Research Article

Depth profiling of polymer samples using Ga$^+$ and C$_{60}^+$ ion beams†

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In this contribution, we focus on the use of C$_{60}^+$ ions for depth profiling of model synthetic polymers: polystyrene (PS) and poly(methylmethacrylate) (PMMA). These polymers were spin coated on silicon wafers, and the obtained samples were depth-profiled both with Ga$^+$ ions and C$_{60}^+$ ions. We observed an important yield enhancement for both polymers when C$_{60}^+$ ions are used. More specifically, we discuss here the decrease in damage obtained with C$_{60}$, which is found to be very sensitive to the nature of the polymer. During the C$_{60}^+$ sputtering of the PMMA layer, after an initial decrease, a steady state is observed in the secondary ion yield of characteristic fragments. In contrast, for PS, an exponential decrease is directly observed, leading to an initial disappearance cross section close to the value observed for Ga$^+$. Though there is a significant loss of characteristic PS signal when sputtering with C$_{60}^+$ ions beams, there are still significant enhancements in sputter yields when employing C$_{60}^+$ as compared to Ga$^+$. Copyright © 2008 John Wiley & Sons, Ltd.

Introduction

SIMS is an extensively used technique for the determination of depth profiles, for example, to study the diffusion phenomena and measure the diffusion coefficients,[1] or to characterize insulating, semiconductor and metallic materials. One of the main advantages that SIMS offers over other depth-profiling techniques (such as X-ray photoelectron spectroscopy[2] or optical microscopy techniques based on infrared (IR) and Raman spectroscopies[3,4]) is its sensitivity to very low concentrations of elements. Using special ion beams such as Cs or O$_2$,[5] three-dimensional elemental analysis has been feasible. But if the state of dynamic SIMS is highly advanced, with many routine applications in materials science and electronics now established, the use of SIMS to characterize molecular surfaces seems more difficult. The rapid accumulation of chemical damage created by the incident ion beam creates a limit to the ion fluence.[6] This greatly reduces the amount of material available for detection, and also raises a problem for the feasibility of depth profiling. Indeed, for molecular solids, beam-induced damage generally destroys the chemical integrity of the sample, making these types of experiments problematic. The use of polyatomic primary ions, and more specifically the development of cluster primary ion sources,[7,8] such as the C$_{60}^+$ ion source, might allow one to overcome this problem. Indeed, unlike monoatomic primary ions, polyatomic primary ions disperse their impact energy among their constituent atoms, resulting in lower penetration depths and increased deposition of their impact energy in the near-surface region.[9−12]

In comparison with monoatomic ions, buckminsterfullerenes induce increased secondary ion yields (measured secondary ions per primary ion) when used as primary particles in ToF-SIMS analysis. Molecular modeling simulations[13,14] provide a microscopic explanation of the different sputtering processes at play with such projectiles. Fullerenes breakup on impact and, because the energy per constituent atom is low, the penetration depth of the primary particle and the damage created in the subsurface region are strongly reduced. As a consequence, C$_{60}^+$ ions appear to be ideal candidates to perform depth profiling of molecular samples. Polyatomic ions, such as SF$_5^+$, were successfully used to depth profile biopolymers[15] and multilayers of polymers,[16] and recent reports of experiments using C$_{60}^+$ ion beams have demonstrated that these clusters could be used for depth profiling of different organic samples.[17−19] In this contribution, we focus on the use of C$_{60}^+$ ions for depth profiling of model synthetic polymers: polystyrene (PS) and poly(methylmethacrylate) (PMMA) and we make a direct comparison between depth profiling with Ga$^+$ and C$_{60}^+$ ions on the same instrument.

Materials and Methods

Sample preparation

PMMA; molecular weight: 30 000 Da and PS; molecular weight: 794 and 2000 Da were purchased from Sigma-Aldrich and were used without further purification. PMMA and PS were dissolved at respectively 10 and 20 mg of polymer/ml of solvent in toluene. Polymer layers were fabricated by spincasting (5000 rpm for 60 s) the polymers onto silicon wafer pieces, which were previously cleaned for about 10 min in a pyranha solution (1/3 H$_2$O$_2$ + 2/3 H$_2$SO$_4$ mixture). With these polymer concentrations in solution and based on a previous calibration by ellipsometry, the film thickness is estimated to be 90 nm for PS 2000 and 40 nm for PMMA 30 000.

