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The effect of incident angle on the C_{60}^+ bombardment of molecular solids

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ABSTRACT

The effect of incident angle on the quality of SIMS molecular depth profiling using C_{60}^+ was investigated. Cholesterol films of ~300 nm thickness on Si were employed as a model and were eroded using 40 keV C_{60}^+ at an incident angle of 40° and 73° with respect to the surface normal. The erosion process was characterized by determining at each angle the relative amount of chemical damage, the total sputtering yield of cholesterol molecules, and the interface width between the film and the Si substrate. The results show that there is less molecule damage at an angle of incidence of 73° and that the total sputtering yield is largest at an angle of incidence of 40°. The measurements suggest reduced damage is not necessarily dependent upon enhanced yields and that depositing the incident energy nearer the surface by using glancing angles is most important. The interface width parameter supports this idea by indicating that at the 73° incident angle, C_{60}^+ produces a smaller altered layer depth. Overall, the results show that 73° incidence is the better angle for molecular depth profiling using 40 keV C_{60}^+.

1. Introduction

Molecular depth profiling using C_{60}^+ has become commonplace in secondary ion mass spectrometry (SIMS) [1]. To explain the basic response of molecule intensity as a function of C_{60}^+ fluence during the experiments, a simple analytical model has been developed [2]. The model considers a number of depth profile parameters, including total sputtering yield, damage cross-section, and altered layer thickness, to describe the concentration of undamaged molecules at the surface during sample erosion. Collectively, the parameters indicate favorable conditions for molecular depth profiling exist when the total sputtering yield is large relative to the damage volume within the solid. Therefore, larger yields are typically consistent with reduced damage during sample erosion [1]. For a number of molecules, the depth profile conditions are easily attained [1,2]. However, several molecules have been identified which do not respond predictably [3].

To overcome the inconsistencies and generalize the strategy, experimental variables need to be optimized to best fit the conditions of the depth profile model. Among the experimental variables which can be varied, incident energy and incident angle of the C_{60}^+ projectile are the most easily tested. The incident energy and incident angle are expected to considerably influence the depth at which the C_{60}^+ energy is deposited into a solid – a factor important in determining sputter yield and damage volume [4,5]. Investigations into the effect of C_{60}^+ incident energy on the quality of depth profile suggest that 40 keV is the most favorable kinetic energy [6]. Here, we show how the depth profile parameters change when the angle of incidence changes from 40° to 73° with respect to the surface normal using a ~300 nm cholesterol film on Si as a model. The experiments indicate that 73° incidence is the better of the two angles for molecular depth profiling using 40 keV C_{60}^+.

2. Experimental

Sample analysis was performed using a ToF-SIMS instrument (BioToF, Kore Technology Ltd.) [7]. A 40 keV C_{60}^+ ion beam system (IOG-40, Ionoptika Ltd.) is mounted onto the instrument at a 40° angle with respect to sample normal [8]. The beam current is 200 pA with a 5 μm ion beam size. The C_{60}^+ incident angle is varied between analyses using a customized sample target to adjust the sample tilt in reference to the ion beam. The C_{60}^+ incident angles used in this research are 40° and 73°.

The cholesterol films were prepared on silicon substrates by physical vapor deposition (PVD) [9]. Cholesterol was chosen as a sample since the molecule is important to biological function and is a target for many SIMS studies [10]. The films were characterized before and after analysis using atomic force microscopy (AFM, Nanopics 2100, TLA Tencor, Inc.). An AFM image of a cholesterol film eroded using 40 keV C_{60}^+ at an incident angle of 40° is illustrated in Fig. 1a. The AFM measurement indicates a 5 nm film

