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SHORT COMMUNICATION

Time-of-flight mass spectrometry depth profiling of sodium-implanted polyethylene terephthalate

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Depth profiling analysis of sodium (Na)-implanted polyethylene terephthalate was performed by using time-of-flight secondary ion mass spectrometry in the cesium-attachment regime. A radical redistribution of the main element due to diffusion and escape of some elements, such as oxygen and hydrogen, and carbonization of a top 550 nm layer were observed. The depth distribution of the implanted sodium was found to be radically different from the "theoretical" distribution calculated by using the Monte Carlo simulation method (TRIM code). We conclude that it is possible to perform an effective depth profiling analysis of an implanted polymer in the "standard" secondary ion mass spectrometry regime without using a big cluster primary ion beam.

KEYWORDS

AFM, CsM$^+$, ion implantation, PET, SIMS

1 | INTRODUCTION

It is well known that ion irradiation of polymers results in a strong modification of a top surface layer composition with an escape of some gas-forming atoms from a polymer and carbonization of a near-surface layer.[1-4] These result in a strong modification of different mechanical, optical, and electrical characteristics of the implanted polymer. Despite the long-term study, there are still some unclear moments in polymer modification and in their restructurization caused by the ion irradiation. Probably, this happens because of the absence of an appropriate analytical technique, which can be used for a complex depth profiling of implanted polymers with a high depth resolution and high enough sensitivity. In the last decade, the time-of-flight mass spectrometry (TOF-SIMS) with different big cluster ion sources has found a wide application in organic chemistry. At the same time, different authors demonstrated a good depth profiling of polymers by a low-energy cesium ion beam sputtering.[5-7] In this report, we are going to show results of the quantitative and molecular depth profiling analysis of Na-implanted polyethylene terephthalate (PET) realized by using the TOF-SIMS in the well-known CsM$^+$ instrument regime.

2 | EXPERIMENTAL

Sodium was implanted into PET with an ion energy of 50 keV and an ion dose of 8×10^{15} ions/cm^2 by using a noncommercial implanter at the Southern Federal University, Rostov-na-Dony. The ion beam was limited by a special diaphragm, which resulted in an approximately

20×20 mm of implanted area. All depth profiling measurements were done with a TOF-SIMS 5 instrument from ION-TOF GmbH. We used a double beam mode: The ion sputtering of the analyzed surface was performed by a 500 eV cesium ion beam, whereas the analytical signal was monitored by using a pulsed Bi$_3^+$ cluster ion beam. Therewith, the cesium beam sputtered a 300×300 μm area and the bismuth beam scanned over 100×100 μm area in the center of the sputter crater. The secondary Cs$_n$M$_m^+$ (where M is the element or cluster of interest) cluster ions were used for quantitative analysis: CsM$^+$ for electropositive and Cs$_2$M$^+$ for electronegative elements. Other cesium-containing clusters were monitored for the chemical (molecular) analysis. The charging effect caused by ion irradiation of the polymer was compensated by using a 20 eV electron beam ("electron shower") with an electron beam current of around 17 μA. The experimental crater depth was measured by a Dektak XT stylus profiler. The quantification of experimental SIMS data (main elements) was performed with the chemical formula of the polymer: $(C_{10}H_8O_4)_n$ at the depth, where the polymer composition was not modified due to Na$^+$ ion irradiation. The surface relief of the polymer film was analyzed by atomic force microscopy before and after the ion irradiation. All measurements were done in the so-called tapping mode with a Solver Next microscope from NT-MDT.

3 | EXPERIMENTAL RESULTS AND DISCUSSION

Figures 1A to 1D show depth distributions of main elements and selected clusters in the Na$^+$ ion implanted area (A and B) in comparison

