

ULVAC's Efforts to Ensure Cleanliness of Organic Electro Luminescence Manufacturing Equipment

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The problem with organic light-emitting diode (OLED) displays is that their service lifetime is affected by impurities in vacuum equipment. Therefore, equipment manufacturers need to ensure the cleanliness of their equipment. We developed a technology to evaluate trace amounts of water-soluble impurities in vacuum equipment by using ion chromatography (IC). As a result, we established our own simple cleanliness evaluation technology.

By using this evaluation technology to monitor and take countermeasures against residual ions in the equipment during each process from manufacturing to delivery, we have been able to manufacture equipment with high cleanliness that meets the required quality.

In addition, we conducted device fabrication and service lifetime tests on OLED deposition equipment to evaluate the impact of equipment components on device lifetime. The evaluation of devices exposed to fluorinated resin-coated cables suggested that the factor causing service lifetime degradation was a gas containing C-F. Meanwhile, it was found that the devices can still be used as device components by reducing the amount of impurities through appropriate cleaning processes. We will contribute to further quality improvement of OLED production equipment by utilizing this technology.

1. Introduction

In recent years, organic light-emitting diode (OLED) displays have become increasingly popular due to their thinness, light weight, contrast, and flexibility, and there is a demand for even higher quality products (higher efficiency and longer service lifetime). As shown in Fig. 1, the service lifetime of an OLED device decreases in proportion to the amount of impurities in the vacuum equipment¹⁾. In particular, the effects of water, organic impurities, and halogen compounds are known²⁻⁴⁾. Therefore, ensuring the cleanliness of the equipment has become an important issue for equipment manufacturers.

Within the chambers of the vacuum equipment, there are various mechanisms such as an evaporation source, a protective plate, a drive mechanism that handles substrates, and doors between chambers. Known substances that may cause impurities in these mechanisms include gases dissolved

in resin materials such as O-rings and resin cables; plasticizers; hardeners; cutting oils and cleaning fluids used during metal machining; and grease used in drive units. There is also a possibility that impurities may be brought in from outside the work area or clean room during equipment manufacturing.

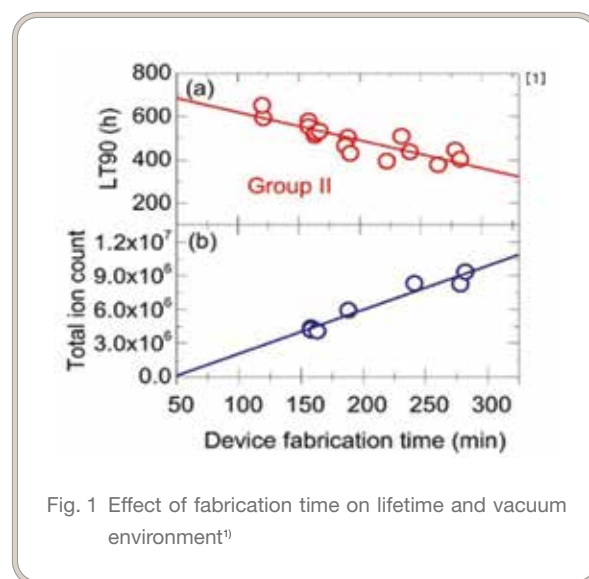


Fig. 1 Effect of fabrication time on lifetime and vacuum environment¹⁾

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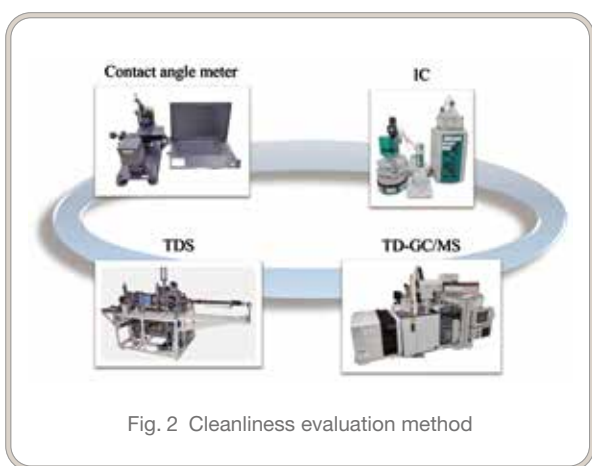


Fig. 2 Cleanliness evaluation method

In response to this issue, as shown in Fig. 2, ULVAC carries out quality control using a wide range of analytical and measurement instruments, including ion chromatography (IC), thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS), thermal desorption spectrometry (TDS), and contact angle meters. Among these instruments, we focused on IC as an analytical method to evaluate residual water-soluble impurities in the equipment, and established an IC evaluation technique.

