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C_{60} molecular depth profiling of a model polymer

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Abstract

The bombardment of a 26 nm poly(methyl methacrylate) (PMMA) film has been studied as a model for depth profiling of polymeric samples using a newly developed C_{60}^+ ion source. Experiments were conducted on a ToF-SIMS instrument equipped with $C_{60}^+$and Ga^+ ion sources. A focused dc C_{60}^+ ion beam was used to etch through the polymer sample at specified time intervals. Subsequent spectra were recorded after each individual etching cycle using both C_{60}^+ 20 keV and Ga^+ 15 keV ion beams at field-of-views smaller than the sputter area. PMMA fragment ion at $m/z = 69$ and substrate Au $m/z = 197$ were monitored with respect to primary ion doses of up to 10^{14} ions/cm^2. Depth resolution as determined by the interfacial region is found to be about 14 nm. A >10-fold increase in sputter yield for C_{60}^+ ion bombardment over Ga^+ ions under similar conditions is observed from quartz crystal microbalance (QCM) measurements and our findings compare to enhanced SF_5^+ cluster bombardment yields of organic species.

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1. Introduction

For SIMS depth profiling experiments of polymeric samples, selecting the correct primary projectile is critical. Atomic and small molecular ion beams (Ga^+, Cs^+, O_2^+, etc.) do not yield useful depth information since too much damage is created on the surface to accurately attain molecular specificity in each layer. Fuoco et al. [1] have reported that polyatomic primary ion beam sources such as SF_5^+ are much better suited for depth profiling through organic substrates. For equal beam energies, polyatomic projectiles penetrate the surface to much lower depths than their atomic counterparts and offer substantial sputter yield and secondary ion yield enhancements for molecular ions.

A C_{60} polyatomic ion source has recently been developed and studied in detail by Weibel et al. [2]. Their results indicate significant yield enhancements that are consistent with previously published C_{60}^+ ion beam enhancements for organic substrates such as Gramicidin D [2], Irganox 1010 [2], and α-cyano-4-hydroxycinnamic acid (ACHA) [3]. Here we explore the possibilities of using the C_{60}^+ ion source as a depth profiling tool for organic species. Poly(methyl methacrylate) (PMMA) is used as a model polymer since direct comparisons can be made to depth profiles reported by Fuoco et al. [1] on PMMA using an SF_5^+ primary projectile. If depth profiling using C_{60}^+ is possible for organic species, new possibilities open for molecular localization within layers of single

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biological cells—making it plausible to obtain 3D molecular maps of cellular constituents.

2. Experimental

The PMMA (Scientific Polymer Products Inc.) film was prepared by dissolving 1 mg of polymer in 1 ml of toluene, followed by spin-coating onto a clean gold quartz crystal microbalance (QCM) crystal. The thickness of 25.8 nm was determined by ellipsometry and a schematic representation of the configuration is shown in Fig. 1. QCM measurements were obtained using a copper block-mounted modified crystal and oscillator from Maxtek. Electrical contacts were made to the QCM controller through gold-plated plungers extending into the block.

Spectra were acquired with a ToF-SIMS apparatus described in detail elsewhere [4]. The analysis chamber was modified slightly to accommodate the fitting of both Ga^+ and $C_{60}{}^+$ ion sources. A detailed depth profiling script was developed to automate the hardware for both sources. For example, it is possible to sputter the surface with either ion beam at wide range of field-of-views, to discontinue sputtering and acquire spectra and/or images with either or both primary ion beams, and to automatically save each spectrum in numerical sequence.

Samples were bombarded by both beams at 2000 μm × 2000 μm field-of-view with 5 s of dc sputtering and spectra were recorded at 1000 μm × 1000 μm field-of-view for 50,000 pulses. The Ga^+ primary ion current was 2.7 nA and $C_{60}{}^+$ ion current was 1.2 nA for this study. Although, generally stable, the $C_{60}{}^+$ ion current exhibits occasional fluctuations, making it important to be able to reference signals to a control. A copper grid was used to be sure that the two ion beams were precisely overlapped. Charge compensation (23 eV electrons, ~1 μA emission) was employed after each pulse during spectral acquisition and was from a dc electron beam during sputtering.

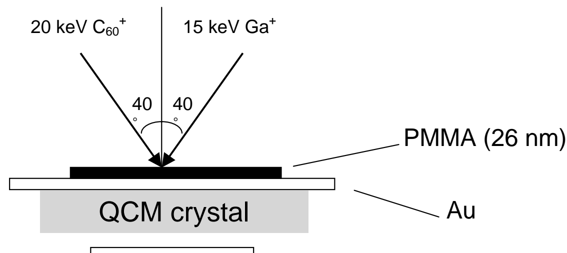

Fig. 1. Schematic representation of substrate orientation, PMMA and primary ion beams with respect to surface normal.

3. Results and discussion

A depth profile of the 25.8 nm PMMA film on Au using $C_{60}{}^+$ projectiles is shown in Fig. 2. For this case, the PMMA fragment ion at $m/z = 69$ and Au^+ substrate ion at $m/z = 197$ were monitored as a function of $C_{60}{}^+$ ion dose. After an initial decay, the $m/z = 69$ reaches a fairly constant value until the film/substrate interface is reached. At this point, the Au^+ ion signal begins to increase as expected. The abrupt drop of both signals at a dose of just over 1.3×10^{14} ions/cm^2 is due to a primary ion beam fluctuation that occurs occasionally with our source. The general features of this profile are quite similar to those reported using $SF_5{}^+$ projectiles [1].