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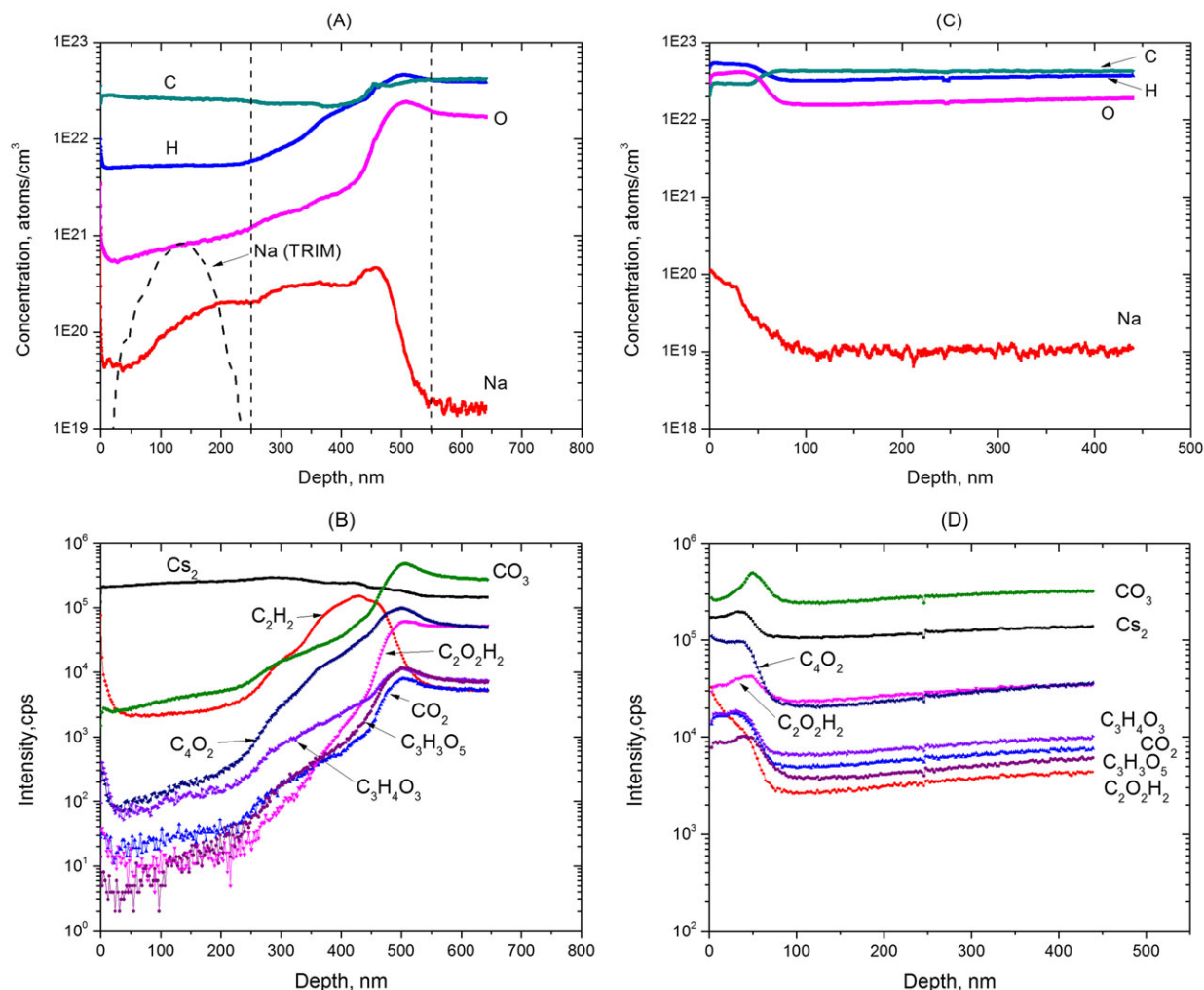
FIGURE 1 Time-of-flight secondary ion mass spectrometry (TOF-SIMS) depth profile of Na^+ implanted in polyethylene terephthalate (PET) A, in comparison with depth distribution of some molecules B, and in comparison with depth profile of main elements C, and molecules D, in the original polymer. All elements and clusters shown in depth profiles were monitored as Cs containing cluster ions

with the nonimplanted polymer (C and D). First of all, we can notice a strong difference between the experimental Na distribution and "theoretical" one obtained by the computer simulation by using the Monte Carlo method (TRIM-2008[8]). The theoretical sodium distribution is shown in Figure 1A by the dashed line. The difference between the experimental distributions and data of computer simulations was already noticed in literature for different polymers and different implanted elements.[1,2,4] We discuss below about possible reasons for this difference.

