Extended Abstract of PSA-19
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TOF-SIMS MS/MS Depth Profiling of OLED Devices -Toward the Elucidation of Degradation Process-

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TOF-SIMS depth profiling is a common way to evaluate the OLED devices. However, the depth profiles of OLEDs are still complicated due to the mass interference from other organic compounds. In this study, in order to extract the accurate depth distributions from conventional depth profiles, MS/MS depth profiling method has been applied. This new method enables us to determine the specific molecular depth distributions of individual organic compounds, and understand the degradation mechanism.

1. Introduction

Recently, OLED (Organic Light Emitting Diode) devices are widely used in many fields such as computers, smartphones, TVs, watches, as well as illumination sources. The advantages of OLEDs include high brightness, slenderness, flexibility and high speed response, etc. OLEDs will be the main light emitting device in the next decade.

One of the major issues of present OLEDs is lifetime. A degradation analysis of OLEDs is necessary to achieve a longer operating life. Generally, the degradation process of OLEDs is complicated, because it has many factors, and they are intricately linked each other. In order to investigate the details of the process, the author has examined the molecular information on deteriorate OLEDs using TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectroscopy). TOF-SIMS is a powerful analysis technique which allows us to directly observe the molecular distribution. Furthermore, after the invention of Ar-GCIB (Ar-gas cluster ion beam), the combination of Bismuth cluster and Ar-GCIB has brought us the three dimensional molecular distributions with high spatial resolution. Nowadays, Bi/Ar-GCIB has become a common and indispensable analysis technique for depth profiling of OLED devices [1]. However, to discuss the accurate molecular distributions in OLED depth profiles is still difficult. The OLED generally has 5 to 7 organic layers, and we often observe that the fragment ions interfere with each other and confuse the interlayer boundaries. In this study, therefore, TOF-SIMS MS/MS depth profiling has been used to obtain the specific compound depth profiles without interference from other organic compounds.

2. Experiment

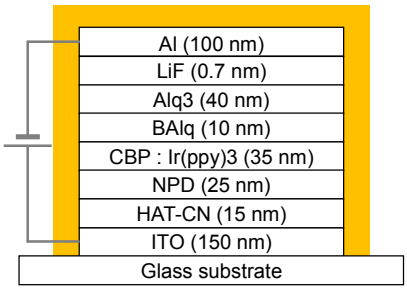
2-1. Sample

The layer structure of the green OLED devices used in this work are shown in Fig. 1. OLED samples with new and 50 % degradation of light brightness were prepared. After peeling off the aluminum layer, the depth profiles were acquired.

2-2. Measurement conditions

A conventional TOF-SIMS instrument (PHI *nano*TOF II, ULVAC-PHI, Inc., Japan) was used in this study. In addition to the Bi and Ar-gas cluster ion columns used for OLED depth profiling, the instrument was also equipped with tandem MS (MS/MS) [2, 3]. A single nominal mass can be selected from the stream of secondary ions, and the selected ions are dissociated at ~1.5 keV collision energy in the CID (Collision Induced Dissociation) cell that was filled with Ar gas. The analysis and sputter ions were 60 keV Bi_5^{++} and 2.5

keV Ar_{2500}^+, respectively. 15 eV electrons were used during the depth profiling for the charge neutralization.



Alq3: Tris(8-hydroxyquinolinato)aluminium
BAlq: Bis(2-methyl-8-quinolinolate)-4-(phenylphenolato)aluminium
CBP: 4,4′-Bis(N-carbazolyl)-1,1′-biphenyl
Ir(ppy)3: Tris(2-phenylpyridinato)iridium(III)
NPD: N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine
HAT-CN: Hexaazatriphenylenehexacarbonitrile

Fig. 1 Layer structure of green OLED device. Chemical name of each organic compound is also shown.

3. Results and Discussions

Figure 2(a) shows the MS^2 product ion spectrum of $C_{18}H_{12}AlN_2O_2^+$ which is the most intense secondary ion peak from Alq3. In this study, the intensities of four major product ions of Al^+ (*m/z* 27), $C_9H_6AlNO^+$ (*m/z* 171), $C_9H_7AlNO_2^+$ (*m/z* 188), and $C_{10}H_6AlN_2O^+$ (*m/z* 197) were summed to describe the MS^2 depth profiles. Figure 2(b) shows the comparison between MS^1 (conventional) and MS^2 depth profiles of $C_{18}H_{12}AlN_2O_2^+$. The intensities were normalized by the $^{115}In^+$ signal of the ITO substrate to recognize the differences easily. The dashed and solid lines denote the depth profiles of new and degraded OLEDs, respectively. The depth distributions of $C_{18}H_{12}AlN_2O_2^+$ in MS^1 especially at organic/ITO interface was unclear because of the unresolved isobaric interference from other organic compounds. In contrast, the MS^2 depth profiles reflect the depth distributions derived from only $C_{18}H_{12}AlN_2O_2^+$. The results indicate that the Alq3 diffused to the substrate as part of the degradation process.

4. Summary

MS/MS depth profiling has made it possible to extract specific molecular depth distributions from conventional depth profiles. This method enables us to discuss the detailed degradation process, and will lead to deep understanding of the degradation mechanism.

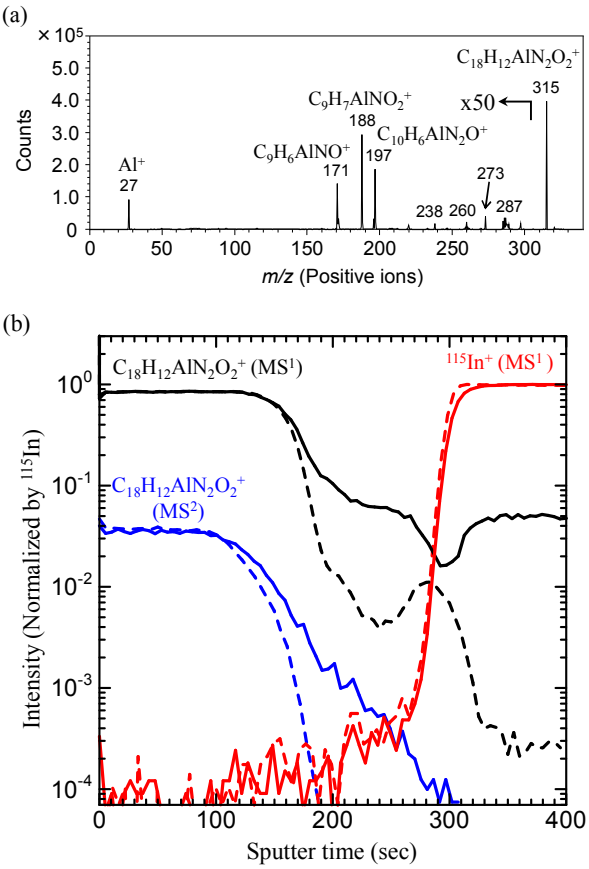


Fig. 2 (a) MS^2 product ion spectrum of $C_{18}H_{12}AlN_2O_2^+$ from Alq3 standard sample. (b) Comparison between MS^1 and MS^2 depth profiles of $C_{18}H_{12}AlN_2O_2^+$. The dashed and solid lines denote the depth profiles of new and degraded OLEDs, respectively.

Acknowledgments

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5. References

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