PHYSICAL ELECTRONICS

OPTIMIZING C_{60} INCIDENCE ANGLE
for Polymer Depth Profiling by TOF-SIMS

INTRODUCTION

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is widely used to obtain molecular information at the surface of organic materials. It is highly desirable to obtain this same molecular information as a function of depth from the polymer surface. Development of new technologies such as OLED's and organic PV materials requires a more detailed understanding of the relationship between molecular distributions and device performance. Obtaining this information by sputter depth profiling has proven difficult due to accumulated damage to the organic structure during the (i.e., depth profiling) sputtering process.

The recent use of cluster ion beams for sputtering, such as SF_5^+ and C_{60}^+, has made it possible to obtain stable molecular secondary ion signals as a function of depth for a number of different polymer materials [1]. This is due to cluster primary ions having a high sputter yield and a thin damage layer, enabling molecular secondary ion signals to be produced up to very high primary ion doses. To obtain stable molecular secondary ion intensities as a function of depth requires that the damage input reaches a steady-state with a majority of damaged material being removed during the sputtering process. For some polymers, this has proven difficult due to cross-linking and other mechanisms that lead to a rapid decrease in the sputter yield. Cramer et al. reported that 10 kV C_{60} sputtering is not suitable for bulk and spin-coated polycarbonate (PC) and polystyrene (PS) materials when sputtering at an incident angle of 45° from normal [2]. It has been reported that

C_{60} sputtering at glancing angle rather than 45° reduces the structural damage of polycarbonate as measured by XPS [3]. In addition, glancing angle C_{60} depth profiling was shown to be more successful than lower angle sputtering for TOF-SIMS depth profiling of thin molecular films [4,5]. The purpose of the present study was to investigate if the use of glancing angle sputtering could be extended to TOF-SIMS depth profiling of polymers such as PC and PS.

EXPERIMENTAL

TOF-SIMS depth profiles were acquired using a PHI TRIFT V *nanoTOF* instrument equipped with a 20 kV C_{60} ion gun. Depth profiles were collected using a single-gun mode by alternating the C_{60} ion gun between the pulsed TOF-SIMS acquisition phase and DC sputtering phase. The C_{60} beam energy, beam current and incidence angle were kept constant for both the analysis phase and the sputter phase. Due to the very wide angular acceptance of the TRIFT analyzer, TOF-SIMS analysis can be done with the sample tilted up to 28 degrees. The C_{60}^+ beam energy was 20 keV, the beam current was 450 pA, and the beam diameter was 10 µm. The raster sizes of the C_{60}^+ beam for sputtering and TOF-SIMS acquisition were 400 µm x 400 µm and 40 µm x 40 µm, respectively. The samples were bulk polymers of PC and PS purchased from Goodfellow, Inc. The polymer sheets were analyzed as received with no pre-treatment.

TOF-SIMS depth profiles were obtained by acquiring negative secondary ions for PC and positive secondary ions for PS. For charge compensation, 10 eV electrons were pulsed onto the sample surface between each C_{60}^+ pulse

during the acquisition phase. Sputtered depths were determined by directly measuring the sputter craters with a mechanical stylus profiler (Dektak 6M, Veeco).

RESULTS AND DISCUSSION

Polycarbonate:

