Organic Depth Profiling by Cluster Ion Sputter

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Depth profiling of model organic thin films composed of Alq_3 and α-NPD on ITO-covered glass has been performed by Ar^+ or C_{60}^{++} ion sputter. In the case of conventional 2keV-Ar^+ ion sputter, as a result of the severe damage there are no peaks characteristic of their molecular structure, and a specific elemental ion of Al^+ is the only sign of Alq_3. Al^+ profiles of Alq_3 with different thickness show a constant sputtering yield. On the other hand, we can observe the survival of $C_{18}H_{12}N_2O_2Al^+$ (Alq_2^+) by use of 20keV-C_{60}^{++} cluster ion sputter. However, Alq_3 films show the quite dose-dependent sputtering yields. The dose dependency is caused by the accumulation of the sample damage, which is represented by the increase of C^+ and C_2^+. The intensities of low mass fragment ions can be available as an index of the accumulating sample damage.

1. Introduction

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is quite powerful technique for practical surface and interface analysis. It is spreading widely in both industry and academia for the characterization of organic surfaces. Recently, cluster ion sputter is at the forefront of current ToF-SIMS research to realize the high-resolution molecular imaging and molecular depth profiling. The main limitation to using ToF-SIMS for organic depth profiling was the extensive damage occurring to organic layers upon ion sputter, leading to a complete loss of molecular information. However, resent studies have shown that cluster ion sputter allows molecular depth profiling in some organic materials [1-4].

Recently Shard et al. has pointed out that some materials (polylactide and Irganox 1010) have a constant and high sputtering yield, whereas Alq_3 has lower, dose-dependent sputtering yield in C_{60} depth profiling [5]. Wucher has proposed the simple erosion dynamics model that describes the essential features commonly observed in molecular depth profiles [6]. To get more insight into the organic depth profiling by cluster ion sputter, we have intended to perform the comparable depth profiling of model organic thin films by Ar^+ or C_{60}^{++} sputter.

2. Experimental

Materials

In this study, we used three model organic thin films on ITO-covered glass, which were evaporated onto the substrate in vacuum. The first and second samples have an Alq_3 (($C_9H_6NO)_3Al$, 459 u) layer sandwiched by α-NPD ($C_{44}H_{32}N_2$, 588 u) layers. Their molecular structure is shown in Fig. 1. The third sample has an Alq_3 film as the top layer. Thickness of each layer is as follows:

Sample 1: NPD (130 nm) / Alq_3 (50 nm) / NPD (130 nm) / ITO,
Sample 2: NPD (130 nm) / Alq_3 (130 nm) / NPD (130 nm) / ITO,
Sample 3: Alq_3 (40 nm) / others (63 nm) / ITO.

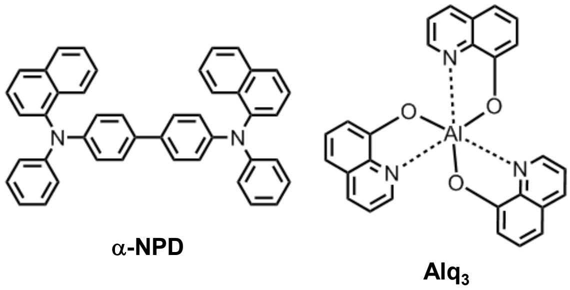

Fig. 1 Molecular structure of the materials used.

Measurements

Depth profiling was carried out using TOF-SIMS IV and TOF-SIMS V (ION-TOF Gmbh, Germany) systems equipped with 50keV-Bi_3^{++} primary ion source for ToF-SIMS analysis. The Bi_3^{++} primary ion current was set to 0.2 pA and rastered over an area of typically 150×150 μm^2 (for Ar^+ sputter) or 100 × 100 μm^2 (for C_{60}^{++} sputter). For surface sputtering, another ion sources of 2keV-Ar^+ or 20keV-C_{60}^{++} were used. The Ar^+ ion

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current was set to 30 nA and rastered over an area of typically 300×300 μm^2. The C_{60}^{++} ion current was set to 1 nA and rastered over an area of typically 200 ×200 μm^2.

Depth profiling was carried out in the "non-interlaced mode", consisting of cycles of 50keV-Bi_3^{++} analysis and 2keV-Ar^+ or 20keV-C_{60}^{++} sputter. The analyzing time was 3.3 sec/cycle (2 scan of 128×128 pixels). The primary ion dose density is estimated to 1.8×10^{10} ions/cm^2 per cycle under these conditions. The sputter time was 120 sec/cycle for 2keV-Ar^+ and 16.4 sec/cycle (10 scans of 128×128 pixels) for 20keV-C_{60}^{++}. The ion dose density is estimated to 2.5×10^{16} ions/cm^2 per cycle for 2keV-Ar^+ and 2.6×10^{14} ions/cm^2 per cycle for 20keV-C_{60}^{++}.

