Depth Profiling of Metal Overlayers on Organic Substrates with Cluster SIMS

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ABSTRACT: Molecular depth profiling of organic thin films by erosion with energetic cluster ion beams is a unique aspect of secondary ion mass spectrometry (SIMS) experiments. Although depth profiles of complex multilayer organic structures can be acquired with little damage accumulation and with depth resolution of <10 nm using either C$_{60}^+$ or Ar$_{x}^+$ with x = 500−5000, hybrid materials consisting of both organic and inorganic layers often yield poor results. To unravel the factors that lead to this difficulty, we developed a model system composed of a thin gold layer of 1.4 to 3.5 nm deposited either on top of or sandwiched within a cholesterol thin film matrix which is several hundred nanometers thick. For these systems, the results show that by erosion with a 40 keV C$_{60}^+$ beam, reliable depth profiles can always be acquired as indicated by the presence of a steady state molecular ion signal. During the erosion process, however, gold atoms from the gold overlayer are implanted into the cholesterol matrix beneath it, resulting in a reduced sputter yield, an increase in the amount of cholesterol fragmentation and an increase in the thickness of the cluster ion-induced altered layer. The results also show that the effects of the metal film on the organic substrate are independent of the gold film thickness once the film thickness exceeds 1.4 nm. In general, this model study provides mechanistic insight into the depth profiling of heterogeneous thin film structures and offers a possible path for improving the quality of the depth profiles by employing low energy atomic ion sputtering in the region of the metal layer.

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Molecular depth profiling with energetic polyatomic ion beams has now been established for polymers and many types of organic molecules. Sophisticated protocols for optimizing these types of measurements using secondary ion mass spectrometry (SIMS) have been developed from both a practical and a theoretical point of view. In general, primary ions such as C$_{60}^+$ are successful at depth profiling since the damage created during a single ion impact is largely removed by subsequent impacts, leading to the creation of a steady state molecular ion signal.

In view of the long-time success of the depth profiling of inorganic materials, there has been an obvious attempt recently to utilize cluster-SIMS for the characterization of hybrid materials containing both organic and inorganic components. A particularly important example involves the study of organic light emitting diodes (OLEDs), which contain a number of organometallic compounds as well as a metallic overlayer coating. This challenging system has not been successfully examined yet. So far, the Al metal overlayer must be removed (delaminated) by physical means prior to analysis since the presence of this material prevents acquisition of a successful depth profile. After that, the remaining materials could be examined using C$_{60}^+$ but only when cobombarding with low energy Ar$_{x}^+$ ions. More successful results have been obtained using Ar clusters for erosion where molecular information with depth resolution of ∼10 nm has been reported for a multilayer system. The reasons behind the dramatic influence of a metal overlayer on molecular depth profiles are currently not known.

There have been few attempts to elucidate the mechanism behind the depth profiling of hybrid metal on organic systems. Using dynamic SIMS, Song et al. have examined a model OLED structure and was able to observe diffusion of a Ag overlayer into the tris(8-hydroxyquinolinato)aluminum (Alq$_3$) substrate layer. Unfortunately, no useful molecular information was found because of the destructive nature of O$_2^+$ bombardment. Aluminum and Ag overlayers on trehalose have been studied using 20 keV C$_{60}^+$ bombardment with the resulting depth profile found to be severely degraded. The results suggest that ion beam induced mixing of metal and organic materials complicate the erosion process, although no solutions were offered to fix this problem. These observations have been qualitatively confirmed by molecular dynamics (MD) computer simulations. These studies utilized thin Ag layers on top of an octetraene crystal as a model. The calculations show that the Ag atoms are indeed implanted into the organic substrate. Moreover, for thicker overlayer films, the implanted Ag is found in the form of large clusters. It is speculated that these
implanted species are largely responsible for the increased damage observed in the experiments. In addition, the calculations show that the primary ion creates a hole in the metal overlayer that its thickness is of the order of 1 nm. The organic molecules are found to sputter from the sample by jetting through this opening.

To better disentangle the molecular-level details associated with the depth profiling of hybrid materials, here we examine a model system comprised of a thick cholesterol film with a gold overlayer of thickness varying from 1.4 to 3.5 nm. The results show that meaningful depth profiles can be acquired for each of these model systems using 40 keV C$_{60}^+$ to erode through the metal–organic interfaces, but there are strong perturbations to yields, damage cross sections and altered layer thickness when compared to nonhybrid systems. The influence of the gold layer on the depth profile remains constant once the gold thickness exceeds 1.4 nm. From these observations, and by comparison to the MD simulations, we propose an approach to largely mitigate these perturbations.