A sheet of PC was depth profiled with C_{60}^+ in the negative SIMS mode at incidence angles of 48°, 66°, and 76°. In general, all the structurally significant peaks for PC showed the same trend as a function of incidence angle. Figure 1 shows an overlay of the depth profiles of $C_{14}H_{11}O_2^-$ (m/z
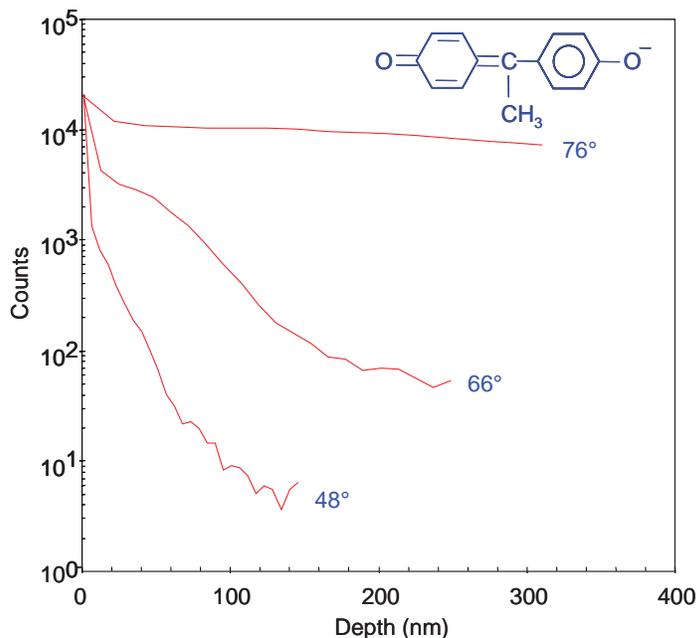
Figure 1: Depth profile of the $C_{14}H_{11}O_2^-$ peak (m/z 211) of PC as a function of depth at different C_{60}^+ incidence angles.

211), which is one of the main structurally diagnostic negative secondary ions from PC, at the three incidence angles studied. The three profiles were normalized to the same starting intensity for ease of comparison. The profile at 48° agrees with the previously reported result [2]. The profile at 66° does not decay as fast; however, a plateau is never reached where the signal is stable. At an incidence angle of 76° the $C_{14}H_{11}O_2^-$ molecular ion is nearly constant over a sputtered depth of 300 nm. This comparison demonstrates that the sputter-induced damage of PC significantly decreases as the C_{60}^+ incidence angle is increased.

A series of sputter craters were made at increasing C_{60}^+ doses at incidence angles of 48° and 76°, and the crater depths were measured in order to determine the sputter rate as a function of dose.   The relationship between crater depth and C_{60}^+ dose is shown in Figure 2. A linear relationship was observed between ion dose and crater depth up to 450 nm for the data acquired at an incidence angle of 76°. At an incidence angle of 48° the sputter rate begins to decrease beyond a depth of 100 nm due to excessive damage to the polymer chemistry.

Figure 3 shows the mass spectrum before sputtering (a) and after sputtering (b) to a dose of 8 x 10^{14} ions/cm^2 at 76° and (c) 48°. The spectrum acquired after sputtering with an incidence angle of 76° (Figure 3b) shows very little change in the relative peak intensities as a result of the sputtering. The spectrum acquired after sputtering with an incidence angle of 48° (Figure 3c) shows dramatic changes in the spectrum. For example, the characteristic peaks of PC such as C_2OH (m/z 41), $C_6H_5O^-$ (m/z 93), and $C_{14}H_{11}O_2^-$ (m/z 211) decrease drastically after sputtering, and peaks such as C_n^- and $(C_n+H)^-$ become dominant.

Polystyrene:
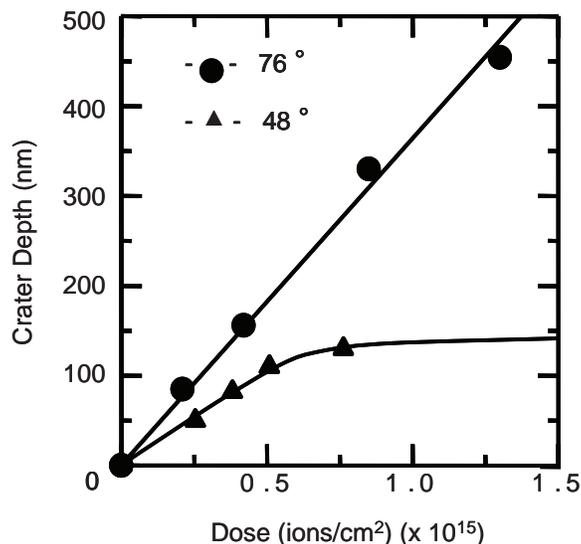
Figure 2: Relationship between C_{60}^+ ion dose and crater depth for 76° and 48° incidence angle on PC.