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Time-of-flight secondary ion mass spectrometry

Positive and negative ion time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiles were obtained using a PHI-EVANS ToF-SIMS (TRIFT 1)[20] equipped with both a 15 keV Ga^+ ion gun (FEI 83-2 liquid metal ion source, 1.2 nA dc current, 5 kHz frequency, 22 ns pulse width bunched down to 1 ns) and a 15 keV C_{60}^+ ion gun[10] (primary ion beam system (IOG-C60-20) from Ionoptika Ltd, 2–100 pA dc current with apertures of 300–1000 µm and a 50 V grid voltage). The contribution from C_{60}^{2+} was eliminated by a double set of blanking plates. The experimental setup has been described in detail elsewhere.[21] The impact angle of the primary ion beam is the same for the Ga^+ ion gun and for the C_{60}^+ ion gun. To improve the measured intensities, the secondary ions were postaccelerated by a high voltage (7 kV) in front of the detector. No charge compensation was needed. The primary ion current was measured in a small aperture of the sample holder, with and without a positive bias of 27 V (to cancel the effects of secondary electron emission).

For depth profiling, a crater was created of a size on the order of 400 µm × 400µm, and the spectra were taken from a zoomed region of 80 µm × 80 µm within the center of the crater to avoid any edge effect. The total fluence per spectrum was less than 10^{10} ions/cm^2 when C_{60}^+ primary ions were used, and less than 10^{11} ions/cm^2 when Ga^+ primary ions were used.

Results and Discussion

Secondary ion yield enhancement

C_{60} has been shown to give increased sputter yields and secondary ions for many samples when used as a primary particle in SIMS analysis.[22] Secondary ion yield enhancements in the range of 30–100 times, as compared with gallium monoatomic analysis, have been demonstrated.[10] We report in this article different secondary ion yields for thin films of PS 2000 and PMMA 30 000 obtained with C_{60}^+ ion beam in comparison with Ga^+ ion beam.

The results for PS 2000 are shown in Figure 1. Secondary ion yields of different characteristic fragments of PS in the positive spectra are reported, namely for m/z 91, 103, 178 and 205 a.u. The primary ion beam energy is 12 keV for the Ga^+ and the C_{60}^+ ion beams. The enhancements obtained are in the range of 50–75 times as compared with gallium monoatomic analysis.

The results for PMMA 30 000 are shown in Figure 2. Secondary ion yields of different characteristic fragments of PMMA in the negative spectra are reported, namely for m/z 85, 141 and 185 a.u. The primary ion beam energy is 18 keV for the Ga^+ and for the C_{60}^+ ion beams. The enhancements obtained are in the range of 30–50 times as compared with gallium monoatomic analysis. Although slightly lower than the ones observed with PS 2000, these enhancements represent more than one order of magnitude.

As stated in previous studies for different organic materials, we observed an important yield enhancement for both PS 2000 and PMMA 30 000 when C_{60}^+ ions were used as primary ions as compared with Ga^+ primary ions. For depth profiling, high secondary ion yields are of crucial importance to characterize appropriately the polymers during the erosion of the film in order to get information as a function of depth. These high secondary ion yields indicate corresponding increased sputter rates for polymers under polyatomic primary ion bombardment.[23,24] These increased sputter rates and secondary ion yields make C_{60}^+ an ideal candidate for molecular depth profiling. However, it
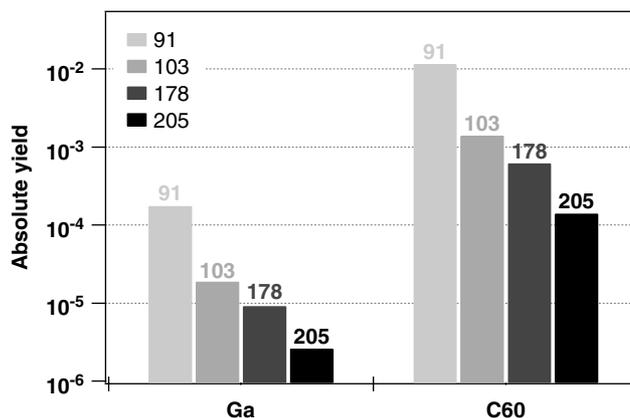