### EXPERIMENTAL SECTION

**Description of the Model System.** A schematic of the model system used in this study is shown in Figure 1. In brief, 5 mm × 5 mm Si wafers (Ted Pella Inc., Redding, CA) serve as the initial building blocks. The substrates were sonicated in methanol for 15 min and rinsed with deionized water three times prior to use. Cholesterol (Avanti Polar Lipids, Alabaster, AL) was then deposited onto cleaned Si wafers to form single-component films in a previously described, home-built physical deposition (PVD) chamber.** The film thickness was monitored by a quartz crystal microbalance (QCM) during deposition and confirmed by atomic force microscopy (AFM) measurements afterward. On top of single-component cholesterol samples, various thicknesses of gold thin films were deposited by ion beam sputtering to form chemically alternating metal–organic two-component films. During the sputter deposition processes, the sputter rate is kept low at 0.001 nm/s in order to allow thin gold films to be uniformly spread onto organic substrates while the thickness of the deposited Au layers is monitored by a QCM. The sputter deposition system has been described in detail elsewhere.** The resolution of 2000 at the molecule-specific peak of cholesterol, m/z 369. All the depth profiling experiments were performed at room temperature (RT).

**Instrumentation.** Sample analysis was performed using a Bio-TOF SIMS instrument, the design of which has been described previously.** The mass spectrometer is equipped with a 40 keV C$_{60}^+$ primary ion source (Ionoptika Ltd., Southampton, U.K.), which is mounted at an angle of 40° with respect to the surface normal. The design and characteristics of the ion source have been described in detail elsewhere.** In this study, singly charged C$_{60}^+$ primary ions were selected by a Wien filter and were focused to provide ~180–200 pA beam current with a 6–8 μm diameter. For depth profiling, the mass spectrometer was set to operate alternatively between erosion cycles and image acquisition cycles. During an erosion cycle, the C$_{60}^+$ ion beam was operated in DC mode to etch through the film at an area of 400 μm × 400 μm in 6 s intervals with an etch fluence of 4.0 × 10$^{12}$ ions/cm² per cycle. Between erosion cycles, SIMS images of 256 × 256 pixels and corresponding mass spectra were collected from a zoomed area of 200 μm × 200 μm within the etched crater using the pulsed C$_{60}^+$ ion beam. The ion fluence applied during each acquisition cycle was kept below 1.0 × 10$^{10}$ ions/cm², ensuring negligible erosion even after collecting several hundred data points in the depth profile. The mass spectrometer was operated in a delayed extraction mode during data acquisition with a delay time of 60 ns between the primary ion pulse and the secondary ion extraction pulse. No sample charging was noticed in the positive SIMS mode and the acquired mass spectra have a mass resolution of 2000 at the molecule-specific peak of cholesterol, m/z 369. All the depth profiling experiments were performed at room temperature (RT).

**Atomic Force Microscopy (AFM) Measurement.** Crater depth and size information were gathered by an AFM (NanoDiscs 2100, KLA-Tencor, San Jose, CA). This unique type of AFM offers a maximum scanning area of 0.8 mm × 0.8 mm in contact mode, allowing a convenient one-step measurement of the entire eroded crater. All AFM measurements in this study were taken immediately after the depth profiling experiment was completed. Surface relaxation after ion...
thicknesses were prepared by PVD to mimic the base material.45
been reported.45 Associated with the sputtering of a pure gold film, shown in Figure 1d and 1e (325 nm). The physical properties of 2.2 nm × 325 nm. The physical properties associated with the sputtering of a pure gold film have already been reported.45

The depth profile of the underlying base cholesterol film is shown in Figure 2a. The secondary ion intensity of the cholesterol molecular ion peak (M − H)+ at m/z 385, the quasi-molecular ion peak (M − OH)+ at m/z 369, and substrate signal at m/z 28 for Si+ are plotted as a function of C60+ ion fluence. Both of the cholesterol molecule related signals exhibit an initial drop in intensity, an intermediate steady-state erosion, and a loss of intensities at the surface features. Moreover, there is no evidence for pinholes or discontinuity from this characterization. It is clear that although the depth profiles are not identical, there are similarities and differences between the trends that merit special attention.