This paper introduces a case study of IC evaluation⁵⁾ conducted as an effort to ensure cleanliness in the manufacturing process of OLED production equipment and a case study of the impact of components used in the equipment on the service lifetime of OLED devices⁶⁾.

2. Evaluation of the cleanliness of OLED manufacturing equipment using IC

IC is an analytical method that separates ion species in aqueous solution by using differences in their affinity with ion exchange resins and then determines their concentrations

from their electrical conductivity. To evaluate water-soluble impurities in vacuum equipment using IC, we wipe the surfaces inside the equipment with a wipe and then measure ions by eluting them in ultrapure water. Since this evaluation method is a trace analysis, the collection site area, elution conditions, and solution handling greatly affect the results, so it is necessary to understand the background variability before evaluating the results.

2.1 Measuring equipment

We measured anions and cations by using equipment manufactured by Metrohm AG. We used the Compact Professional IC881 to measure anions and the 930 Compact IC Flex to measure cations. Equipment details are shown in Table 1.

2.2 Ultrapure water and reagents

To clean the instrument and prepare the solvent and solution for ion elution of the samples, we used ultrapure water purified with the Super-Q and ELIX 70 systems manufactured by Merck to 18 MΩ • cm or higher.

The mobile phase for the anion measurement was 1 mol/L sodium carbonate (for IC) manufactured by Kanto Chemical, and the suppressor regeneration solution was 10 mol/L sulfuric acid (for IC) diluted with ultrapure water. The mobile phase for cation measurement was prepared by dissolving 2,6-pyridinedicarboxylic acid (Wako special grade) manufactured by Fujifilm Wako Pure Chemical in 1 mol/L nitric acid (for IC) manufactured by Kanto Chemical and diluted with ultrapure water. Ions were measured qualitatively and quantitatively by the calibration curve method using a standard solution. For the measurement of anions, we used seven types of anion mixture standard solutions (JCSS) manufactured by Fujifilm Wako Pure

Table 1 Ion chromatography equipment used

Ion	Anion	Cation
Analyzer	Compact Professional IC881	930 Compact IC Flex
Autosampler	858 Professional Sample Processor	
Concentration System	Dosino	Dosino
Separation column	Metrosep A Supp 7-250/4.0	Metrosep C4-250/2.0
Concentration column	Metrosep A PCC2 HC/4.0	Metrosep C PCC1 HC/4.0
Guard column	Metrosep A Supp 5 Guard/4.0	Metrosep C4 Guard/2.0
Suppressor	Yes	No
CO ₂ suppressor	Yes	No

Chemical: F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻. For the measurement of cations, we used six types of cation mixture standard solutions (for IC) manufactured by Kanto Chemical: Li⁺, Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺. All the solutions were prepared with ultrapure water.

2.3 Equipment and sample collection tools used

In IC measurement, ions eluted from a sample are analyzed by using ultrapure water as a solvent. For this reason, it is necessary to reduce ions other than those derived from the sample as much as possible, which is why we selected instruments with few water-soluble impurities. In addition, there is a risk of contamination of the sample due to the dissolution of water-soluble impurities in the laboratory atmosphere. Therefore, the equipment was installed in a class 100,000 clean room. We collected samples from the chambers and components with wipes while wearing polyethylene (Labment brand) gloves. For the wipes, we used the ASPURE Super Wiper Econo, which has a low ion content.

To prepare each sample, we immersed the entire surface of the wipe in a polyethylene bottle containing 50 mL of ultrapure water, closed the lid, stirred the solution about 10 times, and then let it stand for 30 minutes.

