

# Analysis of Organic Thin Films by the Laser Desorption/Ionization Method Using the JMS-S3000 “SpiralTOF”

**Takaya Satoh**

**MS Business Unit, JEOL Ltd.**

Laser Desorption/Ionization-Time of Flight Mass Spectrometry (LDI-TOFMS) is generally used for analysis of organic compounds because this technique generates little fragmentation of molecular ions at ionization. It makes possible to obtain information on molecular weights and molecular structures in organic compounds. In particular, a technique which uses the matrix compounds for enhancing ionization efficiency is well known as Matrix-Assisted Laser Desorption/Ionization-Time of Flight Mass Spectrometry (MALDI-TOFMS). This technique is widely used in the bio markets owing to its capability of ionizing proteins and peptides with the molecular weights of several thousands to several hundreds of thousands. The MALDI-TOFMS is also utilized for analysis of synthetic polymers. In many cases, LDI-TOFMS and MALDI-TOFMS have been used to estimate the molecular weights of organic compounds in solution. But very recently, techniques of imaging mass spectrometry, which controls the laser irradiation position by two-dimensional scan to acquire mass spectra for visualizing localization of chemical compounds with specific molecular weights, have been improved. The application of this innovative technique is increasingly spreading in the bio markets. The technology of Imaging Mass Spectrometry has been advancing for analyzing biological tissue sections, but in the future, it is expected to develop toward the material science markets. It is noted that various surface analytical techniques are already available in the material science markets. In order to study the advantages of LDI-TOFMS as one of effective surface analysis tools, it is essential to consider the complementary analysis of LDI-TOFMS with the existing surface analytical techniques. In this article, the advantages of using LDI-TOFMS for analyzing organic light-emitting diode material thin films, in accordance with comparison with Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy/Energy-Dispersive X-Ray Spectroscopy (SEM/EDS), have been studied. In addition, since LDI-TOFMS is a destructive analytical technique, the influence on the sample surface caused by LDI-TOFMS was also examined.

## Introduction

The surface analytical techniques irradiate an electron beam, an ion beam or X-ray on the surface of the sample for investigation of its morphology and physical characteristics based on the interactions between the beam and substances existing on the sample surface. To observe the sample morphology, an optical microscope and an electron microscope are mainly used. To study the sample characteristics, a wide range of techniques is available depending on the incident particles (beam) and the signals to be detected. They include Electron Probe Microanalysis (EPMA), Auger Electron Spectroscopy (AES), X-ray Photoelectron

Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). In recent years, electronic devices are frequently composed of organic compounds such as organic semiconductor, organic light-emitting diode (OLED) and organic film solar cell, and the use of them will be expected to further expand. It is increasingly important to inspect organic-compounds and their degradation mechanism in the products. Among surface analytical techniques, AES and XPS are capable of obtaining chemical bonding states or information on functional groups in chemical compounds, but those techniques have a difficulty in structural analysis of organic compounds. The TOF-SIMS is a mass spectrometry technique well known as a surface analytical technique. By using the dynamic SIMS, fragmentation of the molecular ions is likely to occur at ionization, thus making it difficult to apply SIMS to analyze organic compounds. Recently, techniques which utilize metallic clusters or gas clusters as a

3-1-2 Musashino, Akishima, Tokyo, 196-8558, Japan.

E-mail: taksatoh@jeol.co.jp

primary ion beam attached to TOF-SIMS have been succeeded to ionize more softly. These techniques are expected to expand the TOF-SIMS applications for organic compounds.

This article reports on Laser Desorption/Ionization-Time of Flight Mass Spectrometry (LDI-TOFMS). As a technique that utilizes the laser desorption mechanism, Matrix-Assisted LDI-TOFMS (MALDI-TOFMS) is in widespread use, which enables ionization of a variety of chemical compounds by properly combining a sample with matrix compounds enhancing ionization. Around 2000 year, the number of installed MALDI-TOFMS has been dramatically increased aiming to analyze proteins and peptides. Moreover in the material analysis fields, MALDI-TOFMS has been utilized for the analysis of synthetic polymers. The use of the matrix is essential for the measurement of these large-molecular weight organic compounds, thus the ionization technique using laser is generally called "MALDI". But, there are many chemical compounds which can be ionized only with laser irradiation. In this case, the used ionization technique is simply called "LDI".

Most of mass spectrometry techniques analyze samples in solution. MALDI-TOFMS also mixes the sample solvent and the matrix solvent to crystallize them by dropping on a target plate. By irradiating the co-crystal of matrix and sample compounds with the ultraviolet, MALDI-TOFMS ionizes various organic compounds contained in the sample and performs mass separation. In recent years, imaging mass spectrometry that adopts MALDI-TOFMS [1,2], which can acquire information about localization on the sample surface, is demonstrating technological improvement and therefore, the use of this unique technique is increasingly spreading. In Imaging Mass Spectrometry, the matrix is sprayed uniformly onto the sample surface and mass spectra are acquired while the laser irradiation position to the sample is two-dimensionally scanned. This process allows acquisition of information on two-dimensional distributions of specific chemical compounds. Imaging Mass Spectrometry has been expanding its applications to the bio markets from its dawn, including proteins, peptides, lipids, drugs and their metabolites. Most of the subjects for this technique are biological tissue section. On the other hand, in accordance with the establishment of biological tissue sectioning techniques, the users gradually start to study the application of Imaging Mass Spectrometry to the material analysis markets and also, this technique is expected to visualize information on localization of organic compounds on a thin film or a solid surface. In order to make Imaging Mass Spectrometry more effective in the material analysis markets, it is very important to carry out complementary analysis with the existing surface analytical techniques. In this article, the fundamental experiments using the JMS-S3000 "SpiralTOF" to examine LDI-TOFMS as one of surface analytical techniques were reported. The comparison with information obtained by XPS and TOF-SIMS and the influence of laser irradiation onto the surface of the organic thin film made of OLED material were examined.