Figure 1. Absolute yields for different characteristic positive fragments of polystyrene (m/z = 91, 103, 178 and 205). Results on the left are obtained when the projectiles are 12 keV Ga^+ ions, and results on the right are obtained with 12 keV C_{60}^+ ions.
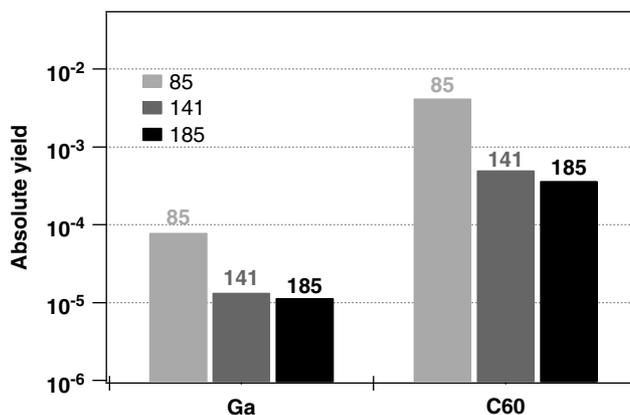

Figure 2. Absolute yields for different characteristic negative fragments of polymethylmethacrylate (m/z = 85, 141, 185). Results on the left are obtained when the projectiles are 18 keV Ga^+ ions, and results on the right are obtained with 18 keV C_{60}^+ ions.

is also necessary to have reduced chemical damage in order to conserve the chemical information during the depth profile.

Recent reports of experiments using C_{60}^+ ion beams have demonstrated not only an increase in yield of secondary ions but also a substantial reduction in chemical damage of the sample, possibly due to the removal of any damage generated with each subsequent impact.[25,26] Low-energy C_{60} bombardment has been used to remove surface contamination from polymers prior to analysis using X-ray photoelectron spectroscopy with no observable chemical change to the sample.[27]

Depth profiling of polystyrene thin films

PS was chosen because it acts as a negative resist, where cross linking is the dominant mechanism, at room temperature, of ion beam damage.[28]

PS thin films spin coated on silicon wafers were depth-profiled both with Ga^+ primary ions and C_{60}^+ primary ions. It is well known that depth profiles of organic layers with monoatomic gallium ions are not feasible, because of the damage created on the surface and in the near-surface region by the projectiles. Nevertheless, these experiments will allow comparison with C_{60} results on the

same ToF-SIMS equipment. The depth profiles of a PS 2000 thin film are shown in Figure 3. Characteristic secondary ion yields of the polymer ($C_8H_7^+$, $m/z = 103$ a.u.) and of the substrate (Si, $m/z = 28$) are studied as a function of the primary ion dose. For Ga^+ projectiles as for C_{60}^+ projectiles, the characteristic signal of PS decreases exponentially as the ion dose increases. This shows that the chemical information in the polymer film is lost because of damage created by the projectiles. This observation was made for different characteristic fragments of PS, under both Ga^+ and C_{60}^+ ion bombardment. Therefore, molecular depth profiling in these films is not feasible. Nevertheless, some differences appear between the use of the monoatomic projectiles and that of the cluster ion beam. One important change is the ion dose for which the interface region is reached. On roughly comparing the ion doses for which the characteristic signal of the substrate begins to rise, we can see that it is about 80×10^{15} ions cm^{-2} when Ga^+ primary ions are used, whereas it is only about 35×10^{13} ions cm^{-2} when C_{60}^+ ions are used, which is lower by less than two orders of magnitude. This is characteristic of a much higher sputter rate for C_{60}^+ projectiles. Another difference is the shape of the silicon signal: when Ga^+ ions are used, this signal reaches a maximum and then decreases for higher ion doses, which is linked to the presence of an oxide layer on the silicon wafer. When C_{60}^+ ions are used, this shape changes significantly, and the silicon signal grows continuously until it reaches a steady state. This illustrates the fact that the physical processes at play with cluster bombardment are not the same as the ones with monoatomic ions bombardment.