By using wipes with few eluting ions, the background was reduced to less than 55 ng for F⁻, Cl⁻, NO₂⁻, Br⁻, PO₄³⁻, SO₄²⁻, Li⁺, NH₄⁺, and Mg²⁺ and less than 500 ng for NO₃⁻, Na⁺, K⁺, Ca²⁺.

2.4 Standard solution measurement variability and detection limits

Using a volumetric flask, we prepared each standard solution by diluting the anion mixture standard solution (JCSS) 500-fold and the cation mixture standard solution

Table 2 RSD and detection limit of standard solution

Ion	Average concentration [ppb] (μg/L)	RSD [%]	Lower detection limit [ppt]
F ⁻	4.67	0.85	1
Cl ⁻	4.71	0.64	2
NO ₂ ⁻	22.2	1.12	3
Br ⁻	22.5	0.67	7
NO ₃ ⁻	22.3	0.90	7
PO ₄ ³⁻	44.5	0.67	15
SO ₄ ²⁻	22.6	0.66	6
Li ⁺	0.50	1.26	6
Na ⁺	2.04	1.58	24
NH ₄ ⁺	2.01	1.72	24
K ⁺	4.99	1.54	59
Ca ²⁺	5.28	2.69	62
Mg ²⁺	5.03	2.20	59

(for IC) 40-fold. We used the Dosino concentration system to inject a prescribed amount of each standard solution for measurement. Table 2 shows the results of the analysis with the number of measurements $N=3$. Measurement variability was defined as relative standard deviation (RSD), calculated as standard deviation/mean value $\times 100$. The RSD values were small at 0.5 to 1.2%, confirming that ppb-level trace analysis could be measured with good reproducibility. The detection limit was calculated as (average concentration $\times 3 \times \text{noise/signal}$)⁹. The detection limits ranged from several ppt to several dozen ppt. By verifying the measurement variability and detection limit, we proved that analysis at the ppb (ng as ion amount) level was possible. The reason for the lower determination limit and lower detection limit for anions compared to cations is thought to be the decrease in baseline noise caused by the suppressor and the increase in the signal of the measured ions⁹.

