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Technical Documents

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OLED

- Identification of Dopant Ratio in Organic EL Device
- Property evaluation of OLED layers in Solution process and Vacuum deposition process
- Impurity Analysis in Solution-processed OLED by TOF-SIMS
- Composition and density analysis in OLED devices using micro-RBS
- Prediction of emission wavelength in Ir complexes for organic EL materials using quantum chemical calculations
- Detailed structural analysis of compounds containing heteroatoms -Analysis of OLED materials-
- Determination of multilayer structure of OLED by cross-sectional TEM
- Photoluminescence (PL) analysis of EMLs in multilayered OLEDs

OLED degradation analysis

- Degradation analysis of p-i-n type OLED
- TOF-SIMS MS/MS for analysis of degradation product in OLED driving test

TFT

- SEM, EDX and SCM evaluation of IGZO-TFT
- Electronic structure of a-IGZO and a-IGZO/metal interface structure in a TFT device
- Precise evaluation for SiN films by mercury probe and XPS

QD-LED

- Degradation analysis of QLED device
- Evaluation of the QD sheet by SEM-EDX analysis and quantitative image analysis

uLED

- Defect analysis of micro-LED with sub-μm level
- Analysis for manufacturing technology of micro LED - Optimization of laser transfer conditions -
- Process optimization and failure analysis of Micro-LEDs and Mini-LEDs

LCD and foreign materials

- Do you have any trouble in LCD panel?
- Composition analysis of foreign substances by optical-photothermal IR spectroscopy (O-PTIR)

Collaboration

- Effective and new solutions for R&D of organic electronics

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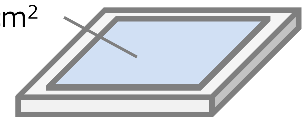
Identification of Dopant Ratio in Organic EL Device

In OLED devices, dopant ratios have a significant effect on luminescence efficiency, color purity, and lifetime. In the case of co-deposition, films are not always deposited at the same ratio as the preparation, depending on the characteristics of the compound. In this report, we present an example of Identification of the dopant ratio in an OLED film with and without standard materials (SMs).

Analysis Samples

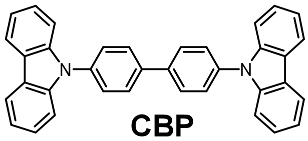
– OLED films –

Thickness: 50 nm
Area: 5 cm^2

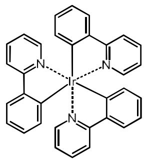


Host : **CBP**
Dopant : **$Ir(ppy)_3$**

–Chemical structure–



CBP
(4,4′-Bis(N-carbazolyl)-1,1′-biphenyl)



$Ir(ppy)_3$
(Tris(2-phenylpyridine)iridium(III))

–Dopant ratio–

Sample	CBP/$Ir(ppy)_3$ *1
①	1/0.010
②	1/0.100

*1 Ratio for preparation

⇒ Solvent extraction followed by quantitative analysis (QA) with LC/UV and LC/CAD.

Detector's Features & Sensitivity

● UV-Vis (PDA)
- Detection of light-absorbing substances
- Large differences in sensitivity by structure

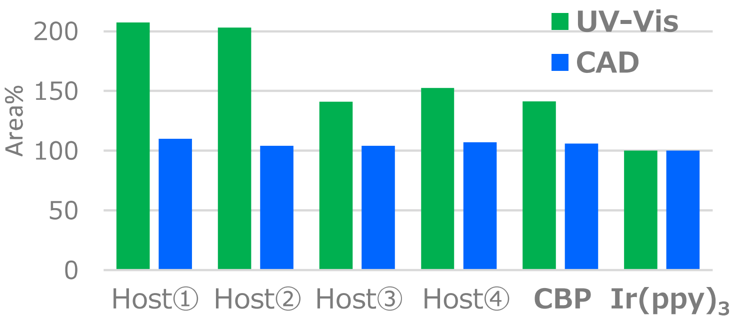
⇒ **SMs are needed for QA**

● Charged Aerosol Detector (CAD)
- Detection of electrically charged compound by corona discharge
- Small differences in sensitivity by structure

⇒ **Quantifiable without SMs**

– Comparison of peak area values in same concentration solution –

※ Normalized with the peak area value of $Ir(ppy)_3$ as 100



UV-Vis: Large variation in peak area values.
CAD: Within 10% variation in peak area value.

Absolute Quantification by LC/UV

1. Preparation of calibration curves for CBP and $Ir(ppy)_3$ using by each standard solution
2. Calculation of quantitative values using each calibration curve

Sample	CBP/$Ir(ppy)_3$
①	1/0.010
②	1/0.149

Quantification using each standard solution clearly showed that sample ② was not deposited at expected dopant ratio.

Semi-quantification by LC/CAD

1. Preparation of calibration curves using standard solution of CBP
2. Calculation of quantitative values using only calibration curve of CBP

Sample	CBP/$Ir(ppy)_3$
①	1/0.010
②	1/0.150

The semi-quantitative value of $Ir(ppy)_3$ using the calibration curve of CBP was less than 1% deviation from the absolute quantitative value.

Dopant ratio and co-deposition ratio of other company's products can be calculated even in absence of standard materials.