Figure 4 shows an overlay of the characteristic m/z 91 peak from PS at 76° and 48° incidence angle normalized to the same starting intensity. The profile at 48° confirms the previously published result that the secondary ions containing aromatic functionality are immediately destroyed [2]. At 76° incidence, the structurally significant molecular ions of $C_7H_7^+$ (m/z 91), $C_8H_9^+$ (m/z 105) and $C_9H_7^+$ (m/z 115) reached a steady state and were almost constant over the sputtered depth.

Figure 5 shows the mass spectra before (a) and after (b) sputtering to a dose of 2×10^{14} ions/cm^2 at 76° and (c) 48° incidence angle. Just as in the case of PC, there was very little change in the relative peak intensities between the spectrum of the initial surface and the spectrum after sputtering at 76°. The spectrum after sputtering at 48° shows the diagnostic aromatic molecular ions for PS (e.g. m/z 77. 91 and 115) are lost and the spectrum is dominated by C_n^+ and $(C_n+H)^+$ peaks. The C_n and (C_n+H) peaks which dominate both the PC and PS
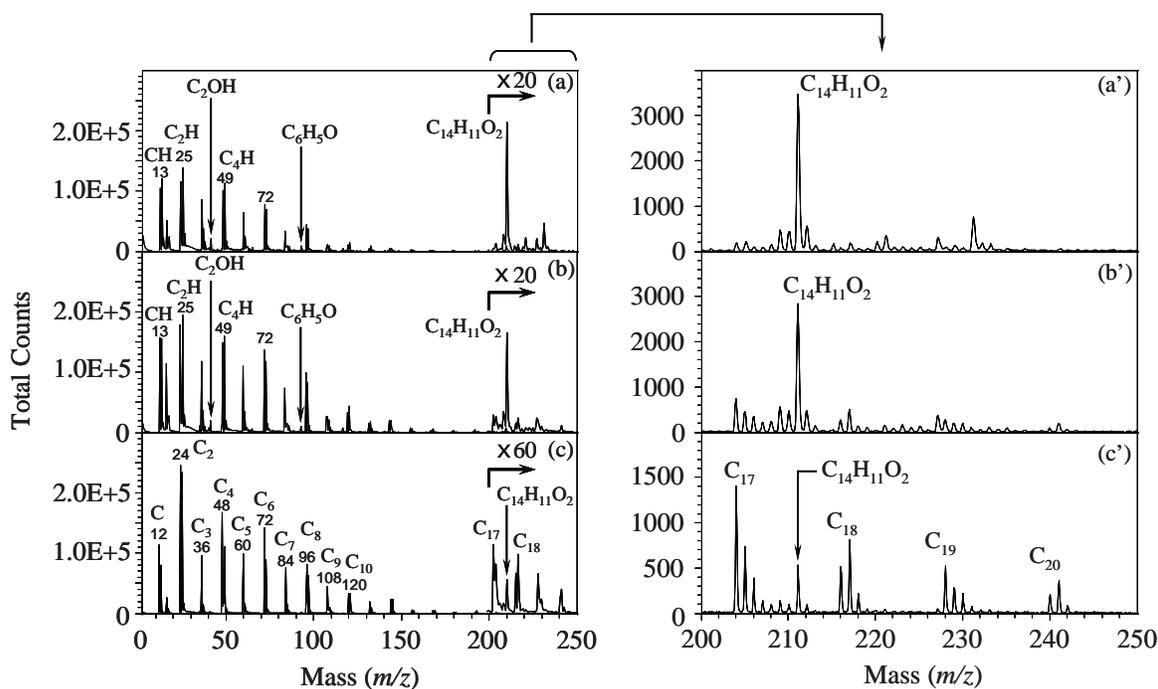
Figure 3: TOF-SIMS spectra from PC samples; before sputtering (a) and after sputtering (b) of 8 x10^{14} ions/cm^2 at 76° and (c) at 48°.
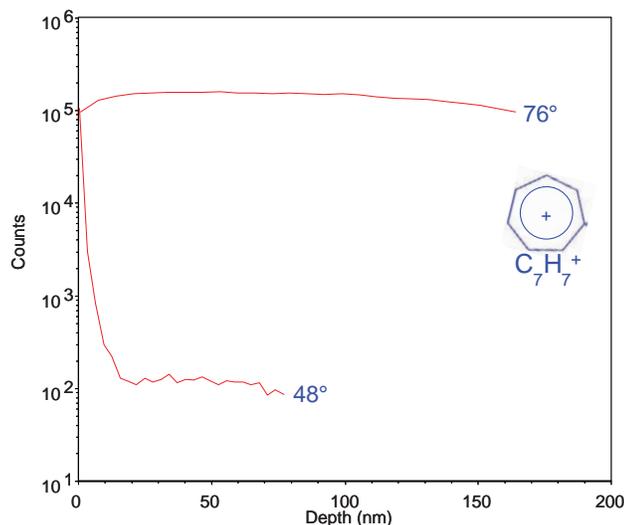
Figure 4: C_{60}^+ depth profile of m/z 91 from PS at (a) 76° and (b) 48° incidence angle.