## Sample

For complementary analysis among LDI-TOFMS, TOF-SIMS and XPS, *N,N'*-Di(1-naphthyl)-*N,N'*-diphenylbenzidine ( $\alpha$ -NPD), which is a material for a hole transport layer of an OLED, was deposited onto a Si substrate with 600 nm thick (hereinafter, called " $\alpha$ -NPD/Si"). In addition, in order to examine the influence of LDI on the sample surface, the author prepared a different sample of another Si substrate where a material for a hole transport layer of an organic EL (4,4',4''-Tris[2-naphthyl(phenyl)amino]triphenylamine (2-TNATA) of a thickness of 700 nm) was deposited onto the substrate and furthermore,  $\alpha$ -NPD of a thickness of 1300 nm was deposited onto the prepared layer (hereinafter, called " $\alpha$ -NPD/2-TNATA/Si").

## Analyses of Organic Thin Film Using LDI-TOFMS, TOF-SIMS and XPS

The JMS-S3000 "SpiralTOF" was used as an LDI-TOFMS. **Figure 1(a)** shows the external view of the SpiralTOF. The biggest feature of the SpiralTOF is adopting a JEOL originally-developed spiral ion trajectory (Fig. 1(b)) and this trajectory is formed by four hierarchical electrostatic sectors. The flight distance of 1 cycle is 2.093 m and the SpiralTOF achieves an effective flight distance of 17 m at 8 cycles. Here, the mass resolution of TOFMS is proportional to the flight distance. The general effective flight distance of the reflectron TOFMS is approximately a few meters, but the SpiralTOF which has an effective flight distance of 17 m can achieve the world-highest mass resolution among MALDI-TOFMSs. Furthermore, the electrostatic sectors which forms the spiral ion trajectory makes it possible to eliminate the fragment ions during their flight, thus a mass spectrum with little noise can be acquired. By attaching the TOF-TOF option [4], it is possible to perform structural analysis with the Tandem Mass Spectrometer (MS/MS). The high energy CID (collision-induced dissociation) could provide much structural information rather than low energy CID used in major MS/MS instruments. The SpiralTOF is equipped with a Newport Nd:YLF (349 nm) as an ionization laser source. The laser irradiation diameter onto the sample surface is approximately 20  $\mu$ m and the laser intensity is 60  $\mu$ J at 100 % laser setting.  $\alpha$ -NPD and 2-TNATA are ionized without requiring the matrix, so the experiments were performed by acquiring the mass spectra using LDI-TOFMS. **Figure 2(a)** shows a mass spectrum ( $m/z$  10 to 800) acquired by fixing the laser irradiation position on the  $\alpha$ -NPD/Si and by accumulations of 250 times. Only molecular ions of  $\alpha$ -NPD are observed in the mass spectrum and it is found that ion fragmentation is very little at the ionization. Using the TOF-TOF option, the author acquired a product ion spectrum by selecting the observed molecular ions. Fig. 2(b) shows the observation result of the created fragment ions and the estimated fragmentation position of fragmentation. By the use of the High-Energy

CID technique, sufficiently much information was obtained to estimate the molecular structure.

The Ar gas cluster ion beam source attached to JEOL JMS-T100LP “AccuTOF LC-plus” developed in Matsuo Group at Kyoto University [5] was used for TOF-SIMS experiments. **Figure 3(a)** shows its external view. Fig. 3(b) shows a mass spectrum ( $m/z$  0 to 800) which was acquired with the primary ion beam of Ar cluster ions (accelerating voltage: 10 kV) that irradiates on the “ $\alpha$ -NPD/Si”. The molecular ion peak of  $\alpha$ -NPD ( $[M]^+$ ) was observed. However, the fragment ions were also observed with noticeable abundance in low mass range, ( $m/z$  100 to 500), compared to LDI-TOFMS. This may be due to two reasons. One is the fragment ions generated from  $\alpha$ -NPD at the ionization. It was considered reasonable because the pattern of the product ion spectrum in Fig. 2(b) is relatively similar to the mass spectrum acquired with TOF-SIMS. On the other hand, the measurement region in depth direction by TOF-SIMS is confined to only 10 nm or less from the top surface of the sample, thus many chemical back ground peaks produced from surface contamination. Since Ar cluster ions are used for the primary ion beam, the mass spectrum achieves the littlest fragmentation among TOF-SIMSs. However compared to LDI-TOFMS, it should be taken into consideration the influence of the fragmentation or a remarkable influence of sample-surface contamination on the mass spectrum. TOF-SIMS makes it possible to perform high spatial resolution

mapping and depth profiling by monitoring molecular ions or major fragment ions. For example during the mapping, a spatial resolution of 1  $\mu\text{m}$  or less is achieved, indicating that this resolution performance is higher than that obtained by Imaging Mass Spectrometry using the present MALDI-TOFMS (typically a few tens of micrometers). But, when taking account of the fact that many fragment ions and the background originating from the surface contamination are observed, this technique is applicable only to the ions of major components. The chemical compounds deriving from the major components in degradations expected to be minor components; therefore, distinction with fragment ions or with surface contamination may become difficult.