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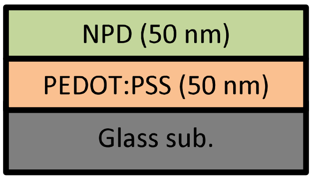
Property evaluation of OLED layers in Solution process and Vacuum deposition process

We compared film properties of OLED layers deposited by solution process and vacuum deposition process in spectroscopic ellipsometry and X-Ray reflectivity (XRR). We can revealed the difference of optical properties, such as refractive index, surface layer on vacuum deposited sample.



NPD deposition process
- Spin-coating with THF solvent
- Vacuum deposition

Polar

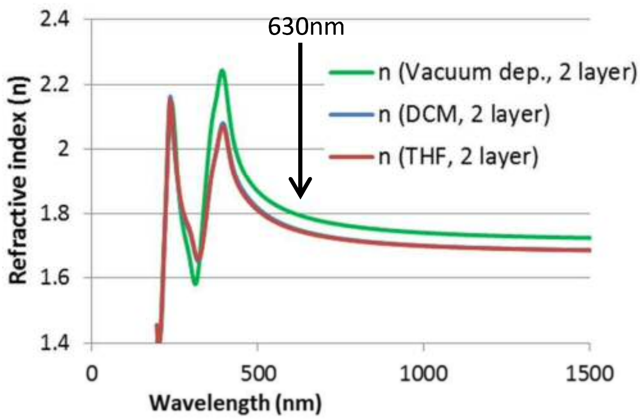
CH_2Cl_2 DCM (dicholoromethane)

THF (tetrahydrofuran)

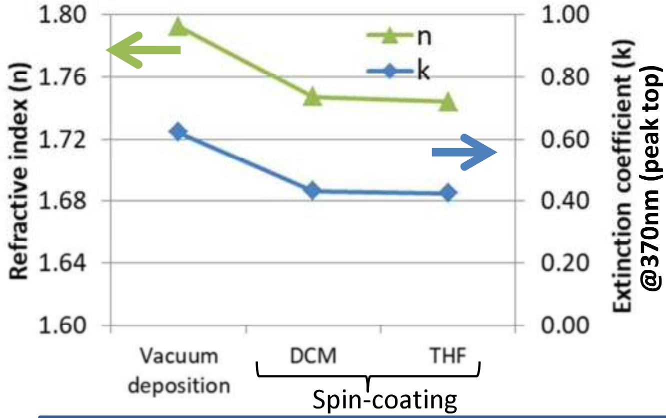
Non-polar

Spectroscopic Ellipsometry

Refractive index of NPD layer



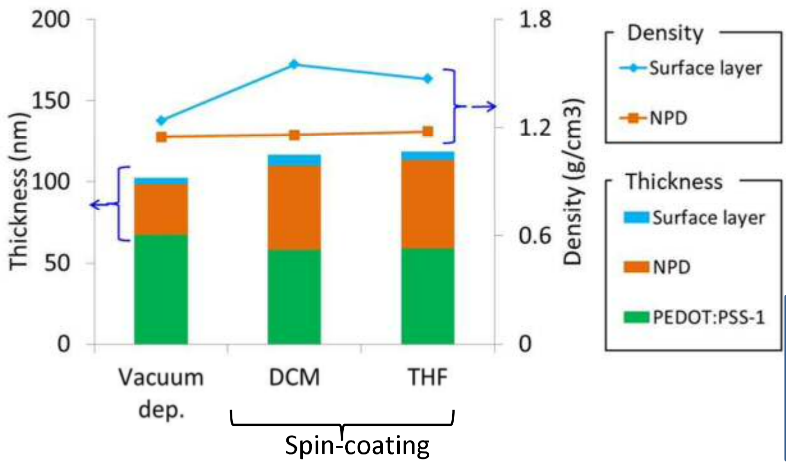
Comparison of refractive index and extinction coefficient



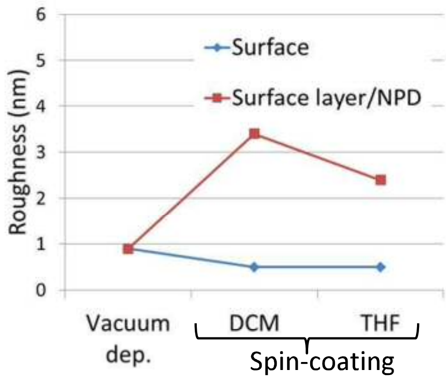
Refractive index and extinction coefficient
: vacuum deposition > spin-coating
→Difference in density or polarizability

X-ray reflectivity analysis (XRR)

Layer thickness, density of each layer

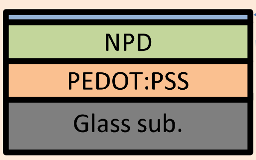


Roughness



- Density of NPD: No significant difference
  → Lower polarizability caused lower refractive index.
- Spin-coating sample: surface layer with higher density.
- Difference of roughness on surface layer / NPD interface

Features of "spin-coating" in comparison to "vacuum deposition"



- Surface layer with higher density
- Higher roughness on surface layer / NPD

- Lower refractive index
- Lower extinction coefficient
- No significant difference on density
  →Difference of polarizability

- Difference of optical property, density, roughness on interface were observed.
  →XRR : Fitting is applicable for multilayer.
- GCIB-TOF-SIMS observed solvent residue, impurity on surface and interface as shown in another document.
  → Integrated analysis by combination of techniques

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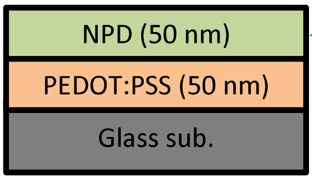
Impurity Analysis in Solution-processed OLED by TOF-SIMS

We performed depth profiling of impurities by GCIB-TOF-SIMS and detailed qualification of impurities by MS/MS in TOF-SIMS as comparison of OLED layers deposited by solution process and vacuum deposition process. Impurities on interface and surface were observed in solution-processed OLED.