For the 1.4 nm Au film deposited on top of the cholesterol film, shown in Figure 3a, the cholesterol molecular ion and gold signal appear at the surface and start to degrade immediately with erosion. A steady state is reached for the cholesterol molecular ion. Here, Au3+ is chosen to represent gold simply because there is less interference in that mass range, although similar results are observed for Au+. Samples with thicker gold layers result in distinctly different profiles. As shown in Figure 3b and c, depth profiles of both the 2.8 nm Au/Chol/Si film and the 3.5 nm Au/Chol/Si film contain three distinct regions. First, the gold signal appears without the presence of the cholesterol molecular ion. Second, both gold and cholesterol signals start to rise. Third, after reaching their peak value, both gold and cholesterol signals start to decline, and become similar to the behavior of the 1.4 nm Au/Chol/Si structure.

Figure 2. Characterization of cholesterol building blocks in the model system. Depth profiles of (a) 1st batch and (b) 2nd batch cholesterol PVD films, sputtered and analyzed with 40 keV C60+ at 40° incidence. The inserted AFM images show the bombarded regions in three-dimensions and line scans taken across the craters showing the two cholesterol building blocks are 622 and 325 nm thick, respectively. Panel a is the bottom cholesterol layer of Au/Chol and Chol/Au/Chol samples, while panel b is the top cholesterol layer of Chol/Au/Chol samples.

The other type of building block used in the hybrid system is a thin gold film. Recently, Yang et al.45 reported that the erosion rate is ∼2.2 nm/s material per primary ion. Their system is equipped with a 20 kV C60+ ion source and is equivalent in kinetic energy to the 40 keV C60+ ion beam employed here. Note that the erosion rate of cholesterol is >100 times that of gold.

RESULTS AND DISCUSSION

Single-Component Films. Before examining the hybrid metal–organic thin film structures shown in Figure 1, it is important to obtain depth profiles of the pure materials to act as controls. Two different cholesterol films of different thicknesses were prepared by PVD to mimic the base film shown in Figure 1b, 1c, and 1e (622 nm) and the overlayer film shown in Figure 1d and 1e (325 nm). The physical properties of the pure materials to act as controls.

Two-Component Au–Cholesterol Films. The next step is to investigate the behavior of the metal–organic interface under C60+ bombardment. The response of cholesterol films with varying thicknesses of Au overlayers to a total ion fluence of 2.0 × 1014 C60+ bombardment are shown in Figure 3. The AFM measurements (see S1 in the Supporting Information) show similar roughness values for all of the hybrid metal–organic thin films, indicating that the samples have similar surface features. Moreover, there is no evidence for pinholes or discontinuity from this characterization. It is clear that although the depth profiles are not identical, there are similarities and differences between the trends that merit special attention.

For the 1.4 nm Au film deposited on top of the cholesterol film, shown in Figure 3a, the cholesterol molecular ion and gold signal appear at the surface and start to degrade immediately with erosion. A steady state is reached for the cholesterol molecular ion. Here, Au3+ is chosen to represent gold simply because there is less interference in that mass range, although similar results are observed for Au+. Samples with thicker gold layers result in distinctly different profiles. As shown in Figure 3b and c, depth profiles of both the 2.8 nm Au/Chol/Si film and the 3.5 nm Au/Chol/Si film contain three distinct regions. First, the gold signal appears without the presence of the cholesterol molecular ion. Second, both gold and cholesterol signals start to rise. Third, after reaching their peak value, both gold and cholesterol signals start to decline, and become similar to the behavior of the 1.4 nm Au/Chol/Si structure.
The observations described above are consistent with MD computer simulations of 15 keV C$_{60}$ bombarding an analogous silver-octatetraene hybrid system. This modeling shows that when the metal overlayer is thick enough, it prevents the underlying organic molecules from disruption by absorbing the incident kinetic energy. Only metal atoms are ejected (Region I in Figure 3b and c). However, as the thickness of the layer is reduced to a critical value, energy deposition begins to occur in the organic phase. Moreover, the primary ion creates a hole in the metal overlayer which allows ejection of the underlying.

**Figure 3.** Depth profiling of cholesterol films with varying thicknesses of Au overlayers: (a) 1.4 nm Au/Chol/Si film, (b) 2.8 nm Au/Chol/Si film, and (c) 3.5 nm Au/Chol/Si film. Both panels b and c are divided into three regions: Region I in blue color shows pure gold etching; Region II in pink color represents the metal–organic interface with rising gold and cholesterol signals; In region III, the trends become similar to those in panel a. Both metal and organic material signals start to decrease.
organic molecules via a jetting mechanism. It is this phenomena that we associate with the rising cholesterol signal in region II of Figure 3b and c. Note also that the cholesterol molecular ion intensity is enhanced at the interface and is associated with the presence of the Au film. The thicker Au overlayers are associated with a higher cholesterol intensity. In addition, the gold intensity also increases to approximately the same level as in the beginning of the depth profile, indicating that the Au$^+$ signal variation within the gold overlayer is mainly caused by matrix ionization effects. Presumably, oxides in the surface contaminants and the presence of oxygen in cholesterol increase the ionization probability of gold. The 1.4 and 2.1 nm gold films (Region I + II in Figure 3b and c) require $0.7 \times 10^{14}$ and $1.2 \times 10^{14}$ ions/cm$^2$ ion fluence, respectively, to remove the film. This fluence corresponds to an average erosion rate of $\sim 2.2$ nm$^3$ gold atoms per primary ion. Eventually, the metal overlayer becomes thin enough to allow primary ions to push metal atoms into the organic layers. These implanted species are presumably associated with the decay of the metal signal (Figure 3a and Region III in Figure 3b and c). It is also clear that the presence of the Au overlayer significantly suppresses the cholesterol molecular ion information when compared to the pure cholesterol film.