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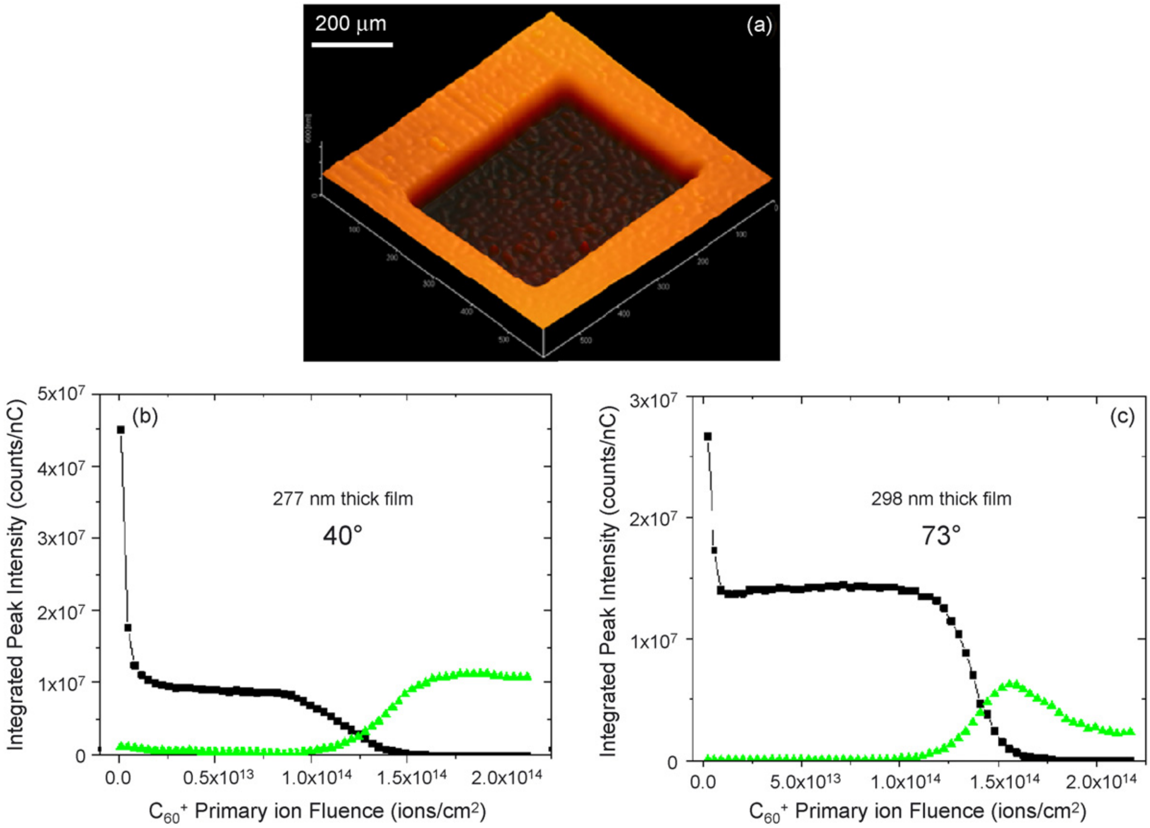

Fig. 1. (a) AFM image of cholesterol film bombarded with 40 keV, 40° incident C_{60}^{+} at 350 µm × 430 µm field. Image is acquired at a 600 µm × 600 µm field and measures the film to have a 5 nm roughness and a 277 nm thickness. (b and c) Depth profile plot of cholesterol quasi-molecular ion (m/z = 369, M-H_2O^+) and silicon substrate ion (m/z = 28, Si^+) intensities as a function of C_{60}^{+} fluence. The depth profiles were acquired using 40 keV C_{60}^{+} at 40° (b) and at 73° (c) incidence. The depth profiles were used to calculate S_{ss}/S_0 and sputter yield.

roughness and a 277 nm film thickness. The measurements were reproducible for each film used in the analyses – making the samples a suitable platform for the day-to-day comparison of molecular depth profiling.

The experiments were performed by alternating between erosion cycles and SIMS acquisition cycles. Erosion cycles involved rastering the C_{60}^{+} ion beam across the sample in direct current (DC) mode. Sputter time (~2–3 s) and sputter field (~350 µm × 350 µm) were chosen to deliver ~1 × 10^{13} C_{60}^{+} ions per cm^2 per erosion cycle. SIMS acquisition cycles involved rastering the C_{60}^{+} ion beam in pulsed mode (~70 ns pulses, 3 kHz repetition rate) across the sample. To eliminate crater edge effects, the analysis field (~50 µm × 50 µm) was chosen to be smaller then the eroded field. Positive SIMS spectra were recorded in single ion counting mode and summed over 2 × 10^5 ion pulses. The depth profiles were characterized by plotting molecule intensities from sequential spectra as a function of C_{60}^{+} fluence. The plots were used to calculate a number of depth profile parameters, including the relationship between steady-state signal and zero fluence signal (S_{ss}/S_0), the total sputtering yield, and the interface width [2,6]. Details for the calculations of the parameters are provided in the discussion.