Second, the ion implantation results in a carbonization of the near-surface layer; this is a well-known effect as well.[1-4] The carbonization is caused by rupture of the majority of chemical bonds and emission of a part of oxygen and hydrogen as gases (like H_2 and probably CO and CO_2) from the near-surface layer of the polymer. In our experiment, the oxygen concentration in the top 250 nm layer decreased by 2 orders of magnitude and hydrogen concentration decreased 20 times. This experimental fact explains a radical decrease of the polymer resistivity (in some cases even by 10-15 orders of magnitude) observed experimentally.[1,2]

Third, we can identify 2 different layers at the surface formed after implantation that are marked in Figure 1A by vertical dashed lines: the carbonized layer (top 250 nm) and the transient region between the polymer volume and the carbonized layer. This layer can be denominated also as a "carbon cluster" layer because of the high-intensity C_2H_2 peak observed in it (see Figure 1B). In this transient region, we observe also the formation of the maximum of sodium. The formation of a carbon cluster in the implanted layer was suggested by different authors,[1-4] but without any specification. The depth of the cluster layer is defined by the primary ion energy dissipation.

Depth profiling analysis of the "molecular signal" was performed in both the original and implanted polymers (see Figures 1B and 1D). An essential part of the mass spectrum (or peaks with the highest intensity) is formed by $Cs_kO_l^+$, $Cs_kC_l^+$, and $Cs_kC_lO_m^+$ clusters. Hydrogen-containing clusters were observed as well, but with surprisingly low frequencies and intensities. Only few molecular fragments of PET ($C_kH_lO_m$) were found in the mass spectrum of both the implanted and original polymers.[9] This fact leads to the conclusion

about a strong depolymerization and rupture of the majority of chemical bonds during cesium and bismuth ion irradiation (during SIMS depth profiling analysis). To find the reason for the small number of hydrogen-containing clusters, we performed an analysis of the residual atmosphere in the analyzing chamber directly during the SIMS depth profiling by using a residual gas analysis (RGA) system. The time profile (P-t) of the partial pressure of H_2, CO, and CO_2 molecules was monitored (see Figures 2A and 2B). The start of the SIMS depth profiling is accompanied in the P-t profile by a remarkable increase in the hydrogen partial pressure (the left vertical arrow in Figure 2). It is important to note that the gas emission is observed during the SIMS depth profiling of both the original and Na-implanted areas. Partial pressures of CO and CO_2 during SIMS depth profiling increase too. We used the RGA system with a Faraday Cup as a detector of ionized molecules; this did not permit us to get a good detection limit for these gases. Then, we compared the effects of the ion irradiation of the polymer resulting from the 30 keV, 0.3 pA Bi_3^+ ion beam irradiation and the 500 eV,

45 nA Cs^+ ion beam irradiation and did not find any remarkable difference in the residual gas composition and partial pressures of emitted gases. This RGA experiment leads us to the conclusion that an essential part of hydrogen emits from ion-irradiated polymers as H_2 molecules, and therefore, we observe a limited number of molecular fragments in the SIMS mass spectrum.[4]

After all, we would like to give a brief "reconstruction" of different processes accompanying the implantation process and discuss possible reasons for a strong difference in sodium experimental and theoretical distributions observed. Ion bombardment results in rupture of the majority of chemical bonds between atoms in the polymer along the entire trajectory of the primary ion and during a complex track formation.[1-3] This process is accompanied by an escape of volatile elements from the polymer due to both a local heating and the radiation enhanced diffusion. The heating of a top surface layer depends, among other things, on the primary ion density; a very high ion density can result in an evaporation of a top surface layer of a polymer (the thermolysis effect). When the ion fluence exceeds approximately 10^{13} ions/cm^2, the single-track regime, where the individual primary ion tracks are isolated from each other, transforms into an overlapping regime.[2] This leads to formation of a top porous surface layer. The porous structure of the irradiated surface facilitates the escape of gas-forming atoms. The atomic density of the porous surface is low with respect to the original one; this, in its turn, leads to an essentially deeper penetration of the following implanted ions. At the same time, carbon clusters are accumulated at the irradiated surface. And, finally, when the ion fluence is high enough and all volatile elements have escaped from the polymer, a new carbonized structure with a relatively high density is formed. As a result, the complex final distribution of the implanted ions is formed, which includes different ion ranges corresponding to different steps of polymer surface modification described above. Moreover, the radiation-enhanced diffusion of elements forming the polymer as well as the implanted element occurs during the entire irradiation process; this explains the observed sodium distribution but generally complicates the interpretation of the experimental results.