Initial disappearance cross sections obtained for characteristic fragments of PS are another difference between the use of monoatomic projectiles or of the C_{60}^+ ion beam. Disappearance cross sections for the $C_8H_7^+$ and $C_{16}H_{13}^+$ fragments are plotted in Figure 4. It can be seen in this figure that the initial disappearance cross section obtained with C_{60}^+ projectiles (for instance 6.29×10^{-14} cm^2 for $C_{16}H_{13}^+$) is slightly higher than the one obtained with the Ga^+ projectiles (2.57×10^{-14} cm^2 for $C_{16}H_{13}^+$). This corresponds to secondary ion formation efficiencies of 10^{-2} cm^{-2} with th Ga^+ projectiles and of 2.2×10^{-1} cm^{-2} with the C_{60}^+ projectiles, for $C_{16}H_{13}^+$.

Eventually, a spectrum can be seen in Figure 5, which is obtained with the C_{60}^+ ion beam, of the PS film after an exposure of about 9×10^{13} ions cm^{-2} to C_{60}^+ ions. It has been seen previously (Figure 5) that in this area of exposures, the characteristic signal of PS had dramatically decreased and damages had been created on the surface and in the near-surface region by the projectiles. Nevertheless, we can observe on this spectrum that PS can still be identified: characteristic fragments of masses 91, 103, 178 and 205 a.m.u. are still significant.

The fact that depth profiling of PS 2000 thin films with C_{60}^+ primary ions is not feasible might be connected with the chemical nature of the polymer: as stated above, for PS, cross linking is the dominant mechanism of ion beam damage. This cross-linking phenomenon might be a disadvantage for the removal of damage generated by the projectiles. To test this hypothesis and to study the influence of the polymer chain length on depth-profiling feasibility, we tried to depth profile PS thin films with a lower molecular mass PS. A 794 Da molecular weight PS was used to make a thin film spin coated on a silicon wafer. The depth profile of this film with C_{60}^+ ions is shown in Figure 6. We can observe
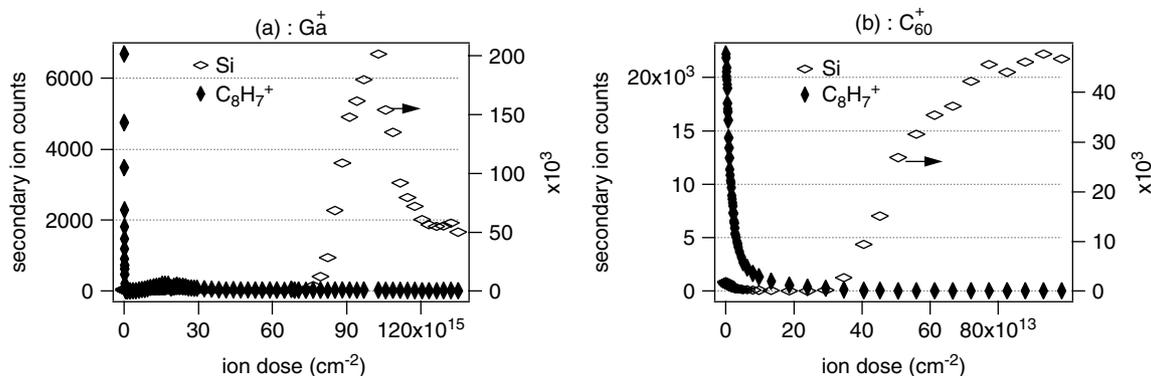