3. Results and discussion

The objective of the research is to investigate the influence of incident angle on the quality of molecular depth profiling. The two incident angles of 40° and 73° were chosen to illustrate the contrasting configurations of off-normal and glancing angle conditions. The resulting depth profiles are shown in Fig. 1b and c. The depth profiles are plots of the cholesterol quasi-molecular ion (m/z = 369, M-H_2O^+) and the silicon substrate ion (m/z = 28, Si^+) intensities as a function of C_{60}^{+} fluence. In general, the response of the cholesterol quasi-molecular ion signal has a similar trend for both the 40° and 73° experiments. Specifically, the trend is characterized by three distinct regions: an initial loss of signal attributed to molecule damage, an intermediate quasi steady-state erosion, and a complete disappearance of signal at the film/substrate interface. The extent of molecule response in each region, however, varies according to C_{60}^{+} incident angle.

An example of the effect of C_{60}^{+} incident angle on molecule signal is the degree of chemical damage induced during the experiments. Specifically, the amount of signal loss in the initial damage region decreases as the incident angle increases. Therefore, 73° incident C_{60}^{+} inflicts less molecule damage than 40° incident C_{60}^{+}. The degree of molecule damage can be quantitatively compared by calculating the ratio of the steady-state (S_{ss}) signal to the molecule signal intensity at zero fluence (S_0) (Table 1) [2]. A value of 1 for the S_{ss}/S_0 relationship indicates no molecule damage. For 40° incident C_{60}^{+}, the value of S_{ss}/S_0 is 0.17. For 73° incident C_{60}^{+}, this value is 0.45. Hence, glancing C_{60}^{+} incident angles, such as 73°, are better for reducing molecule damage and retaining molecule signal than more normal C_{60}^{+} incident angles such as 40°.

The dependence of the total sputtering yield on incident angle is another important parameter. This dependence can be calculated from the C_{60}^{+} fluence required to remove a cholesterol film from an area of known thickness. In our case, for the 40° geometry as seen from the data in Fig. 1b, 1.53 × 10^{11} C_{60}^{+} ions are required to remove 7.7 × 10^{13} cholesterol molecule equivalents, corresponding to a yield of 503. The number of cholesterol molecules is determined

Table 1
Summary of depth profile parameters, including S_{ss}/S_0, total sputtering yield, and interface width, for the depth profiles acquired using 40 keV C_{60}^+ at 40° and 73° incidence

40 keV C_{60}^+ incident angle (±5°)	S_{ss}/S_0 – damage parameter (±0.06)	Y_{tot} – sputter yield (±32 molecule equivalents)	Interface width (±6 nm)
40	0.17	503	32
73	0.45	425	19

Details for the calculations of the parameters are provided in the discussion.