The JEOL JPS-9010 was used for XPS experiments. **Figure 4(a)** shows its external view of the JPS-9010. The analysis area was set to be 1 mm diameter. Fig. 4(b) and (c) show the measurement result of  $\alpha$ -NPD/Si. A spectrum shown in Fig. 4(b) is a wide spectrum (energy resolution: 1.7 eV equivalent to  $\text{Ag}3d_{5/2}$ ) and the peaks of C and N which are constituent elements of  $\alpha$ -NPD are clearly observed. In the spectrum obtained by XPS, which is a top-surface analysis instrument like TOF-SIMS, a Si peak originating from a substrate is not observed. Furthermore, a narrow spectrum (energy resolution: 0.5 eV equivalent to  $\text{Ag}3d_{5/2}$ ) was acquired from the vicinity of the C peak. It was able to understand the peaks including the information on C-C

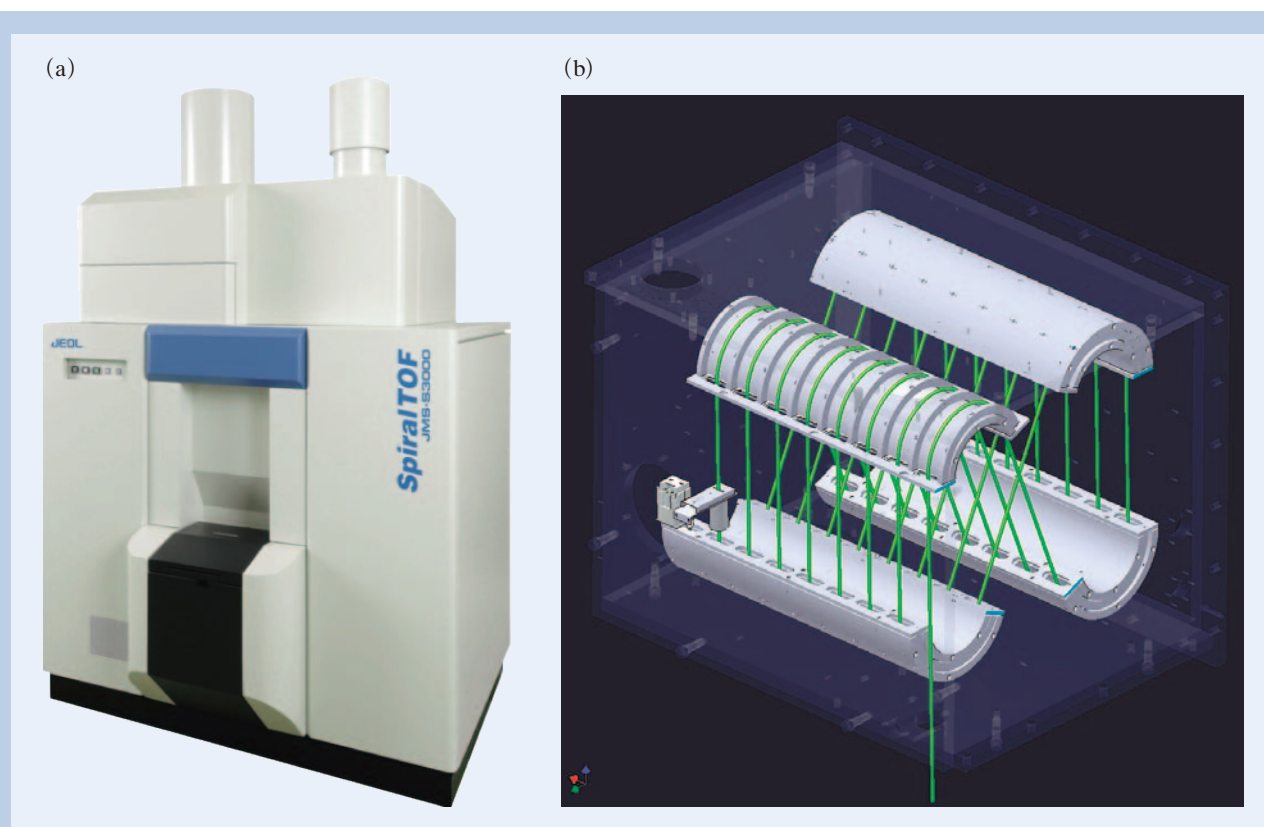


Fig. 1 (a) External view of the JMS-S3000 (when the Linear TOF option and the TOF-TOF option are attached), and (b) the schematic of the spiral ion trajectory in the JMS-S3000.

bonding and the C-N bonding. As compared to mass spectrometry techniques (LDI-TOFMS, TOF-SIMS, etc.), XPS provides non-destructive analysis and also can perform quantitative analysis which is difficult in mass spectrometry caused by ionization uncertainty. However, when the sample is an organic compound formed by a combination of limited elements, it is not easy to quantitatively analyze mixtures in the compounds with an XPS instrument. In particular, it is estimated that, when the limited elements are mixed as minor components where the composition of a degradation product does not

change largely, the separation of their spectral peaks becomes more difficult.