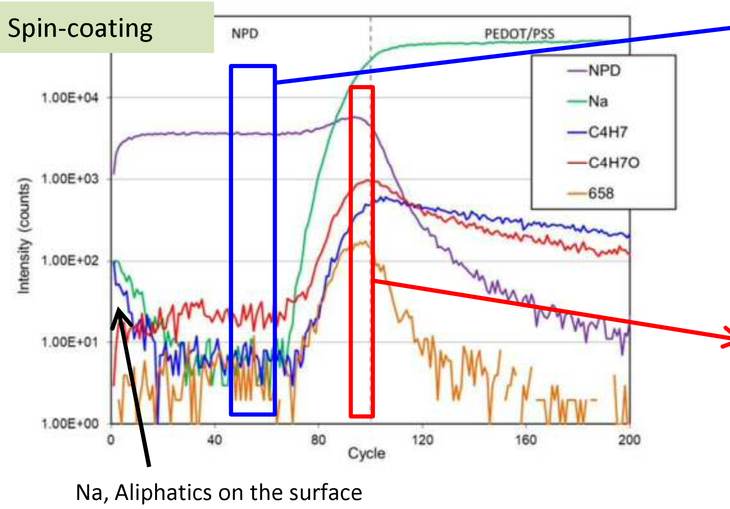


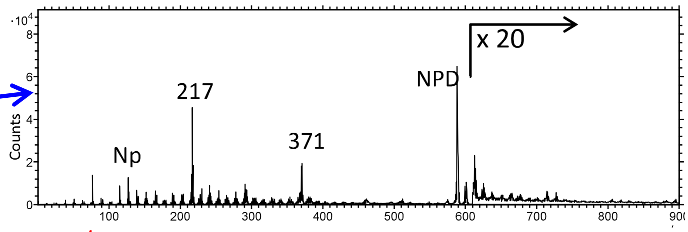
NPD deposition process
- Spin-coating with THF solvent
- Vacuum deposition

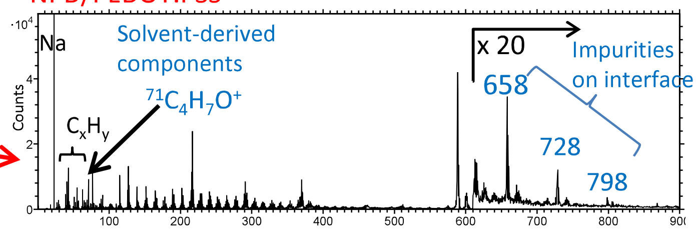
* Results in spin-coating sample is shown below. Comparison to vacuum deposition sample is discussed in summary.

* THF(tetrahydrofuran):

1. GCIB-TOF-SIMS depth profiling of impurities

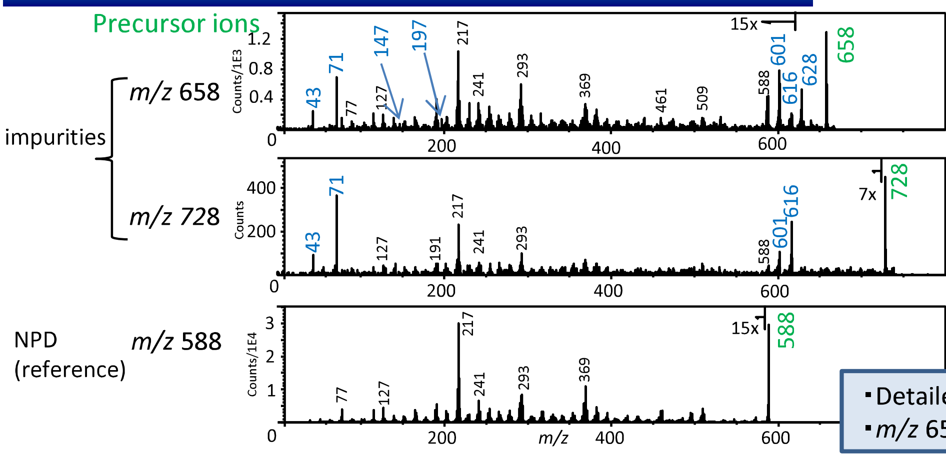




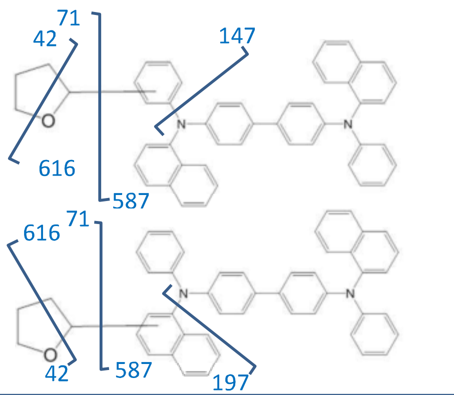


- Detection of solvent-derived components on interface and in NPD layer
- Detection of impurities on spin-coated samples