Figure 1C shows the depth profile of a nonimplanted polymer. A top surface layer with a modified composition (reduced C and elevated O and H) is observed. This modification is caused by a special treatment of the polymer made to prepare a half-finishing product for a future fabrication of cine film. A high stability of the analytical signals during the depth profiling is evident in Figure 2B (please note that the shown experimental intensities were not normalized).

As the last step, we analyzed by atomic force microscopy the original polymer surface and the polymer surface after ion implantation (not presented here): In both cases, a smooth surface was measured with some insignificant details. Then, we compared the surface roughness of the sputtered crater bottom arising after the depth profiling performed in sodium-implanted and nonimplanted areas (see Figure 3). Three different analytical images were monitored: the surface height distribution, the phase, and the amplitude modulation contrasts. All 3 images show a strong difference between these 2 analyzed areas. For sodium-implanted area, we observe a structured surface; this suggests that the C_xH_y clusters observed in the SIMS depth profile (see Figure 1B) form a specific grain structure in the irradiated polymer
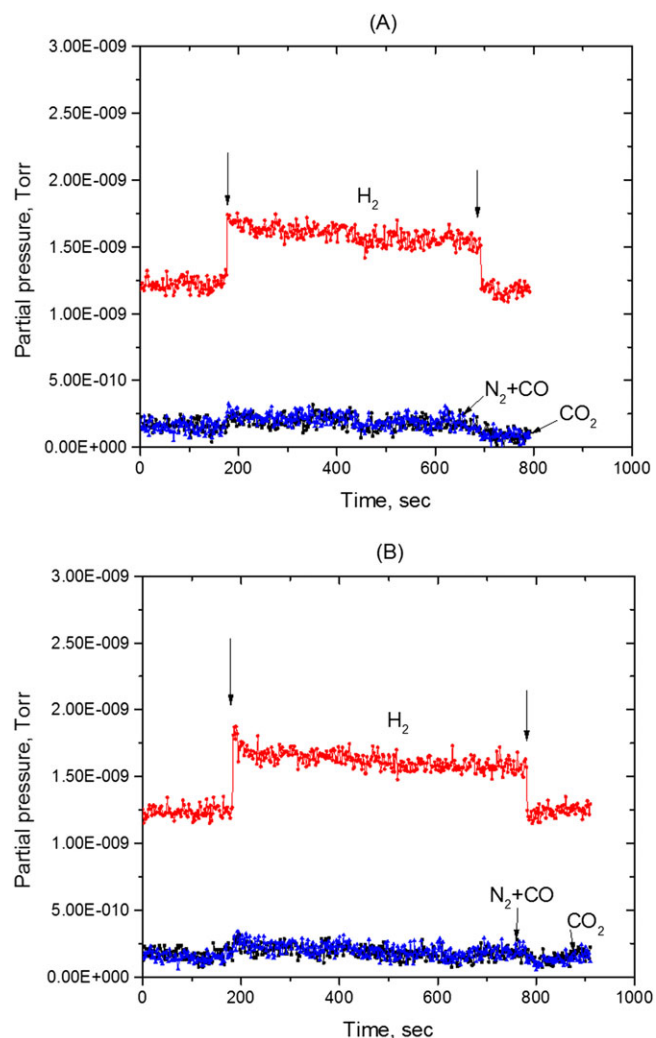
FIGURE 2 Partial pressures of H_2, CO (plus N_2), and CO_2 in the main chamber of the secondary ion mass spectrometry (SIMS) instrument during depth profiling of nonimplanted polyethylene terephthalate (PET) A, and sodium-implanted PET B,. The vertical arrows show the start and the end of the SIMS depth profiling
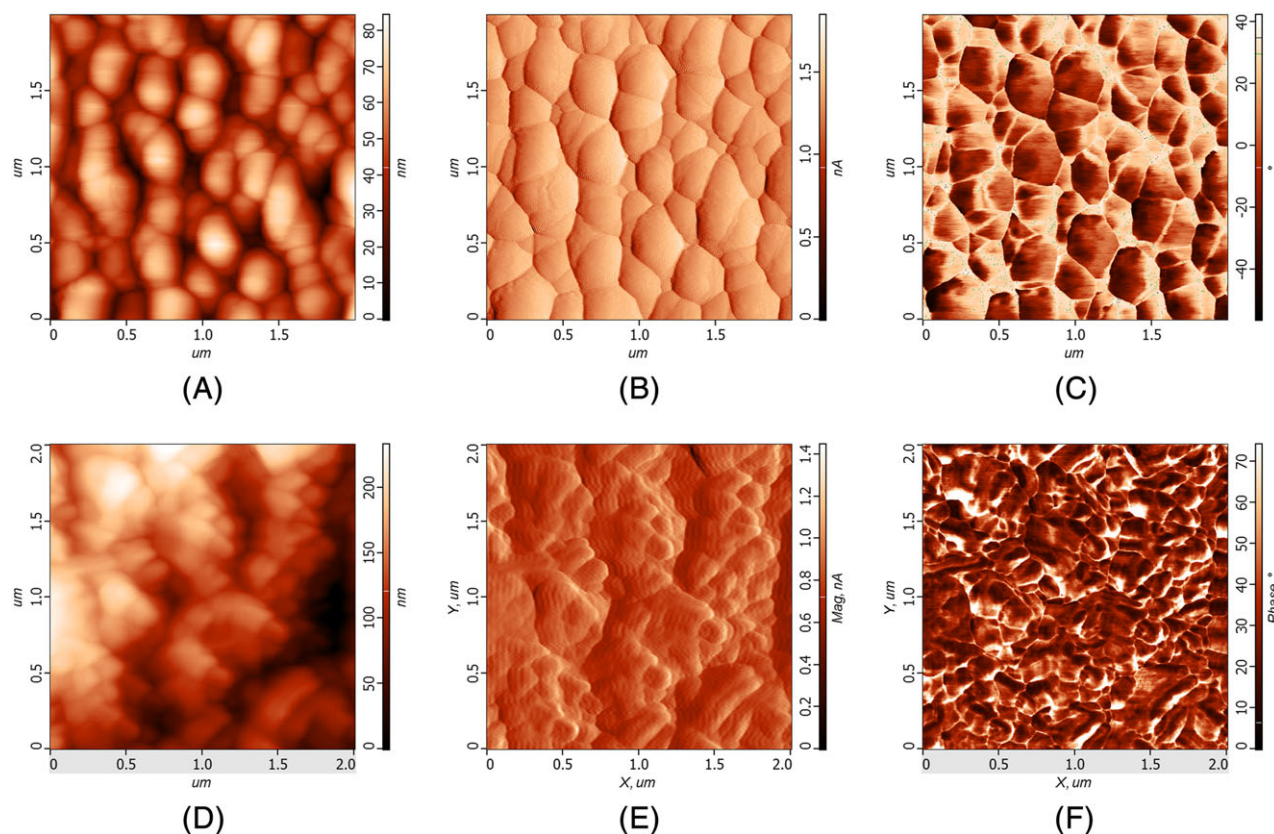