As described above, the chemical information from LDI-TOFMS with both TOF-SIMS and XPS, which are the existing surface analytical techniques, are compared. The advantages of LDI-TOFMS in the analysis of organic compounds are the followings. LDI-TOFMS enables one to confirm mainly molecular ions from the mass spectrum and also, makes it possible to perform structural analysis through MS/MS analysis. These powerful features play a significant role especially in the analysis of

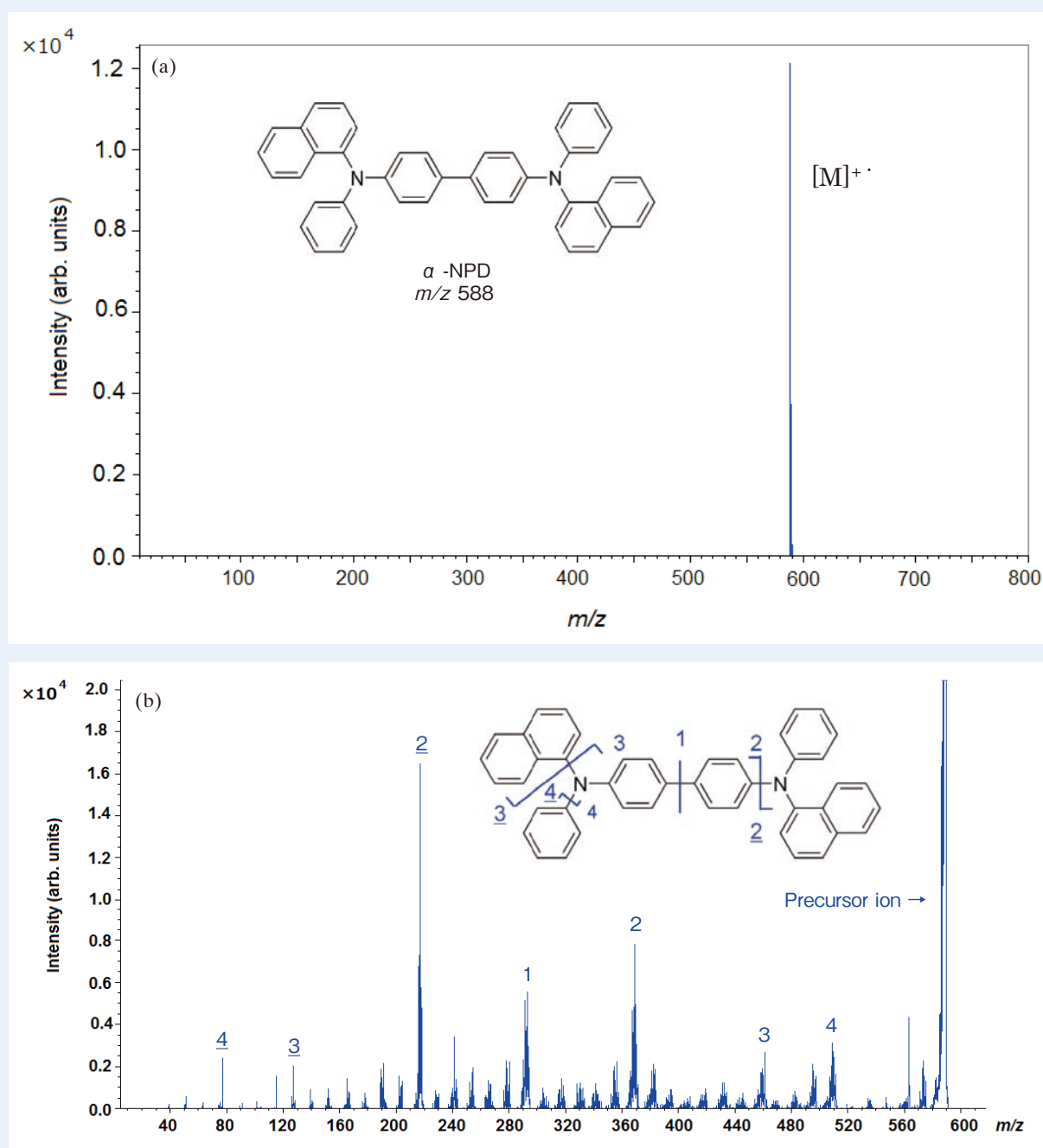


Fig. 2 (a) Mass spectrum of  $\alpha$ -NPD acquired by LDI-TOFMS. Peaks indicating the molecular information on  $\alpha$ -NPD are clearly observed. (b) MS/MS spectrum of  $\alpha$ -NPD. Peaks well reflecting the structures of  $\alpha$ -NPD are observed.

organic mixtures which exist on the sample surface. Also in degradation analysis, this technique is expected to allow the analysis of a minor component which is a degradation product created from the major component.