2. Qualification of impurities by MS/MS in TOF-SIMS

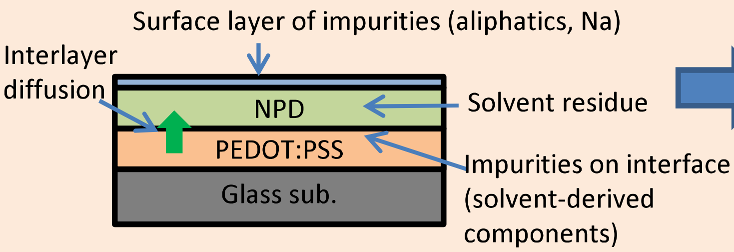


Assignment of peaks from *m/z* 658



- Detailed qualification of impurities
- *m/z* 658 : two type of "Solvent-adduct to NPD"

Features of "spin-coating" in comparison to "vacuum deposition"



- Solvent residue, impurities on interface and surface were observed in "spin-coating" by GCIB-TOF-SIMS.
  - →Detailed qualification of impurities on interface by MS/MS in TOF-SIMS as 2nd step
- Spectroscopic ellipsometry, XRR observed difference of refractive index, high density on surface layer as shown in another document.
  - →Integrated analysis by combination of techniques

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Composition and density analysis in OLED devices using micro-RBS

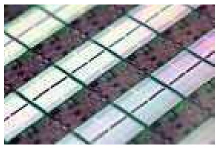
We have the world's first introduced a high spatial resolution RBS system.
Accurate composition and density evaluation of small area can be realized by using High energy micro-ion-beam. The composition and density analysis of the IGZO layer in the flexible OLED device and Ir quantification in the emission layer are shown.

1. Introduction of New RBS

	Conventional RBS	New RBS
Available Information	Accurate composition, depth distribution / density (film thickness is required)	
Minimum spot diameter	2 mmφ	2 μmφ
new feature		Micro analysis: μRBS High mass resolution - Highly sensitive detection light elements

Conventional RBS:
Spatial resolution 2 mmϕ
Applicable only for blanket/model sample

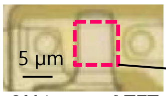
New RBS:
Spatial resolution 2 μmϕ
Applicable also for actual devices



- **It is possible to perform high-precision compositional analysis using the same method through all stages from material development to production.**

2. Elemental composition and density analysis of the small area of IGZO layer in TFT

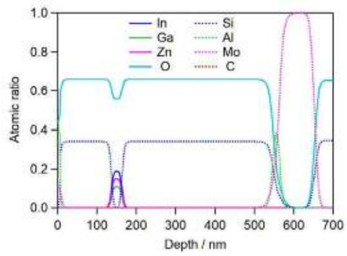
Sample : Flexible OLED device
Objective: Accurate composition and density analysis of IGZO layer in TFT
Conventional method : Composition can only be semi-quantified by Auger electron spectroscopy or TEM-EDX.
There is no method for density evaluation in micro region..



OM image of TFT

μRBS measurement & simulation analysis

Microion beam.(~2 μmϕ) irradiated to the gate area.



Depth profile

Composition and density quantification results

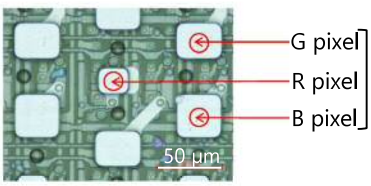
[atomic %]				density [g/cm3]
In	Ga	Zn	O	
18.8	10.8	14.8	55.6	6.6

- Advanced pretreatment + Measurement of microscopic area
  → Accurate compositional analysis of micro areas is possible.

- **Density evaluation of micro areas made possible for the first time.**

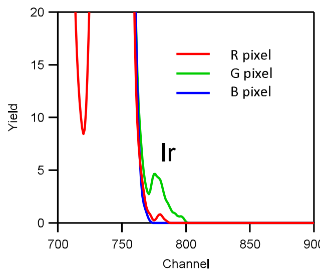
3. High-sensitivity quantification of dopants in OLED emitting layers

Sample : Flexible OLED device
Objective : Accurate determination of Ir complex in the luminescence layer in each RGB pixel
Conventional : SIMS is the only method sample comparison, accurate quantification difficult



OM image of RGB pixel

Microion beam.(~2 μmϕ) irradiated to each RGB pixel.



μRBS spectrum

Ir quantification results for each pixel

pixel	Ir [atomic %]
R	0.01
G	0.09
B	LOD

- **Establishment of a method for accurate determination of Ir in the luminescent layer.**

Realization of high-precision composition and density analysis using the same method from raw materials to final products. ⇒ Direct comparison of OLED device characteristics and fabrication conditions is possible. Our new RBS contributes to accelerating the research and development and clarifying the essential causes.

