix characteristic peaks. Our tentative explanation is that inclusions such as graphene nanoplatelets act as crosslinking centers and lead to the gradual degradation of the polymer as the sputtering proceeds. Highly crosslinked materials would in turn be harder to sputter, causing increased topography. Interestingly, cesium bombardment seems to prevent this degradation, but in that case, the topography development is significant for all samples, including the reference polycarbonate matrix. In order to provide a more complete assessment of the dynamics of the topography development, a detailed study as a function of the primary ion areic dose should be carried out. Nevertheless, our current results already indicate that alternative approaches such as beveling might be the only solution for retrieving molecular depth profiling information from such samples.

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