Figure 3. Depth profiles of PS 2000 thin films spin coated on silicon wafers with Ga^+ primary ions (a) and C_{60}^+ primary ions (b).
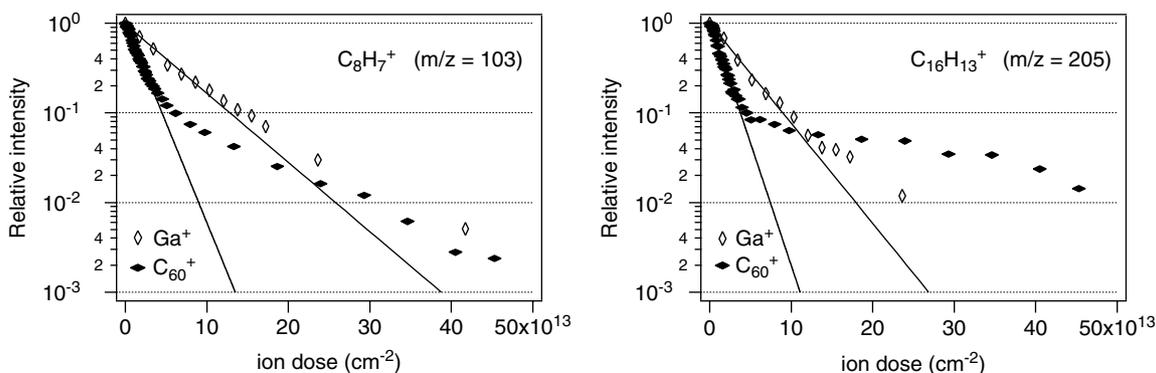

Figure 4. Disappearance cross sections obtained with Ga^+ and C_{60}^+ projectiles for characteristic fragments of polystyrene: $C_8H_7^+$ (a) and $C_{16}H_{13}^+$ (b).
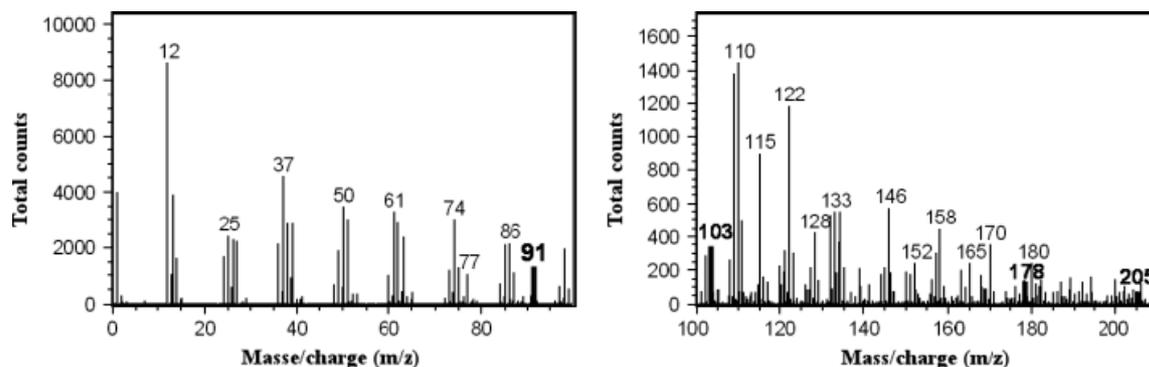
Figure 5. Spectrum, obtained with the C_{60}^+ ion beam, of the polystyrene film after an exposure of about 9×10^{13} ions cm^{-2} to C_{60}^+ ions. Additional peaks ($m/z = 12$ for instance) present after bombardment with C_{60}^+ ions are indicative of carbon deposition.
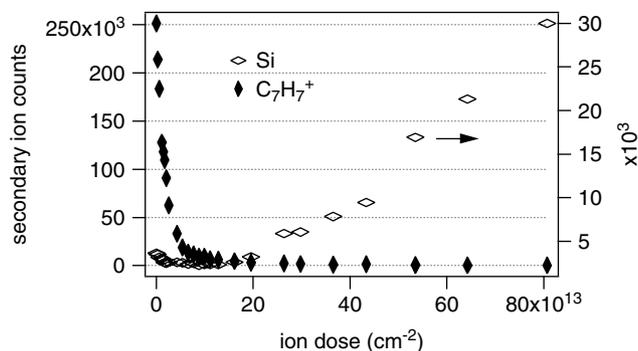

Figure 6. Depth profile of a PS 794 thin film spin coated on a silicon wafer with C_{60}^+ primary ions.

that, as in the case of the PS 2000 film, there is an exponential decrease of the signal corresponding to a characteristic fragment of PS. The chemical characterization of the polymer is lost whereas the interface region is not yet reached (the signal corresponding to the substrate has not started to rise). This indicates that even with this shorter chain length polymer, depth profiling with C_{60} is not feasible.