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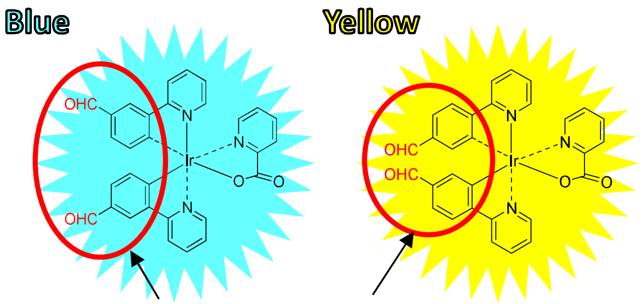
P02313表面科学第2研究室20210902-1

Prediction of emission wavelength in Ir complexes for organic EL materials using quantum chemical calculations

We performed quantum chemical calculations on Ir complexes for organic EL materials and accurately predicted the difference of emission wavelength between the structural isomers. From this result, it is possible to determine the ligand structure by confirming the agreement between the experimental emission wavelength and calculated one, or to predict the emission wavelength of the product denatured by deterioration etc.

1. Change of emission wavelength in Ir complex

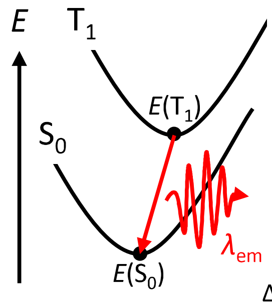
It has been reported that **slight differences in the ligand structure inside Ir complexes lead to changes of emission wavelength**[*a*, *b*]. Controlling the ligand structure is important in the design of organic EL devices.



It is difficult to determine the detailed ligand structure from instrumental analysis alone.

2. Calculation method of emission wavelength

Quantum chemical calculations allow us to **accurately predict the difference of emission wavelengths** between Ir complexes with similar ligand structures.



The emission wavelength can be evaluated approximately from the energy difference between the T_1 and S_0 states.

Emission wavelength $\lambda_{em} \approx \Delta E$

$$\Delta E = E(T_1) - E(S_0) + \Delta ZPE$$

ΔZPE: Zero-point energy correction

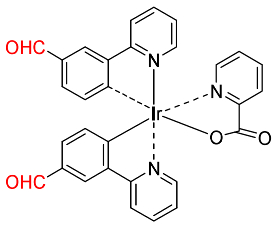
✓ Compound containing a **heavy element (Ir)**
✓ Ground state (S_0) and **triplet excited state (T_1)**

Need to ***professionally set conditions***

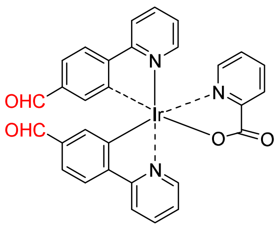
3. Emission wavelengths in structural isomers of Ir complexes

The emission wavelengths of the two structural isomers were calculated and compared with experimental values.

Different substitution sites of CHO groups

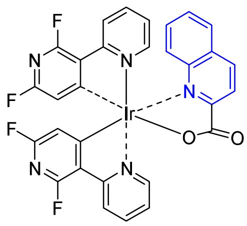


Compound A1

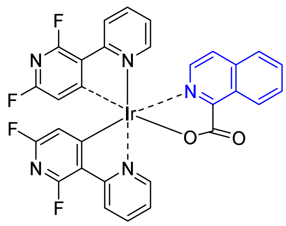


Compound A2

Different arrangements of quinoline rings



Compound B1



Compound B2

Calculated and experimental emission wavelengths

	Compound A1	Compound A2	Compound B1	Compound B2
Calc. (nm)	488	590	532	562
Expt. (nm)	[a]487	[a]579	[b]539	[b]555
Relative error with Expt. (%)	0.2	1.9	−1.3	1.3

[a]D. Wang *et al.*, Org. Electron. **14**, 2233 (2013).
[b]H. Oh *et al.*, Organometallics **32**, 6427 (2013).

The tendencies of the emission wavelengths between the isomers were reproduced **with sufficient accuracy**.

By **professionally and skillfully setting calculation conditions**, we can **determine the ligand structure**, which is **difficult with instrumental analysis**, or **predict the emission wavelengths of denatured products**.

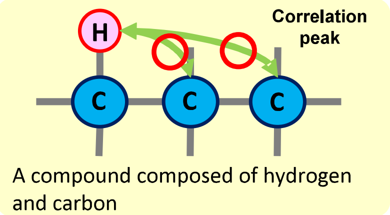
Detailed structural analysis of compounds containing heteroatoms
-Analysis of OLED materials-

2D NMR measurements using hydrogen and carbon nucler are often used for detailed structural analysis of organic compounds, but when the structure contains heteroatoms, structural information may not be sufficiently obtained. Here, we introduce an example in which 2D NMR measurements using multinuclear are effective for detailed structural analysis of OLED materials.

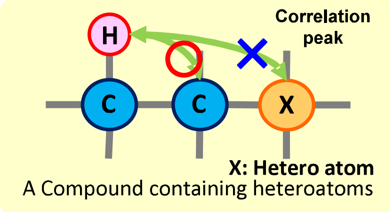
Background

HMBC: HMBC is one of 2D NMR methods that can provides information on the positional relationships between atoms separated by 2-3 bonds.

^{1}H-^{13}C HMBC measurement



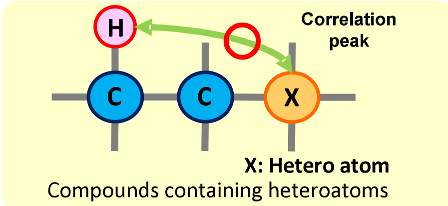
Correlation peaks of hydrogen and carbon distant from 2-3 bonds are detected. **Structural information can be obtained.**



Some correlation peaks are not detected. Enough structural information is not available.