3. Results and Discussion

3.1 50keV-Bi_3^{++} Dose Profile

Prior to the depth profiling, the damage cross section [7] of α-NPD caused by the primary ion bombardment was evaluated. The dose profile of positively-charged characteristic ions bombarded by 50keV-Bi_3^{++} was acquired. The counts per 2 scan of interested secondary ions are plotted against the primary ion dose density (PIDD), as shown in Fig. 2. We can observe the exponential decay curve of the molecular ion of $C_{44}H_{32}N_2^+$ with increasing PIDD. The ions of $C_6H_5^+$ and $C_{16}H_{11}N^+$ do not show the exponential decay because they are the fragmentation products. The C^+ and C_2^+ ions of highly fragmentation products keep the constant and low intensity level.

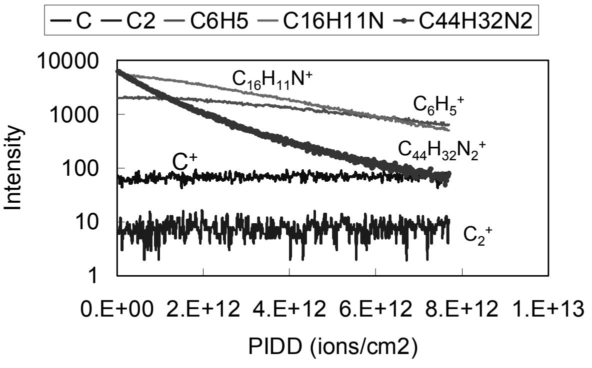

Fig. 2 Dose profile of α-NPD by Bi_3^{++} bombardment.

The damage cross section, σ, can be calculated from the slope of the respective decay curve. The σ determines the average size of the surface area damaged by one single primary ion bombardment. For the molecular ion of $C_{44}H_{32}N_2^+$, the obtained value of σ is 8.9×10^{-13} cm^2. From this σ value we can estimate the static limit of α-NPD as 1.1×10^{12} ions/cm^2 for 50keV-Bi_3^{++}. The primary ion dose density of 1.8×10^{10} ions/cm^2 per depth profiling cycle, described above, is quite below the static limit. For this reason, the 50keV-Bi_3^{++} primary ion dose may be negligible to the intensity variation observed in the depth profiles.

3.2 2keV-Ar^+ Sputter Depth Profile

Positive ion depth profiling of each sample was performed. Typical result of the sample 1 is shown in Fig. 3. In the case of Ar sputter, there is no molecular information on either α-NPD or Alq_3, and we can see the almost constant and high intensity of C^+ and C_2^+ through the layers. The low mass fragment ions such as C^+ and C_2^+ are originated from the organic materials as a consequence of severe damages caused by the ion bombardment. At the middle layer of Alq_3, Al^+ and $AlOH^+$ originating from Alq_3 were clearly observed. The Al^+ profile has a long tail toward the third layer, which was considered as the sign of knock-on effect.

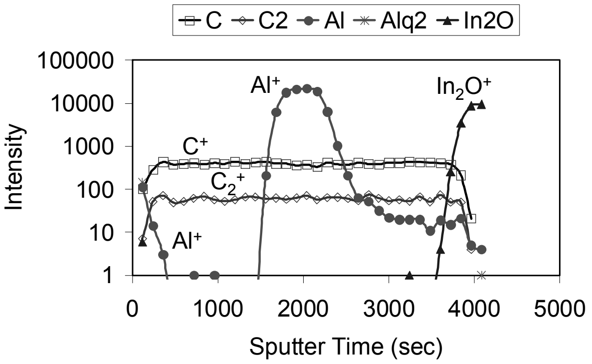

Fig. 3 Positive ion depth profile of α-NPD (130nm) / Alq3 (50nm) / α-NPD (130nm) / ITO obtained by 2keV-Ar^+ sputter.

The Al^+ profiles obtained from three samples are compared in Fig. 4. We can see the almost constant sputtering yield of Alq_3. Obtained sputtering rates for Alq_3 are tabulated in Table 1.

Table 1 Obtained sputtering rates for Alq_3 estimated from each Al^+ profile.

Alq_3 layers	2keV-Ar^+	20keV-C_{60}^{++}
top 40 nm	0.11 nm/sec	0.81 nm/sec
middle 50 nm	0.10 nm/sec	0.08 nm/sec
middle 130 nm	0.09 nm/sec	not measured

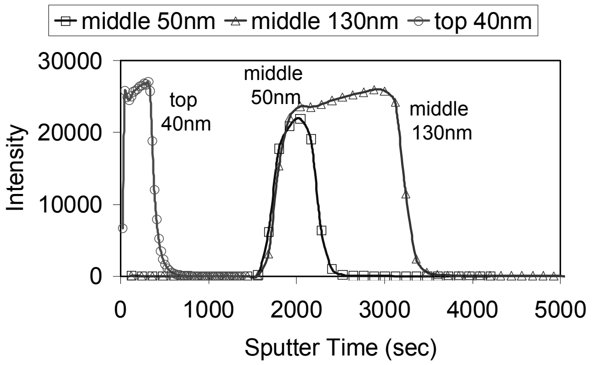

Fig. 4 Comparison of Al$^+$ ion depth profiles among three samples obtained by 2keV-Ar$^+$ sputter.