## Influence of Laser Irradiation on the Sample Surface

The influence of laser irradiation on the sample surface by using the Scanning Electron Microscope/Energy-Dispersive X-ray Spectrometer (SEM/EDS)

was confirmed. **Figure 5(a)** shows the external view of the instrument used for this experiment, JEOL SEM JSM-7001FTTLLV equipped with the OXFORD Instruments AZtec Energy Standard X-Max50. Fig. 5(b) shows an SEM image of an irradiation scar after the sample surface was irradiated with a laser beam under the conditions of laser intensity 40% and the number of laser shot of 250. From this SEM image, the ablation of organic thin-film layers was observed at a diameter of 35  $\mu\text{m}$  in the scar after the laser irradiation. In addition, Fig. 5(c) and (d) respectively show the analysis result of EDS spectra acquired from the irradiation scar

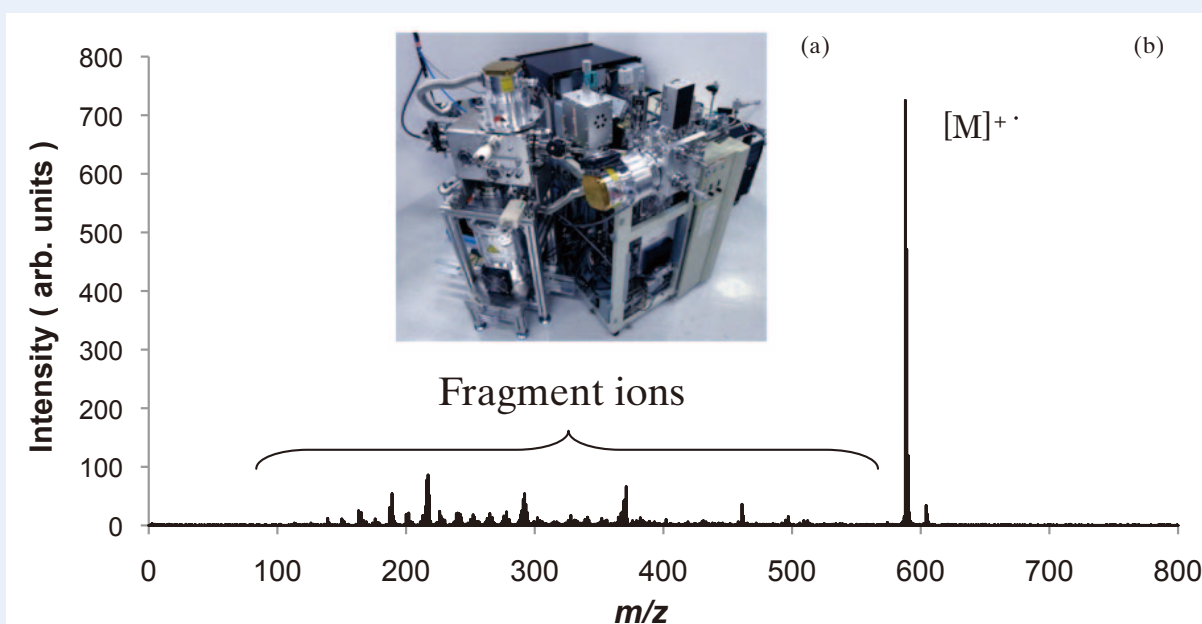


Fig. 3 (a) TOF-SIMS possessed by Matsuo Group, and (b) a mass spectrum of  $\alpha$ -NPD mass spectrum acquired with TOF-SIMS. In addition to peaks indicating the molecular information on  $\alpha$ -NPD, many peaks are observed, which are considered to originate from the fragment ions of  $\alpha$ -NPD and the surface contamination.

