Organic Depth Profiling by Cluster Ion Sputter

Yoshimi Abe
Yokohama Laboratory, Mitsubishi Chemical Group Science and Technology Research Center, Inc.
1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan
1105863@cc.m-kagaku.co.jp
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Depth profiling of model organic thin films composed of Alq3 and \( \alpha \)-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 Alq3. Al\(^+\) profiles of Alq3 with different thickness show a constant sputtering yield. On the other hand, we can observe the survival of C\(_{18}H_{12}N_{2}O_{2}Al\(^+\) (Alq\(_{2}\)\(^+\)) by use of 20keV-C\(_{60}\)\(^{++}\) cluster ion sputter. However, Alq3 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, recent 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 Alq3 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 Alq3 ((C\(_{9}H_{6}NO\)\(_{3}\))Al, 459 u) layer sandwiched by \( \alpha \)-NPD (C\(_{44}H_{32}N_{2}\), 588 u) layers.

Their molecular structure is shown in Fig. 1. The third sample has an Alq3 film as the top layer. Thickness of each layer is as follows:

- Sample 1: NPD (130 nm) / Alq3 (50 nm) / NPD (130 nm) / ITO,
- Sample 2: NPD (130 nm) / Alq3 (130 nm) / NPD (130 nm) / ITO,
- Sample 3: Alq3 (40 nm) / others (63 nm) / ITO.

![Fig. 1 Molecular structure of the materials used.](image)
current was set to 30 nA and rastered over an area of typically 300 \times 300 \, \mu m^2. The C_{60}^{++} ion current was set to 1 nA and rastered over an area of typically 200 \times 200 \, \mu m^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 \times 128 pixels). The primary ion dose density is estimated to 1.8 \times 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 \times 128 pixels) for 20keV-C_{60}^{++}. The ion dose density is estimated to 2.5 \times 10^{16} ions/cm\(^2\) per cycle for 2keV-Ar\(^+\) and 2.6 \times 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 \(\alpha\)-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_{6}H_{5}^{+} and C_{10}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.

For the molecular ion of C_{44}H_{32}N_{2}^{+}, the obtained value of \(\sigma\) is 8.9 \times 10^{-13} \, cm\(^2\). From this \(\sigma\) value we can estimate the static limit of \(\alpha\)-NPD as 1.1 \times 10^{15} ions/cm\(^2\) for 50keV-Bi_{3}^{++}. The primary ion dose density of 1.8 \times 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 \(\alpha\)-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 \(\alpha\)-NPD (130nm) / Alq_{3} (50nm) / \(\alpha\)-NPD (130nm) / ITO obtained by 2keV-Ar\(^+\) sputter.](image)

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.](data_table)

<table>
<thead>
<tr>
<th>Alq_{3} layers</th>
<th>2keV-Ar(^+)</th>
<th>20keV-C_{60}^{++}</th>
</tr>
</thead>
<tbody>
<tr>
<td>top 40 nm</td>
<td>0.11 nm/sec</td>
<td>0.81 nm/sec</td>
</tr>
<tr>
<td>middle 50 nm</td>
<td>0.10 nm/sec</td>
<td>0.08 nm/sec</td>
</tr>
<tr>
<td>middle 130 nm</td>
<td>0.09 nm/sec</td>
<td>not measured</td>
</tr>
</tbody>
</table>
3.3 20keV-C₆₀⁺⁺ 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 C₆₀ sputter, we can clearly observe the characteristic ion of Alq₂⁺ (315 u) along with Al⁺ and AlOH⁺, which is due to the cluster ion effect of less sample damage. Thus, C₆₀ 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 C₂⁺ 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 C₂⁺ in the third α-NPD layer reached to the similar high level of the Ar sputter, as shown in Fig. 6.

4. Conclusion

For C₆₀ cluster ion sputter, films of Alq₃ 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 C₂⁺. 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