Detailed structural analysis is difficult!

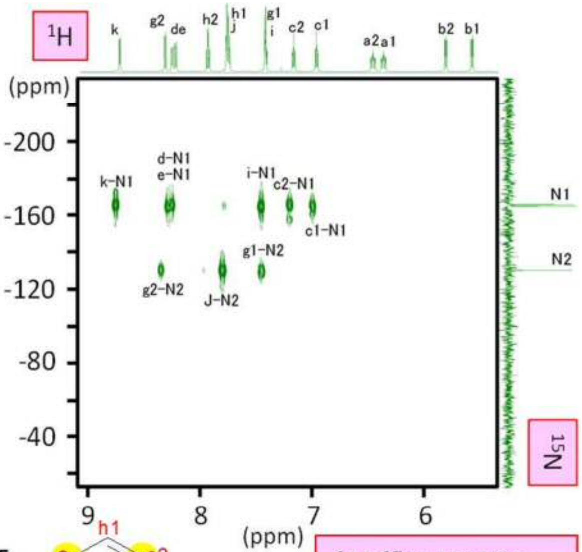
Multinuclear HMBC measurement

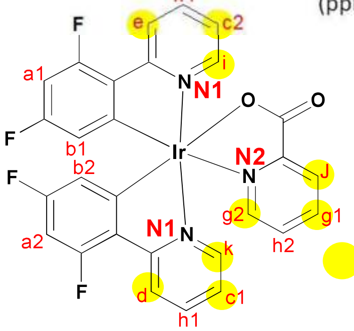


Structural information around heteroatom can be obtained.

It is an effective tool for detailed structural analysis by combining the results of ^{1}H-^{13}C HMBC measurement !

Analysis of OLED materials using multinuclear 2D NMR measurement

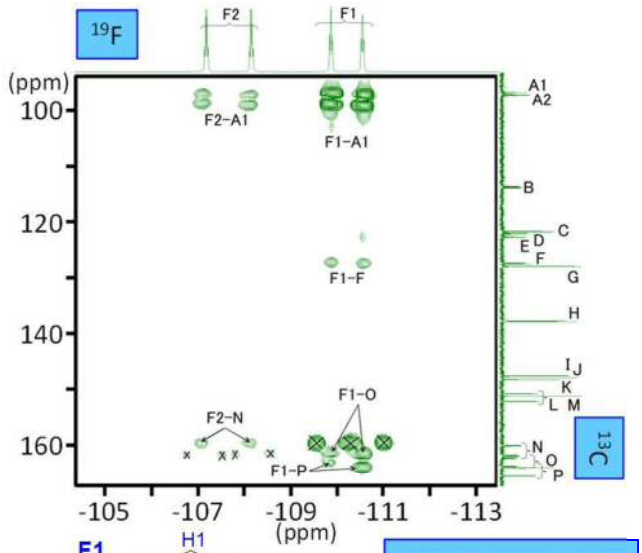


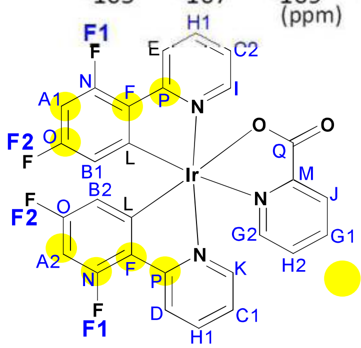


^{1}H-^{15}N HMBC measurement

The positional relationship between hydrogen and nitrogen separated by 2-3 bonds is cleared.

: Hydrogen for which correlation peaks with nitrogen (peak N1, N2) is observed





^{19}F-^{13}C HMBC measurement

The positional relationship between carbon and fluorine separated by 2-3 bonds is cleared.

: Carbons for which correlation peaks with fluorine (peak F1, F2) is observed

The structural information around nitrogen and fluorine was obtained, which enabled more detailed structural analysis!

Determination of multilayer structure of OLED by cross-sectional TEM

Organic layers with similar composition can be distinguished by TEM with our original contrast enhancement. By cross-sectional TEM-EDX of the defect which was found in surface SEM, we can reveal the detailed structure and the composition of it.

Multilayer structure of OLED

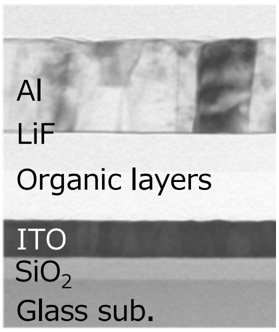
Cathode	Al
EIL	LiF
EML/ETL	Alq3(60nm)
HTL	NPD(40nm)
HIL	2-TNATA(30nm)
Anode	ITO

- Dismantle a panel
- Surface SEM to confirm the small defect
- Make a cross-section of the multilayer of OLED
- TEM analysis

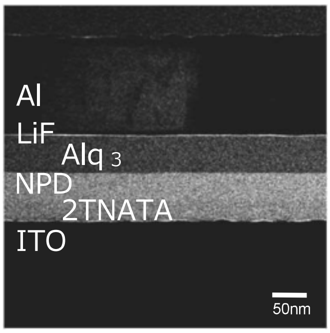
Analysis 1: Our original method, High-Contrast TEM for OLED

Organic layers with similar composition can not be distinguished with conventional TEM method, but with our original contrast enhancement they can be revealed.