**Cholesterol/Au/Cholesterol Structure.** The next level of complexity involves creating a sandwich-like sample which consists of a thin embedded Au layer of 1.4 nm thickness. Depth profiling of this sample is possible. After removal of the top cholesterol layer, the C$_{60}$ cluster penetrates through the thin gold layer and continues to etch away the buried organic layer. The cholesterol molecular ion remains detectable through the entire sample, as shown in Figure 4. The depth profile can conveniently be divided into two regions. The first region (green) encompasses the top 325 nm cholesterol film, while the second region (yellow) represents the bottom 622 nm layer.

The differences in the behavior of cholesterol within these two regions are clear. First, the absolute signal levels vary significantly. The molecular ion intensity of the buried cholesterol film at the steady state drops by a factor of 40,
which is presumably due to the reduction of sputter yield or enhancement of fragmentation. The mass spectrum shown in the inset of Figure 4 indicates that the cholesterol molecular related information is retained. Second, the erosion rate of cholesterol is reduced in the buried cholesterol area. From the data shown in Figure 2a, we know that it requires \( \sim 2.2 \times 10^{14} \) ions/cm\(^2\) to etch through a 622 nm cholesterol film. However, with the addition of the 1.4 nm thick gold layer, an ion fluence 4\( \times \) larger is required to achieve the same erosion. Since the drop in erosion rate mimics the drop in total sputtering yield, the fragmentation must be enhanced in the buried cholesterol film.

The results for the depth profile through a thicker buried gold layer of 2.8 nm are shown in Figure 5. For this case, it is possible to extract information from the gold layer. In general, the cholesterol signal in the overlayer behaves in a normal fashion. There is a reduction of intensity at the surface, followed by a steady-state erosion period before reaching the Au layer. A quasi-steady state of the Au layer is observed with ionization enhancements at both metal/organic interfaces. After a short period of etching, the gold layer loses its ability to fully cover the bottom metal-cholesterol interface. Here, the cholesterol signal is observed via the jetting mechanism discussed previously. Significant amounts of Au continue to be mixed into the bottom cholesterol layer. Moreover, the ratio of the integrated area of the Au signal to the integrated area of the cholesterol signal in the bottom cholesterol layer is found to be independent of the thickness of the gold layer. The observation suggests that the amount of implanted Au is about the same in these cases.

The relative amount of the cholesterol fragment ion \( (m/z = 95) \) to the cholesterol molecular ion \( (m/z = 369) \) is plotted as a function of ion fluence in Figure 6. The origin of this characteristic fragment has been described previously. Note
that the formation of these two cholesterol ions is simply dependent on proton transfer. Therefore, the presence of gold should not cause variations in ionization of these two ions. The fragment/molecular ion ratio profile exhibits the opposite trend of cholesterol molecular signal as shown in Figure 5. At steady state, the cholesterol molecular ion intensity in the top cholesterol film is higher than it is in the bottom cholesterol film as shown in Figure 5. Hence, this ratio profile clearly shows that the presence of the gold layer increases the amount of cholesterol fragmentation. This finding is in agreement with some early static SIMS studies which state that sample metallization induces a dramatic increase of the fingerprint fragment ion yields of polymers.48,49 A similar ratio profile is also observed in the sample with 1.4 nm Au layer in-between two cholesterol films (see S2 in the Supporting Information).

**Erosion Model.** Within the two separated cholesterol areas of the sandwich-like samples, the molecular ion signal exhibits a similar trend, namely a rapid decay into a steady state value. This behavior has been successfully interpreted in terms of a simple model19,20 describing the erosion and fragmentation dynamics in various systems.9,13,18 Here, the same cholesterol molecular ion displays different signal levels at both the initial state and the steady state. Therefore, the shapes of the molecular depth profiles in the two areas are different, as shown in Figure 7. We have employed the erosion dynamics model to investigate some important factors which could lead to the difference.