FIGURE 3 Atomic force microscopy (AFM) images of the sputter crater bottom prepared inside (A-C) and outside (D-F) of the implanted area. The 2 × 2 micron scans show topography A and D, amplitude B and E, and phase C and F, modulation contrasts

(something like the "secondary polymerization"). The surface roughness of both craters bottoms is higher than the roughness of the original polymer surface; this effect is typical of many other materials.

4 | CONCLUSIONS

We have performed an effective depth profiling analysis of an implanted polymer by using the CsM$^+$ regime, which is "standard" for SIMS depth profiling of semiconductor heterostructures. We did not use big argon or carbon clusters believed by many authors to be a necessary tool for the effective depth profiling of polymers by SIMS. We obtained complete information about depth distributions of all elements in a near-surface layer of the implanted polymer.

A number of different processes in a polymer occurring during ion irradiation, such as density decrease and then increase up to a new value, volatile component evolution, a strong diffusion of almost all components of the polymer including the implanted element, all together lead to formation of a final distribution of the implanted element, which differs strongly from the one calculated from ballistic collisions.

Both the low-energy cesium and high-energy bismuth ion irradiations destroy the majority of chemical bonds in a near-surface layer; this results in gas emission from the "original" and implanted polymer just during SIMS depth profiling analysis. So, the molecular (chemical) analysis was found to be quite difficult in the experimental SIMS regime used because an essential part of hydrogen leaves the ion-irradiated surface as H_2 neutral molecules.

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