Conventional TEM image



Our original High-contrast TEM image



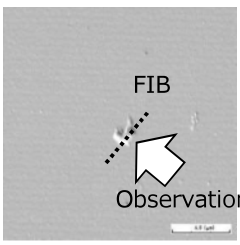
Cross-sectional TEM reveals
- Layer thickness
- Interface structure
- Crystallinity

with nanometer-level resolution.

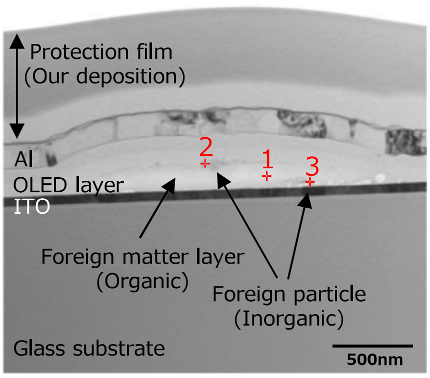
Analysis 2: Observation of detailed structure of defect (Bright spot)

Cross-sectional TEM-EDX is applied to defects identified by low-voltage imaging-EL.

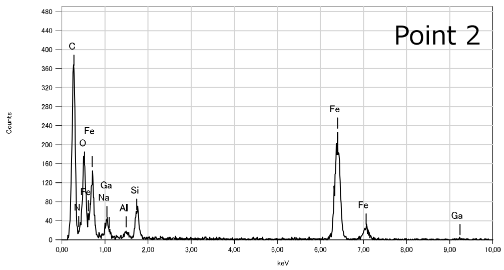
Bright spot



SEM image of surface



FIB-TEM image



	C	N	O	Fe	In	Si	Na
Point 1	96.9	1.6	1.6	–	–	–	–
Point 2	61.9	2.6	12.5	18.9	–	2.4	1.4
Point 3	78.8	1.5	12.2	–	1.3	1.6	3.8

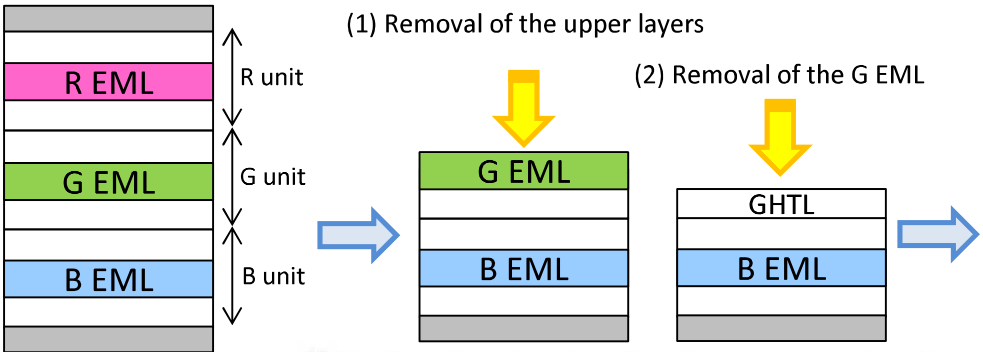
TEM-EDX results

- A convex-shaped foreign matter is observed under the OLED layer.
- From EDX, the foreign matter is suggested to be hydrocarbon organic matter (point1), which contains impurity elements such as Fe or In (point2, 3).

Photoluminescence (PL) analysis of EMLs in multilayered OLEDs

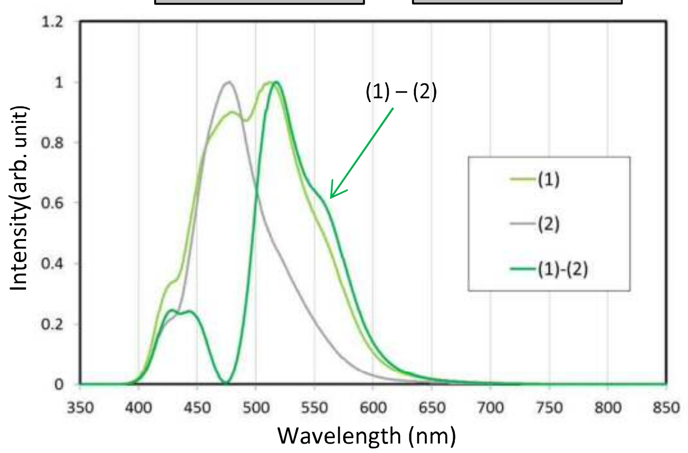
We have developed a method which enables to separate each PL signals in multilayered OLEDs. Pure PL spectra of each EMLs can be obtained by using a precise etching technique and a difference-spectrum method.