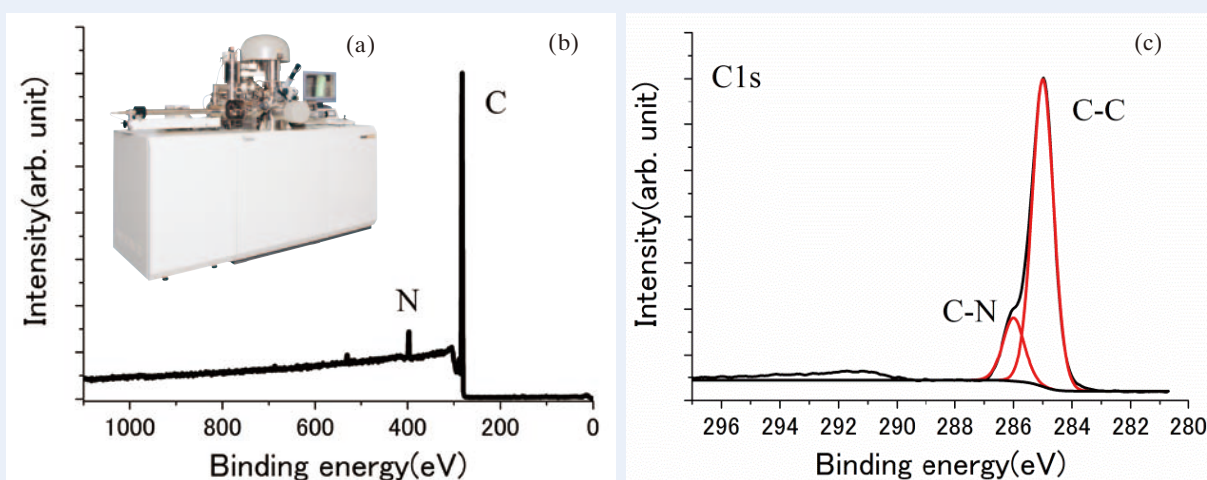


Fig. 4 (a) External view of the JPS-9010, and (b) A wide spectrum of  $\alpha$ -NPD/Si. C and N which are constituent elements of  $\alpha$ -NPD are clearly observed. (c) A narrow spectrum of  $\alpha$ -NPD/Si and a narrow spectrum in the vicinity of C allows observation of peaks indicating the C-C bonding and C-N bonding.

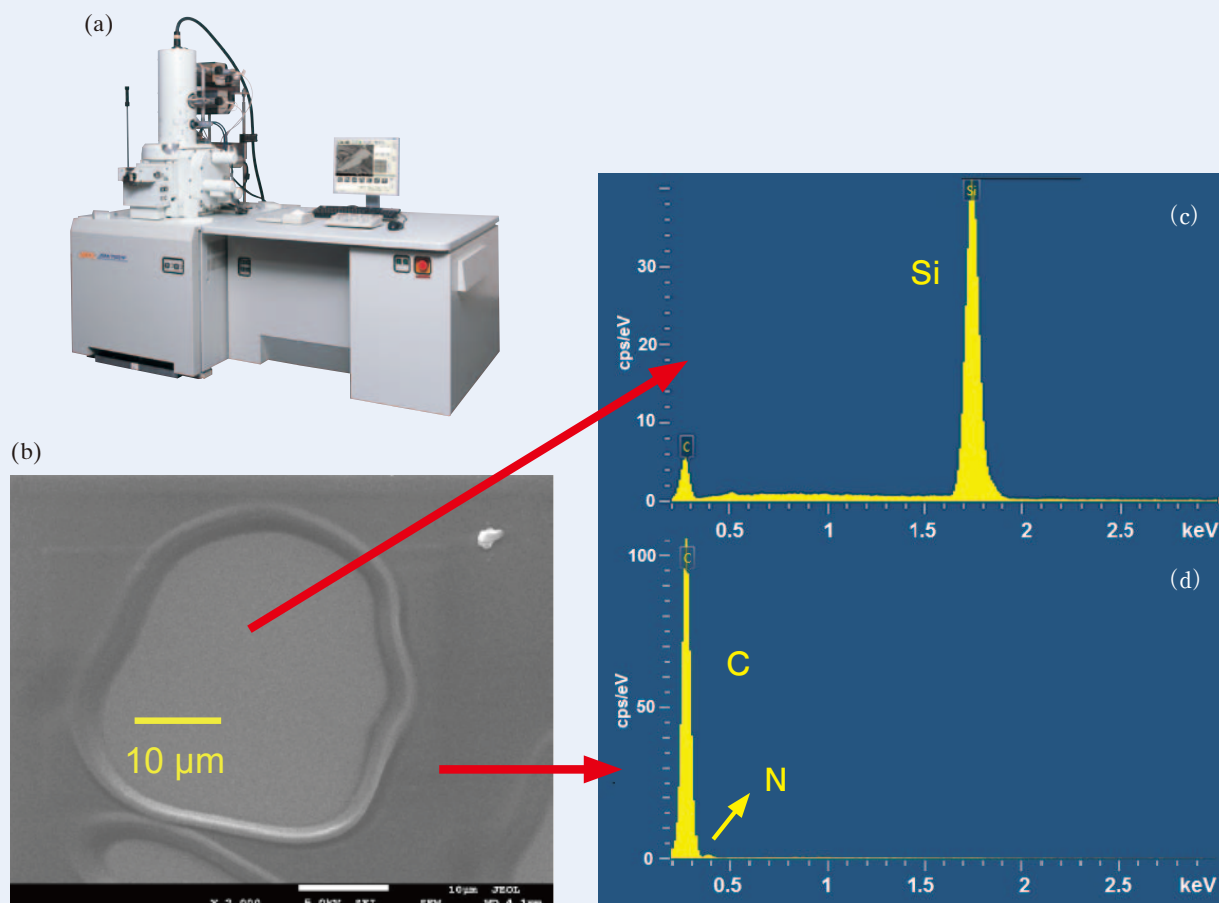


Fig. 5 (a) External view of the JSM-7001FTTLV. (b) SEM image of an irradiation scar acquired after laser irradiation of the sample surface with laser intensity 40 % and the number of laser spot of 250. (c) EDS analysis result obtained from an area of a laser irradiation scar and an area in the vicinity of a laser irradiation scar. The result indicates that organic thin-film layers penetrate into the scar, confirmed by observation of Si from the laser irradiation scar and of C from the vicinity of the irradiation scar.