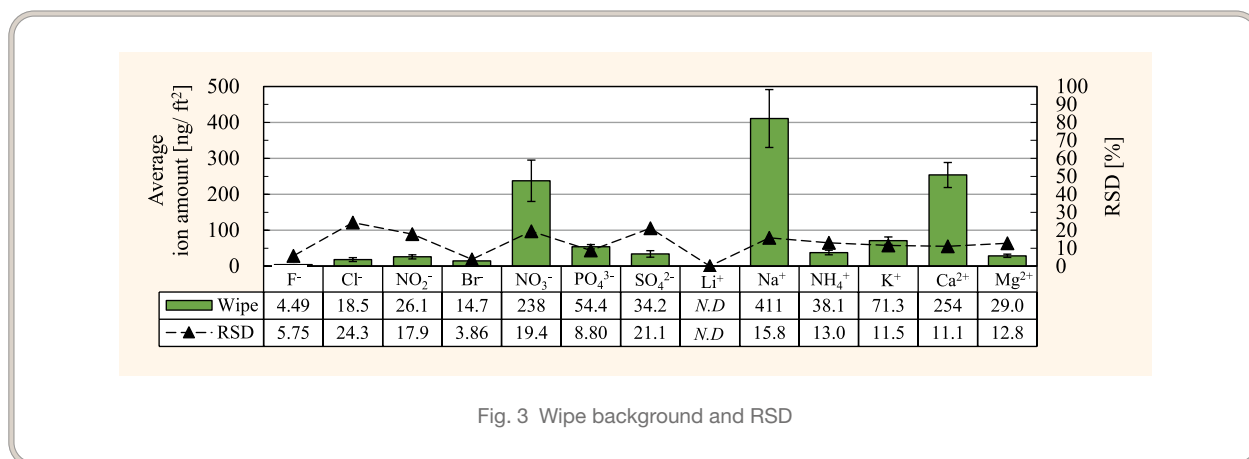


Fig. 3 Wipe background and RSD

2.5 Background variability

To measure the background of the wipes used to collect the samples, we used data from five samples from the same lot. The average ion amount and RSD for each ion are shown in Fig. 3. Error bars indicate expanded uncertainty (4.0 effective degrees of freedom, inclusion factor $k=2.78$). The average ion amounts of the wipes were higher for Na^+ , Ca^{2+} , and NO_3^- , while the RSDs were greater for Cl^- , SO_4^{2-} , and NO_3^- . The catalog values are Cl^- : 172 ng, Na^+ : 636 ng, K^+ : 80 ng, Ca^{2+} : 768 ng, Mg^{2+} : 146 ng. In contrast, the observed ion amounts were Cl^- : $19 \text{ ng} \pm 6 \text{ ng}$, Na^+ : $411 \text{ ng} \pm 81 \text{ ng}$, Ca^{2+} : $254 \text{ ng} \pm 35 \text{ ng}$, Mg^{2+} : $29 \text{ ng} \pm 5 \text{ ng}$. Except for K^+ , the ion amounts were lower than the catalog values. When we evaluated a different lot of wipes other than those used in this study, the ion amounts were about the same as the catalog value, which may be due to a difference in quality. The ion amounts from the wipes varied from lot to lot, but the RSD did not change significantly. This suggests that there should be no problem with the evaluation so long as it is performed after measuring the background of the wipe to be used.



Fig. 4 L-shaped evaluation sample

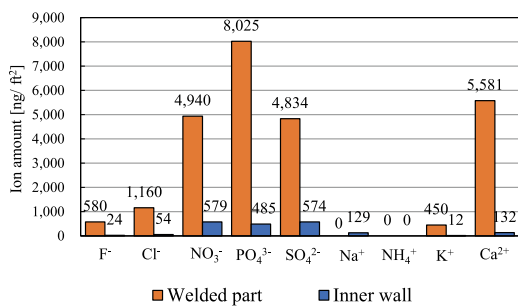


Fig. 5 Cleanliness evaluation of L-shaped part

2.6 Example of cleanliness evaluation

The L-shaped welded SUS304 stainless steel part shown in Fig. 4 was used as the cleanliness evaluation sample. It is approximately 15 cm square with a plate thickness of 25 mm. The part was subjected to general electrolytic polishing and precision cleaning treatment in the vacuum equipment.

We used the wipes to collect samples from two locations on the L-shaped part: the welded part and the inner wall. To collect samples from the part, it was wiped three times with a wipe 900 cm² (approx. 1 ft²) in size, and the wiped surface was folded inward and stored in a centrifuge tube. In cases where the sampling area was less than 900 cm², the ion amounts were calculated by converting the measurements to values per 900 cm². Each collected sample was analyzed using the methods described in section 2.3.

The evaluation of the L-shaped part was performed after measuring the background of the wipes used for sampling. The results of the cleanliness evaluation of the L-shaped part are shown in Fig. 5. The ion amounts in the samples were obtained by subtracting the average background value from the measured value.

The results show large differences depending on the location being evaluated. With the exception of Na^+ , the ion amounts of the water-soluble impurities were greater at the welded part than at the inner wall. This is thought to be due to the fact that the weld marks at the joined edges are difficult to clean, so the impurities were not completely removed during the cleaning process. The following three factors can be considered to be responsible for the residual presence of the respective ions.

- PO_4^{3-} , SO_4^{2-} : Residues from chemicals used in the electrolytic polishing process
- F^- , NO_3^- : Residues from chemicals used in the passivation process