According to the model, the signal intensity at zero fluence ($S_0$) decreases exponentially to a steady-state value ($S_{ss}$) as the depth profile evolves. The initial exponential decay in signal intensity is defined by disappearance cross section, described in detail elsewhere.20 Therefore, an exponential decay is fit to the cholesterol molecular ion signal in the low fluence region via

$$S(f) = S_{ss} + (S_0 - S_{ss}) \exp \left[ \frac{-f Y}{d + \sigma_0} \right]$$

where $Y$ is the total sputtering yield volume, $d$ is the altered layer thickness, $\sigma_0$ is the damage cross section, and $f$ is the primary ion fluence. The acquired exponential slope represents the value of what appears in parentheses in the exponent of eq 1.

In addition, under steady-state conditions, the value of $S_{ss}$ is related to $Y$ and primary ion beam induced damage as

$$S_{ss} = S_0 \frac{Y}{Y + d \sigma_0}$$

The ratio of $Y$ to $d \sigma_0$ is termed as “cleanup efficiency, $\epsilon$”, which describes the ability of the projectile to remove chemical damage produced by its own impact. It is clear that under ideal conditions, $Y \gg d \sigma_0$, the bombardment debris is removed efficiently during each impact and no chemical damage is accumulated.

Within the above equations, $S_0$, $S_{ss}$, $Y$, and $f$ are known from experiment. The remaining two variables, $d$ and $\sigma_0$, can then be extracted from eqs 1 and 2. For our sample, at the top cholesterol layer, the value $S_0$ is determined by extrapolating the erosion model fit to zero fluence. The fit excludes the first acquired data point, since we notice that the signal level at the first data point is variable, which may arise from different levels of surface contamination. Using $S_0/S_{ss}$ as $\sim0.5$, $Y$ as $\sim259$ nm$^3$ per C$_{60}$ impact as measured for this sample, $\sigma_0$, and $d$ are calculated to be $\sim5$ nm$^2$ and $\sim35$ nm, respectively. The cleanup efficiency is $\sim1.5$. The same method may be applied to calculate those parameters associated with the bottom cholesterol layer. In this case, $S_0$ is determined by extrapolating the erosion model fit to the point where the cholesterol signal starts to recover. With the presence of gold, $Y$ for cholesterol is reduced to $\sim70$ nm$^3$ per C$_{60}$ impact. The results show that the $\sigma_0$ value in the bottom cholesterol layer is similar as that in the top layer, however, the value of $d$ increases nearly 4-fold. From the depth profile of the bottom cholesterol film, we notice that the cholesterol signal does not maintain a steady state after consuming $\sim3/4$ of its total erosion ion fluence. This result indicates that during erosion of the last 170 nm of the bottom cholesterol film, the supply of undamaged material ends, a finding which is in accordance with the altered layer thickness determined from the erosion dynamics model. Owing to the reduced sputter yield, the cleanup efficiency in the bottom layer is reduced to $\sim0.1$, reaching the lower limit required to obtain useful information from molecular depth profiling.

**CONCLUSION**

Molecular depth profiling of hybrid metal–organic structures is shown to be feasible using 40 keV C$_{60}$ erosion, although the sputter yield, altered layer thickness, and cleanup efficiency of the organic molecule is severely degraded by the presence of metal. For the specific case of cholesterol/Au/cholesterol, we find that a Au layer thickness of 1.4 nm or greater induces these deleterious effects. The mechanism for this degradation, as deduced from molecular dynamics computer simulations and our experimental observations, involves the continuous mixing of Au atoms and clusters that are implanted into the organic phase by the eroding cluster beam. Despite these difficulties, however, steady state signals are observed in all layers, and depth profiling of the entire hybrid structure occurs in a meaningful fashion. We anticipate that the protocols developed here will be useful in elucidating the behavior of other hybrid systems using different metal compounds.

It is of interest to speculate about developing approaches to improve the quality of depth profiles for these types of systems, especially when considering the importance of producing reliable protocols for characterizing OLED materials. The major issue appears to be the implantation of metal into the organic phase by the eroding cluster beam. Despite these difficulties, however, steady state signals are observed in all layers, and depth profiling of the entire hybrid structure occurs in a meaningful fashion. We anticipate that the protocols developed here will be useful in elucidating the behavior of other hybrid systems using different metal compounds.

**ASSOCIATED CONTENT**

Supporting Information

Additional material as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.
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Notes
The authors declare no competing financial interest.

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