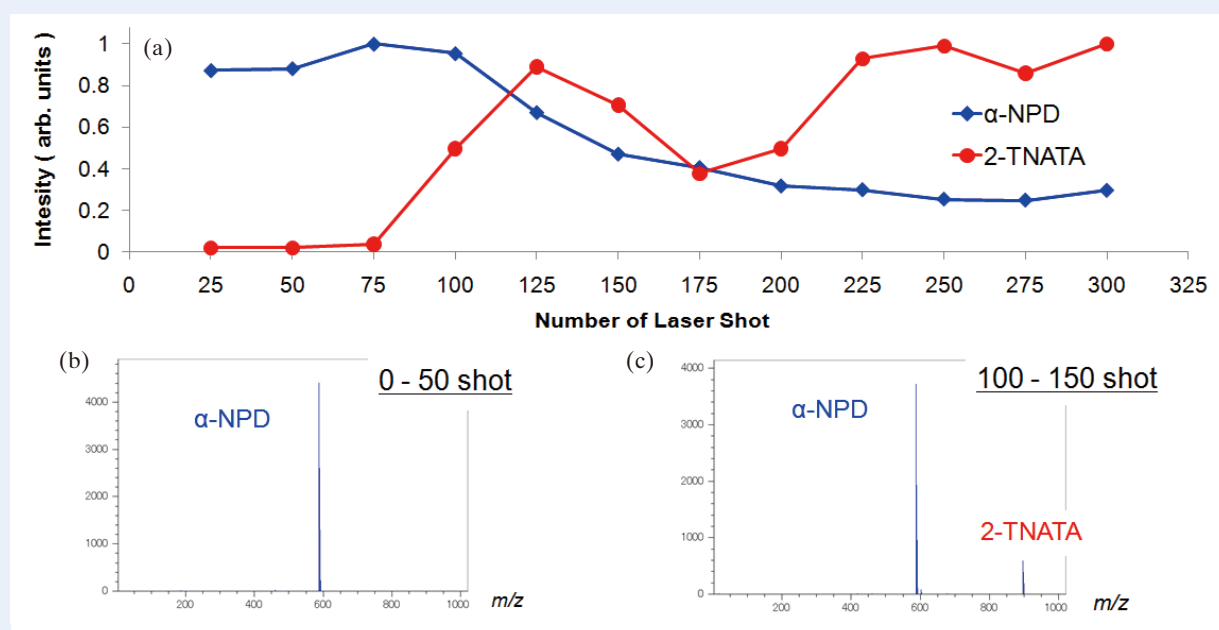


Fig. 6 (a) Ion intensity transitions of  $\alpha$ -NPD and 2-TNATA when  $\alpha$ -NPD/2-TNATA/Si is fixed and measured. Mass spectra acquired with the number of laser shot of 0 to 50 (b) and 100 to 150 (c) are also shown, respectively.

and from an area on which organic thin-film layers exist near the irradiation scar. The peaks of Si and C were observed from the former and latter spectrum, respectively, indicating that the laser irradiation allows penetration of the organic layers into the scar to be confirmed.

Mass spectra of  $\alpha$ -NPD/2-TNATA/Si were acquired under the conditions of laser irradiation position fixed and laser intensity 40%. **Figure 6(a)** shows the plot diagram of ion intensity variations of molecular ions of  $\alpha$ -NPD and 2-TNATA with respect to the number of laser shot. The ion intensity of  $\alpha$ -NPD on the upper layers decreased as the number of laser shot increases. On the other hand, 2-TNATA on the lower layers started to be observed in the mass spectrum when the number of laser shot reached 100. Fig. 6(b) and (c) respectively show the accumulation mass spectrum acquired with the number of laser shot of 0 to 50 and 100 to 150 are shown in Fig. 6(b) and (c), respectively. The fragment ions are hardly observed in both spectrum and the 2-TNATA is clearly appeared in only Fig. 6(c). However,  $\alpha$ -NPD on the upper layers was still observed even after 2-TNATA on the lower layers started to be observed. It is expected that as the number of laser shot increases, the ionization region spreads in the plane direction as well as in the depth direction. The variation of the number of laser shot for the appearance of 2-TNATA in the mass spectrum according to the laser intensity is shown in **Fig. 7**. It is found that, as the laser intensity increases, 2-TNATA appears even when the number of laser shot is decreased. This result indicates that

the influence of depth is affected by the number of laser shot and the laser intensity.

From these results, the author found that the influence of laser irradiation on the sample surface changes greatly depending on the laser irradiation conditions (laser intensity and the number of laser shot). For the depth direction, the present experiments indicate that the comprehensive information on regions between 100 nm and 1  $\mu$ m is obtained. Compared to the measurement results obtained by top-surface analytical techniques such as XPS and TOF-SIMS, the present depth regions are considerably large. When increasing the number of laser shot and the laser intensity, the ionization region increases for not only in the depth direction but also in the plane direction, thus care is required for mapping.