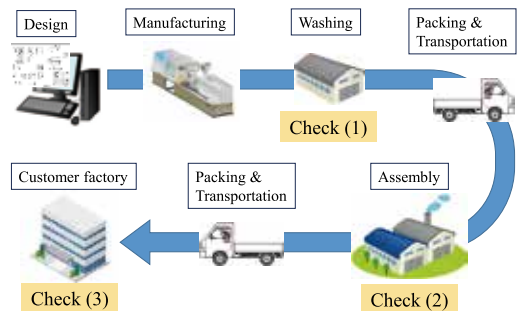


Fig. 6 Cleanliness evaluation from equipment manufacturing to delivery

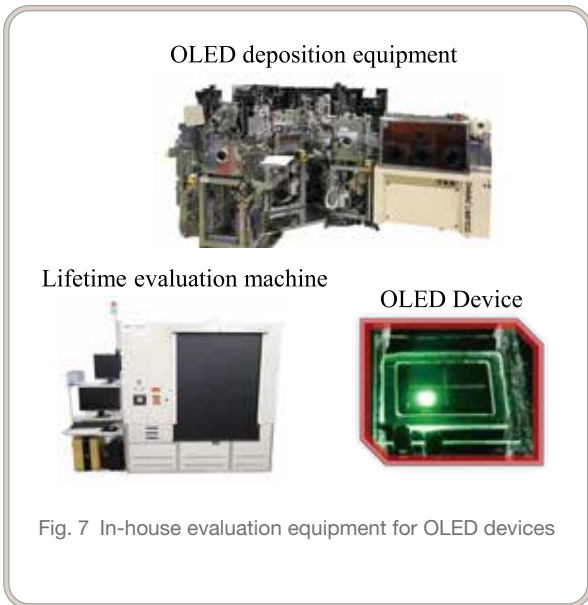


Fig. 7 In-house evaluation equipment for OLED devices

- Cl⁻, Na⁺, K⁺, Ca²⁺: Contamination from the environment and from the packaging and transportation of parts

Based on these results, we were able to establish our own simple cleanliness evaluation technique.

2.7 Efforts to ensure the cleanliness of our OLED manufacturing equipment

Fig. 6 shows the cleanliness evaluation flow of ULVAC's OLED manufacturing equipment. The evaluation is conducted by using a stainless steel chamber and in three stages: check (1) (after washing), check (2) (after cleaning), and check (3) (after delivery to customer). In addition, we regularly evaluate and certify cleaning manufacturers on the basis of our own independently developed standards. By monitoring and taking countermeasures against residual ions in the equipment at each stage, we have established a system to manufacture equipment with high cleanliness that meets the quality requirements of our customers.

3. Evaluation of impurities affecting OLED device lifetime

In addition to manufacturing highly clean equipment using the analysis and evaluation techniques described in section 2, ULVAC fabricates OLED devices using the OLED deposition system in Fig. 7 and conducts lifetime testing of the devices in order to evaluate the impact on device lifetime of the parts used in the equipment.