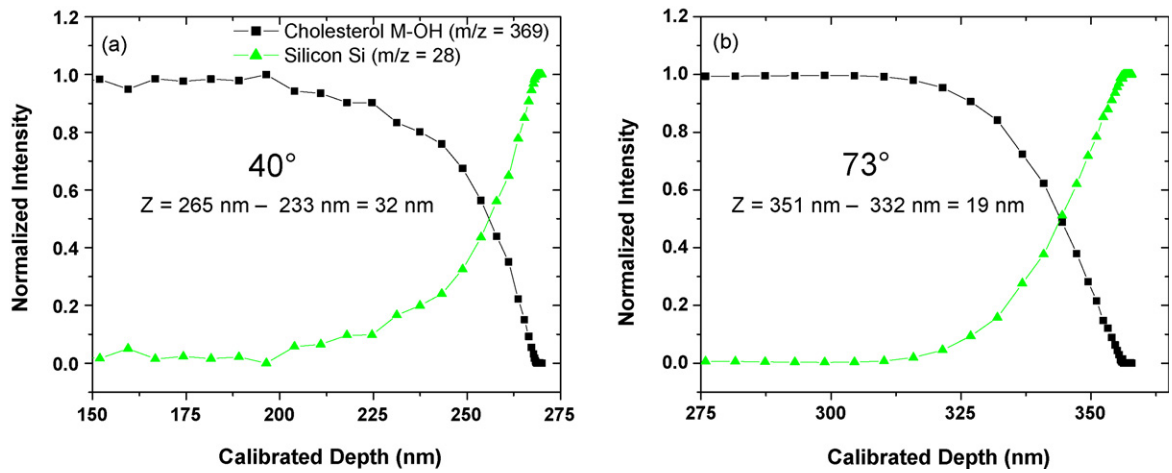

Fig. 2. (a and b) Depth profile plot of cholesterol quasi-molecular ion (m/z = 369, M-H_2O^+) and silicon substrate ion (m/z = 28, Si^+) normalized intensities as a function of calibrated film depth. The normalized intensities were calculated by taking the ratio of a specific ion intensity to the sum of cholesterol and silicon ion intensities. The depth profiles were acquired using 40 keV C_{60}^+ at 40° (b) and 73° (c) incidence. The depth profiles were used to calculate the film/substrate interface width.

from the known bombardment area of 350 μm × 430 μm, the measured film thickness of 277 nm, and a molecular density of 1.85×10^{21} molecules/cm^3. The yield for the 73° case is 425, with the data summarized in Table 1. These results are consistent with molecular dynamics (MD) computer simulations which suggest that the C_{60} incident energy is deposited closer to the surface at glancing angles and that part of the energy is reflected back into the vacuum, leading to smaller sputtering yields [4].

Finally, it is interesting to examine the broadening of the interface between the organic film and the Si substrate due to the ion bombardment process since this width ought to be related to the degree of ion beam mixing during erosion. The thickness of this altered layer is an important parameter in determining the behavior of the molecular depth profile overall. To obtain this quantity, the fluence must be converted to a depth scale by correcting for the varying erosion rates through the film and the substrate. For our case, the overall sputter rate (SR) can be calculated from the following: $\mathrm{SR}_{\mathrm{overall}} = \left(\frac{I_{\mathrm{si}}/I_{\mathrm{si}}^{\max}}{I_{\mathrm{si}}/I_{\mathrm{si}}^{\max}+I_{\mathrm{chol}}/I_{\mathrm{chol}}^{\mathrm{ss}}}\right)\mathrm{SR}_{\mathrm{si}} + \left(\frac{I_{\mathrm{chol}}/I_{\mathrm{si}}^{\mathrm{ss}}}{I_{\mathrm{si}}/I_{\mathrm{chol}}^{\max}+I_{\mathrm{chol}}/I_{\mathrm{chol}}^{\mathrm{ss}}}\right)\mathrm{SR}_{\mathrm{chol}}$, where I is the integrated peak intensity of the indicated species [6]. With this correction, the fluence data can be converted to a depth scale as indicated in Fig. 2a and b. The interface width is then estimated by subtracting the calibrated depth at 84% maximum Si intensity from the calibrated depth at 16% maximum Si intensity, with the results summarized in Table 1. As expected from the MD simulations, this width is considerably smaller for the glancing incidence geometry, suggesting that the energy is indeed deposited closer to the surface.

4. Conclusions

Experimental depth profiles at incident angles of 40° and 73° of C_{60}^+ bombardment at 40 keV show that chemical damage, total sputtering yield, and interface width decrease as the incident angle increases. In our view, the most useful depth profiles are those where the amount of chemical damage is the least and where the steady-state region of the profile is as close to the zero fluence value as possible. From this perspective, the 73° geometry is clearly an improvement over the 40° geometry. The results are consistent with a simple erosion model reported earlier where the degree of chemical damage is controlled by the relative values of the total sputtering yield to the product of the damage cross-section with the magnitude of the altered layer thickness [2]. In our case, it is apparent that the decrease in the altered layer thickness with increasing incident angle more than offsets the concomitant decrease in total sputtering yield. Since these effects are quite dramatic, it will be important in the future to examine the incident angle and kinetic energy effects in considerably more detail [11].

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