spectra after sputtering at an incidence angle of 48° suggest a highly reduced and carbon rich surface composition. From these results alone it is not possible to determine if this carbon rich surface results completely from irradiation damage of the polymer, from carbon deposition from the C_{60}^+ primary ion beam, or a combination of both.

CONCLUSION

This study has demonstrated that depth profiling of PC and PS can be significantly improved by using glancing angle C_{60}^+ sputtering at an incidence angle of 76°. Sputtering at glancing incidence provides stable molecular ions up to the doses used in this study. Although glancing angle sputtering has some disadvantages, such as elongated beam shape and reduced sputter yields, the improvement compared to the standard incidence angle of 48° was significant for both PC and PS in terms of molecular depth profiling over the first few hundred nanometers of the surface.

REFERENCES

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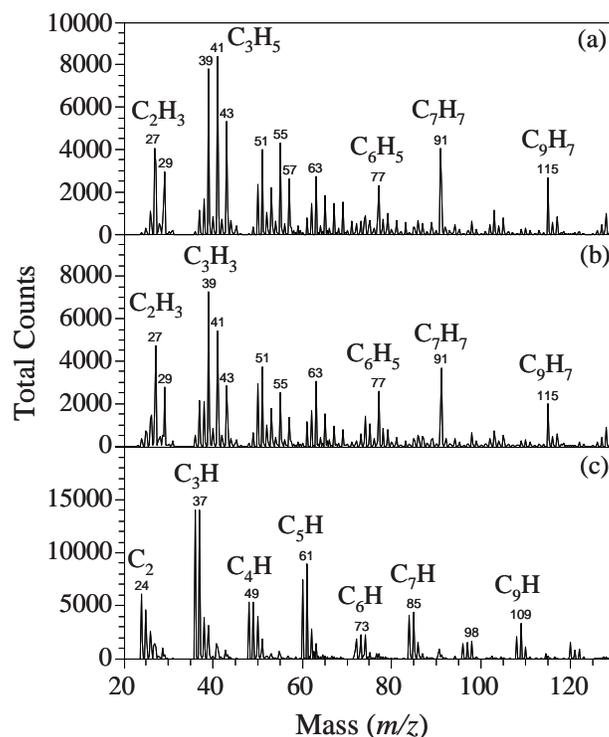
Figure 5: TOF-SIMS spectra from PS samples; before sputtering (a) and after sputtering (b) of 2 x10^{14} ions/cm^2 at 76° and (c) at 48°.

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