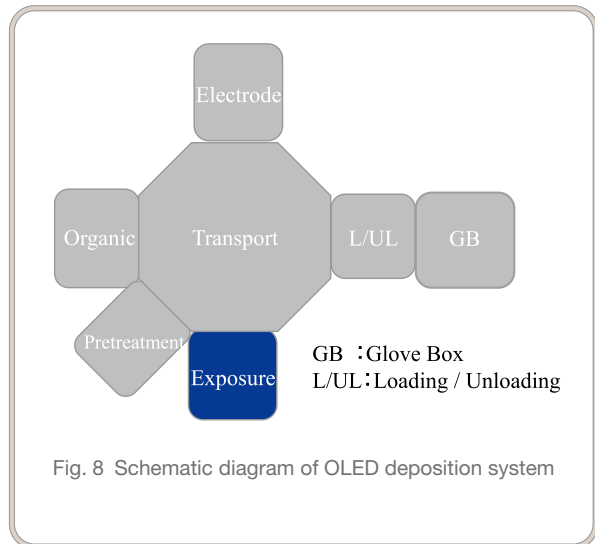


Fig. 8 Schematic diagram of OLED deposition system

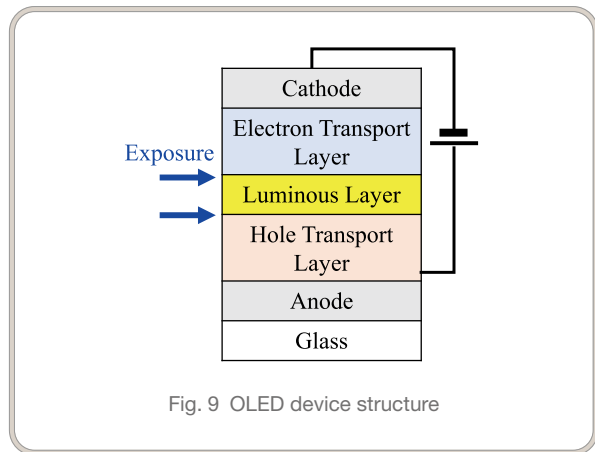


Fig. 9 OLED device structure

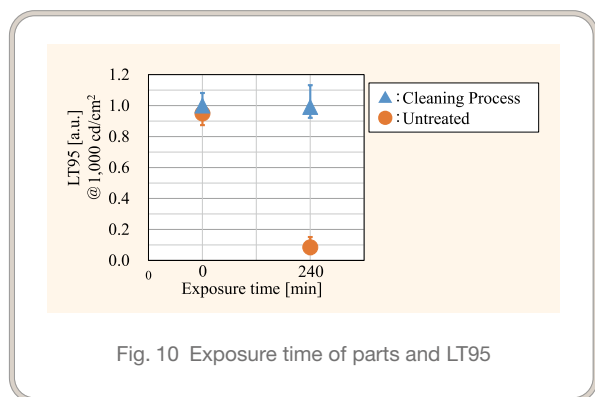


Fig. 10 Exposure time of parts and LT95

3.1 OLED deposition system and device fabrication

We prepared an exposure chamber in one chamber of the OLED deposition system shown in Fig. 8. The parts to be evaluated were placed in the exposure chamber and the chamber was evacuated by vacuum. We moved the OLED device shown in Fig. 9 into the exposure chamber during device fabrication to expose the device to the gases released from the parts being evaluated. For the parts, we used

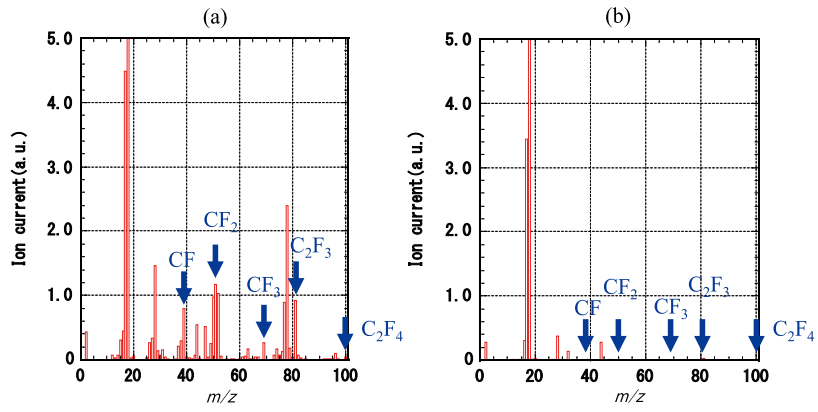


Fig. 11 Mass spectra of fluoropolymer-coated cable
(a) Untreated, (b) After cleaning process