3.3 20keV-C$_{60}^{++}$ Sputter Depth Profile

Positive ion depth profiling of samples 1 and 3 was performed. Typical result of the sample 1 is shown in Fig. 5. In the case of C$_{60}$ sputter, we can clearly observe the characteristic ion of Alq$_2^+$ (315 u) along with Al$^+$ and AlOH$^+$, which is due to the cluster ion effect of less sample damage. Thus, C$_{60}$ sputter depth profiling is believed to be one of the key technologies to realize the molecular depth profiling. However, it should be pointed out that the gradual increases of C$^+$ and C$_2^+$ within the first α-NPD layer were observed. These increases are considered to be a sign of accumulation of the sample damage on the depth-profiling surface. The intensities of C$^+$ and C$_2^+$ in the third α-NPD layer reached to the similar high level of the Ar sputter, as shown in Fig. 6.

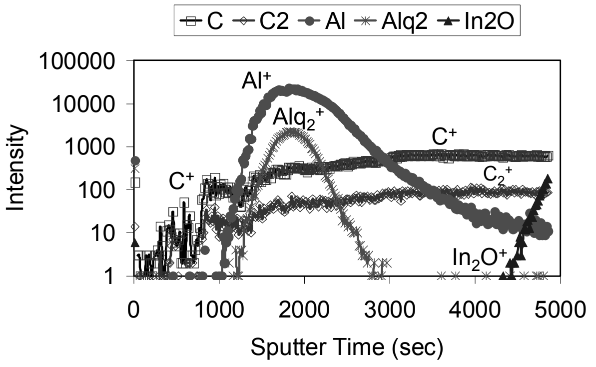

Fig. 5 Positive ion depth profile of α-NPD (130nm) / Alq3 (50nm) / α-NPD (130nm) / ITO obtained by 20keV-C$_{60}^{++}$ sputter.

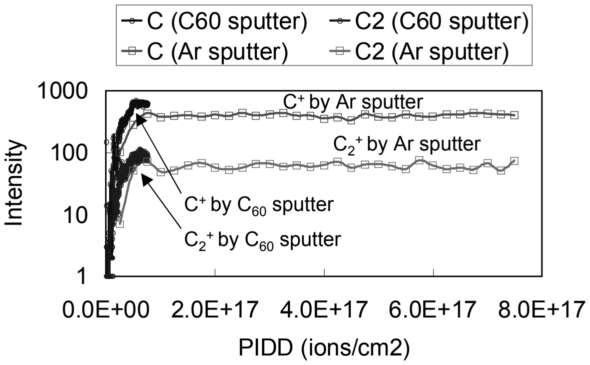

Fig. 6 Comparison of C$^+$ and C$_2^+$ ion depth profiles of the sample 1 obtained by 2keV-Ar$^+$ and 20keV-C$_{60}^{++}$ sputter.

The Al$^+$ profiles obtained from two samples are compared in Fig. 7. Although their thickness is close, we can see the quite different sputtering yield of Alq$_3$. The sputtering yield is very high when the Alq$_3$ layer is the top layer whereas the yield is much lower for the underneath layer. This dose dependency is caused by the accumulation of the sample damage, which are represented by the gradual increases of C$^+$ and C$_2^+$ intensity within the first α-NPD layer.

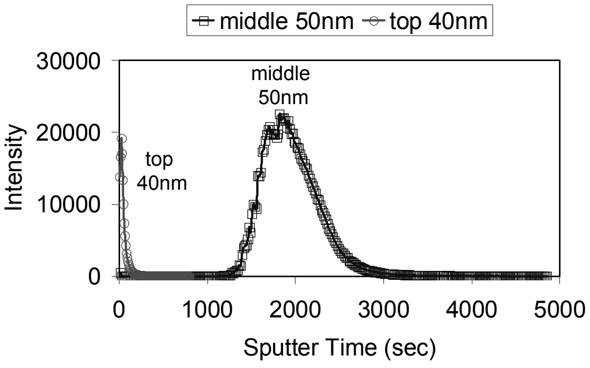

Fig. 7 Comparison of Al$^+$ ion depth profiles between two samples obtained by 20keV-C$_{60}^{++}$ sputter.

4. Conclusion

For C$_{60}$ cluster ion sputter, films of Alq$_3$ show the quite dose-dependent sputtering yields. The dose dependency is caused by the accumulation of the sample damage, which is represented by the increase of C$^+$ and C$_2^+$. These intensities of low mass fragment ions can be available as an index of the accumulating sample damage.

5. Acknowledgement

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6. References

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