To continue the study of the feasibility of depth profiling with C_{60}^+ primary ions, and to test a possible influence of the chemical nature of the polymer on this feasibility, we used another model polymer, PMMA.

Depth profiling of poly(methylmethacrylate) thin films

PMMA was chosen because it is the prototype of positive tone resist, where chain scission is the prevailing irradiation induced chemical event.[29] Thus, the mechanism of ion beam damage for PMMA is very different from the one for PS. Depth profiling of this model polymer was previously studied both with SF_5^{+} [23] and C_{60}^+ [30–32] ion beams.

We studied the evolution of secondary ions of characteristic fragments of PMMA (e.g. $C_4H_5O_2^-$) and of the silicon substrate (SiO_3H^-) as a function of the ion dose both with Ga$^+$ primary ions and C_{60}^+ primary ions. The results obtained are shown in Figure 7.

For monoatomic gallium projectiles, we observed, as for PS, an exponential decrease of the signal corresponding to the polymer: any chemical characterization is lost far before the interface region is reached. During the C_{60}^+ sputtering of the PMMA layer, we observed a different behavior: after an initial decrease of the signal corresponding to the PMMA, a steady state is observed. Before starting erosion, the secondary ion counts during one analysis for the characteristic fragment $C_4H_5O_2^-$ is of about 39×10^3, and when the steady state is reached, these counts are of about 19×10^3, which means that only half of the signal has been lost. The spectra acquired in this area are still characteristic of PMMA, and no chemical information has been lost. The $C_4H_5O_2^-$ decreases again after this steady state, but this decrease is coincident with the increase of the signal corresponding to the substrate, which shows that the interface region has been reached. This figure illustrates the feasibility of depth profiling of PMMA thin films with C_{60}^+ primary ions.
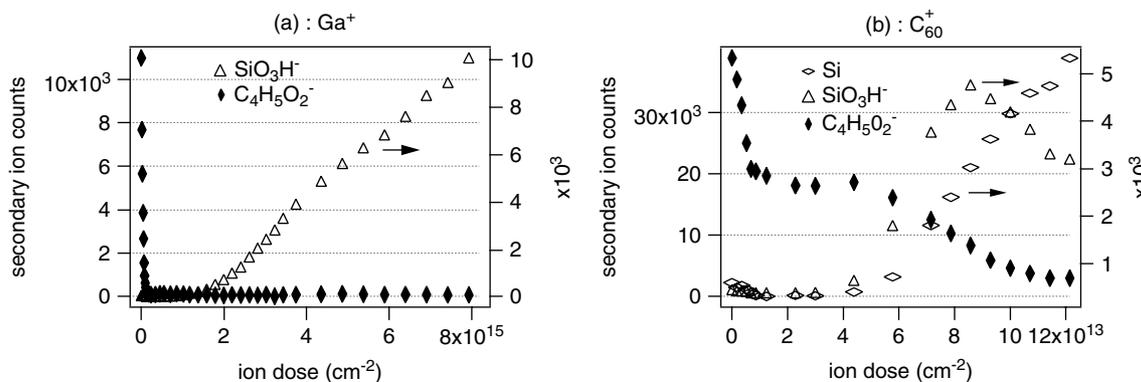

Figure 7. Depth profiles of poly(methylmethacrylate) thin films spin coated on silicon wafers with Ga$^+$ primary ions (a) and C_{60}^+ primary ions (b).

Conclusion

We used a C_{60}^+ ion beam to depth profile model synthetic polymers, PS and PMMA. C_{60}^+ projectiles are associated with high sputter yields and low penetration depths, and therefore are considered as ideal candidates for depth profiling of molecular solids. We have shown in this study that this assertion has to be moderated. Indeed, the results obtained indicate that the feasibility of depth profiling of polymer films is dependent on the nature of the polymer. In the case of PS, a negative resist depth profiling is not feasible with C_{60} under our experimental conditions: there is creation of damage on the surface, and the chemical characterization of PS is lost before the interface region is reached. On the contrary, in the case of PMMA, a positive resist depth profiling with C_{60} is feasible.

Acknowledgements

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