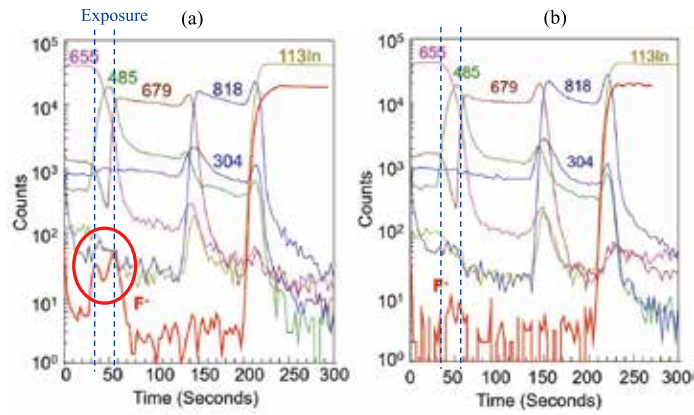


Fig. 12 TOF-SIMS depth profile
(a) Exposed, (b) Not exposed

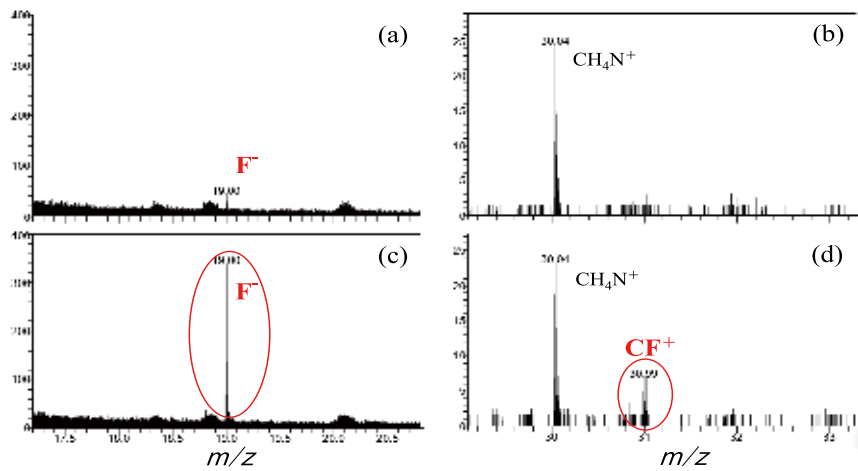


Fig. 13 Mass spectra of luminous layer
(a), (b) Not exposed (c), (d) Exposed

fluorinated resin-coated cables, prepared in both cleaned and untreated versions. We exposed the device to the parts for 120 minutes before and after the fabrication of the luminous layer (240 minutes in total), and heated the chamber to 150°C as an accelerated test. For comparison, we also fabricated a device that did not pass through the exposure chamber.

3.2 Lifetime evaluation of OLED devices

Device lifetime was evaluated in terms of LT95, which is the time required to reduce the luminous intensity to 950 cd/m² from 1000 cd/m². The relationship between LT95 and the time of exposure to each fluorinated resin-coated cable is shown in Fig. 10. From Fig. 10 it can be seen that the LT95 of a device exposed to an untreated cable was about 1/10th that of an unexposed device. On the other hand, the LT95 of a device exposed to cables treated with the cleaning process was comparable to that of an unexposed device. These results indicate that appropriate cleaning processes can reduce the impact on device lifetime.

3.3 Emission gas analysis of exposed OLED devices

To investigate the factors affecting device lifetime, we used TDS to obtain mass spectra for fluorinated resin-coated cables, both untreated and cleaned. Fig. 11 shows the measurement results at 150°C, which is the temperature during device fabrication. Peaks derived from C-F were hardly detected in the cleaned product, but were detected in abundance in the untreated product. This suggests that emitted gases including C-F from the untreated product shorten the device lifetime, whereas cleaning the product improves the device lifetime by reducing the emitted gases including C-F.

3.4 Analysis of impurities in OLED devices

To reveal changes in impurities and organic materials in exposed OLED devices, we performed an analysis by time-of-flight secondary ion mass spectrometry (TOF-SIMS). Fig. 12 compares the results for a device exposed to untreated cables and an unexposed device. The numerical values in Fig. 12 are *m/z*, and the values other than 113 (In) indicate

organic materials that make up the OLED device. The figure shows that the device in (a), which was exposed to the untreated cables, contained F. Meanwhile, no changes were observed in organic materials other than F (*m/z*: 655, 485, 679, 818, 304). Furthermore, the results from mass spectra of the luminous layer of the device are shown in Fig. 13. The figure shows that the device exposed to the untreated cables showed an increase in F⁻ and CF⁺.

4. Summary

We introduced a case study of IC evaluation conducted as an effort to ensure cleanliness in the manufacturing process of OLED production equipment and a case study of the impact of components used in the equipment on the service lifetime of OLED devices.

By using our IC-based cleanliness evaluation technique to monitor and take countermeasures against residual ions in the equipment at each stage from manufacture to delivery, we are able to manufacture equipment with high cleanliness that meets the required quality.

In-house evaluation using our OLED deposition system suggested that the C-F-containing gases emitted from an untreated fluorinated resin-coated cable affected the device lifetime. Meanwhile, it was found that the amount of impurities could be reduced by appropriate cleaning processes, thereby allowing use of such parts in the equipment. ULVAC will use these techniques to contribute to the further improvement of the quality of our OLED manufacturing equipment.

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