## Summary

This article reported on comparison and examination of organic thin-film analysis for LDI-TOFMS, TOF-SIMS and XPS. The XPS and TOF-SIMS have a difficulty in applying the techniques to multi-component samples. This is because XPS can obtain information only on elements and chemical bonding states, and TOF-SIMS makes a mass spectrum complicated caused by fragment ions. To the contrary, LDI-TOFMS can mainly observe molecular ions, thus it is suitable for the analysis of multi-components. In degradation analysis of organic chemical compounds in electronic parts, it

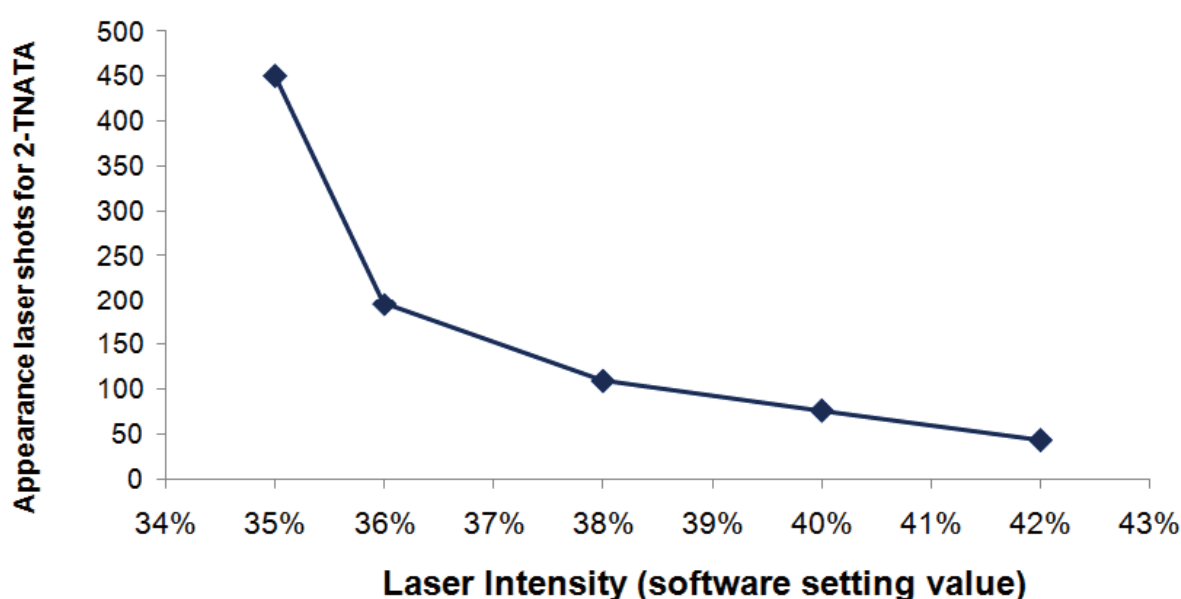


Fig. 7 The number of laser shot at which 2-TNATA starts to be observed when the laser intensity is changed. As the laser intensity increases, the influence of laser irradiation on the sample surface becomes large.

is expected that the total element composition ratio does not change largely, thus LDI-TOFMS can be used as an important tool for identifying degradation components because this technique enables one to confirm molecular ions and to perform structural analysis by MS/MS. In addition, it may be considered that the amount of the degradation product is not so large compared to original compound; therefore, the use of LDI-TOFMS allows one to expect clear analysis because LDI-TOFMS produces almost no fragment ions at the ionization.

Furthermore, the SEM observation result which revealed the sample-surface states after laser irradiation clarified that the comprehensive information of 100 nm or more was obtained in the depth direction of a thin film in an organic EL material. Influence of laser irradiation on the depth direction depends on the laser intensity and the number of laser shot. When LDI-TOFMS is used, the information of depth direction is considerably larger than that obtained by XPS and TOF-SIMS, in which the typical analysis depth is 10 nm or less. In the analysis of thin films having structures in the depth direction using XPS or TOF-SIMS, it is often combined with ion etching because they are top-surface analytical technique. In this case, it is possible to perform depth profiling with high resolution to depth direction. On the other hand, when LDI-TOFMS is used, clear acquisition of the information in the depth direction is rather difficult compared to XPS and TOF-SIMS, but it may be considered that LDI-TOFMS can classify chemical compounds contained in the same thin-film layer.

Now, the use of the (MA) LDI-TOFMS is making it possible to acquire two-dimensional distributions of chemical compounds on the specimen surface in accordance with the progress of Mass Imaging technologies. In the future, by accumulating the knowledge about ionization of samples of thin films and the influence of laser

irradiation on the sample surface, LDI-TOFMS will widely be applied as one of powerful surface analytical techniques.

## Acknowledgments

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Table 1 Comparison of LDI-TOFMS with the other surface analytical techniques.

	Probe	Detected signal	Spatial resolution	Depth direction	Chemical information
Energy-Dispersive X-ray Spectroscopy (EDS)	Electron	X-ray	1 $\mu\text{m}$	< 1 $\mu\text{m}$	Element
Auger Electron Spectroscopy (AES)	Electron	Auger electron	10 nm	< 10 nm	Element, Chemical bonding states
X-ray Photoelectron Spectroscopy (XPS)	X-ray	Electron	10 $\mu\text{m}$	< 10 nm	Element, Chemical bonding states, Functional group
Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)	Ion	Ion	100 nm	< 10 nm	Element, Partial molecular structure
Laser Desorption/Ionization-Time of Flight Mass Spectrometry (LDI-TOFMS)	UV light	Ion	10 $\mu\text{m}$	a few 100 nm	Molecular structure