To obtain a clearer picture of how the monitored signal intensities vary as a function of depth into the sample, normalized PMMA and Au intensities are plotted in Fig. 3. The normalized intensities are computed by taking the ratio of a specific ion intensity to the sum of intensities at $m/z = 69$ and $m/z = 197$. The depth scale is determined from the known film thickness of 25.8 nm and by identifying the halfway point of the PMMA disappearance curve. This point is reached at a total $C_{60}{}^+$ ion dose of 8.5×10^{13} ions/cm^2, yielding a sputter rate of 0.215 nm/s. A constant

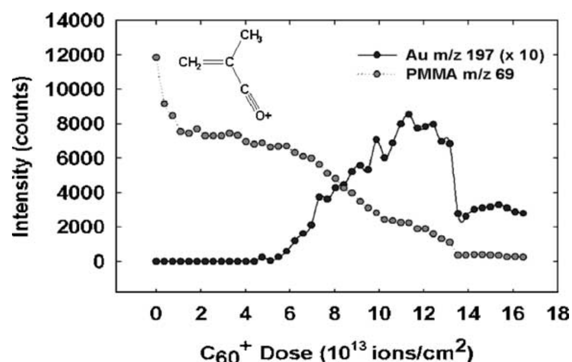

Fig. 2. Plot of depth profile data for PMMA fragment ion $m/z = 69$ (○) and Au ion $m/z = 197$ (●) with respect to dose. The chemical structure represents the PMMA fragment ion at $m/z = 69$.

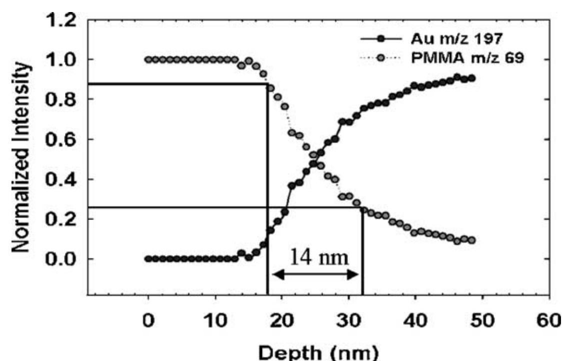

Fig. 3. Plot of normalized depth profile data for PMMA fragment ion $m/z = 69$ (○) and Au ion $m/z = 197$ (●) with respect to sample depth, as described in the text.

sputter rate was assumed throughout the entire depth profile. Using the 84–16% interface width [5] and assuming a constant sputter rate throughout the entire depth profile, the depth resolution for the C_{60}^+ 20 keV bombardment of PMMA is about 14 nm.

Similar attempts to produce these depth profiles using Ga^+ ion bombardment were unsuccessful, as were those of Fuoco et al. [1] using Ar^+ bombardment. However, it is possible to use the C_{60}^+ ion source as the digging probe while using the Ga^+ ion as the projectile for acquiring SIMS data. In this modality, depth profiles that are nearly as good as those acquired using only C_{60}^+ can still be achieved. These results are significant since they suggest that it may be possible to utilize the high lateral resolution of the Ga^+ ion source in conjunction with C_{60}^+ ion sputtering to produce 3D molecular maps.

The QCM was employed to estimate the total sputtering yield of PMMA under Ga^+ ion and C_{60}^+ ion bombardment. Removal rates of between 10^{-8} and 10^{-7} g/cm^2 were measured for each case with a reproducibility of about $\pm 3 \times 10^{-9}$ g/cm^2. The ratio of the 20 keV C_{60}^+ to 15 keV Ga^+ ion bombardment yield for PMMA is 11.0 ± 0.6. This enhancement is slightly higher than that observed by Fuoco et al. [1], who showed a 2.2-fold enhancement in sputtering yield from PMMA with SF_5^+ ion bombardment over Ar^+ ion bombardment at the same impact energy. Finally, we note that the observed intensity ratio of C_{60}^+ to Ga^+ ion bombardment for the $m/z = 69$ peak, corrected for ion beam current and raster area, is approximately 40 on the unperturbed sample. This observation suggests that both the sputtering yield and the ionization efficiency are enhanced using the cluster ion source.

We have observed that for many insulating samples, bombardment with C_{60}^+ ions results in much less charging than found for other projectiles. This effect may arise due to the fact that owing to the high total sputtering yield, absolute positive secondary ion yields may reach values close to unity and, hence, the surface is more electrically balanced under the cluster bombardment.

4. Conclusions

Depth profiling of thin polymer films appears to be feasible using the C_{60}^+ ion probe, yielding results comparable to those acquired using SF_5^+ ion bombardment. The sputtering yield and accompanying molecular specificity is enhanced by at least a factor of 10 over corresponding atomic ion bombardment. Moreover, it is possible to combine C_{60}^+ and Ga^+ probe experiments to achieve higher lateral resolution. C_{60}^+ ion beams are particularly suitable for depth profiling of insulators since the samples appear to be less susceptible to the charging phenomenon.

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