Measurement procedure of each EML spectrum

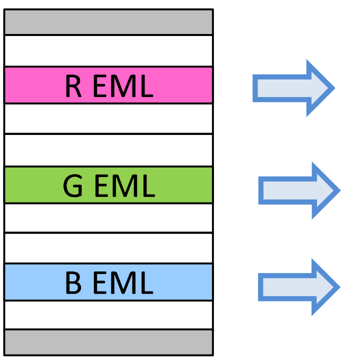


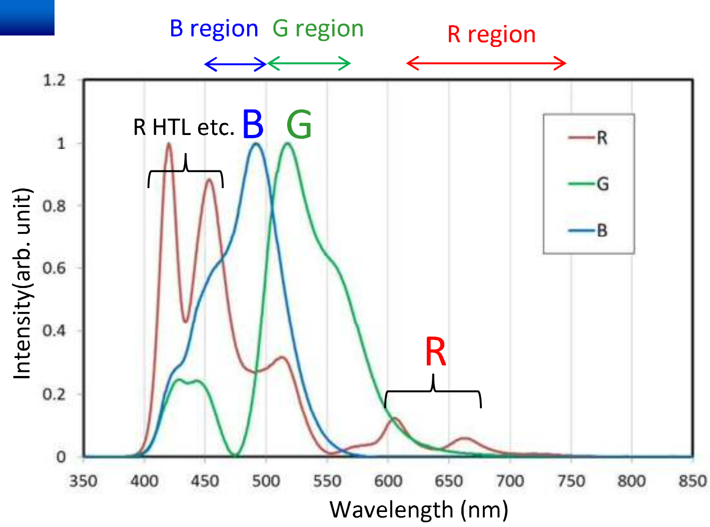
Three-color tandem OLED

PL spectrum of the pure G EML is obtained by subtracting (2) from (1).



PL spectra of R, G, and B EMLs





・The difference spectra of R, G, and B EMLs in this sample correspond to the general RGB color regions.
・PL spectra of each EMLs in multilayered OLEDs can be obtained by this technique.

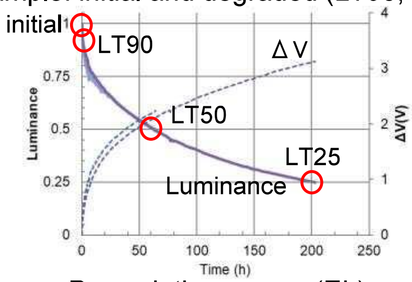
Degradation analysis of p-i-n type OLED

OLED devices mostly have positive-intrinsic-negative (p-i-n) doped layers, which drastically improve performance of OLED devices. Highly sensitive techniques are effective to analyze the small-amount components such as a degradation product or dopant.

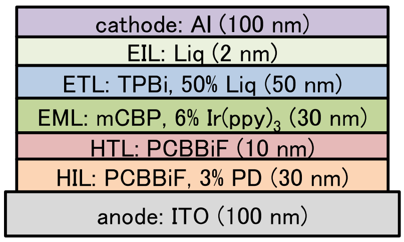
OLED: Organic light emitting diode

1. Sample

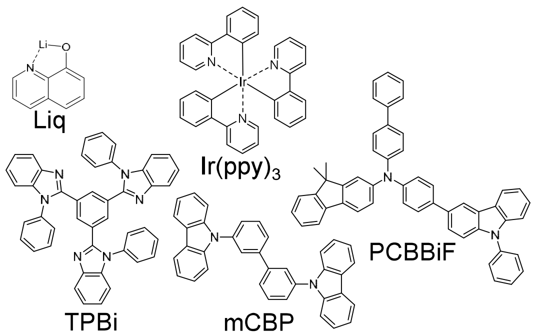
Sample: initial and degraded (LT90, 50, 25) OLED devices



Degradation curves (EL)



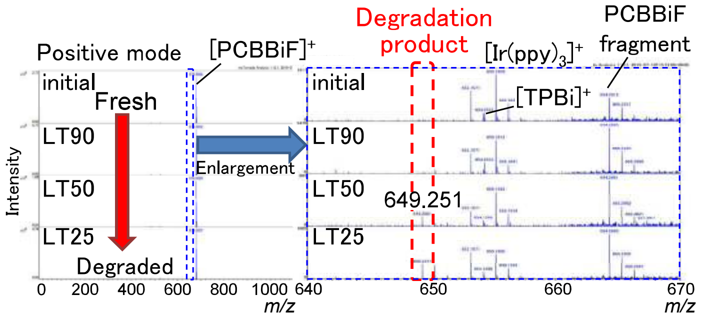
OLED stack



Chemical structures of the components

2. LDI-MS

Features;
High sensitivity, high mass resolution and accuracy



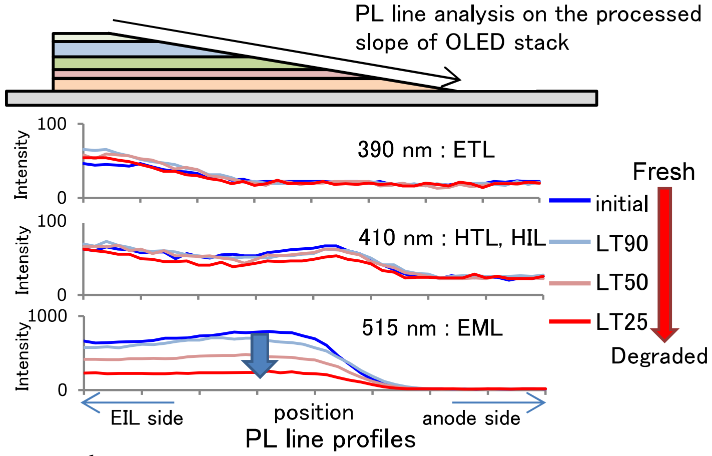
LDI-MS spectra of OLEDs

✓ Detection of a degradation product

✓ Identification of *m/z* 649.251 peak as $C_{48}H_{31}N_3^+$

3. Photoluminescence (PL)

Features;
Direct observation of luminescence property of each layer



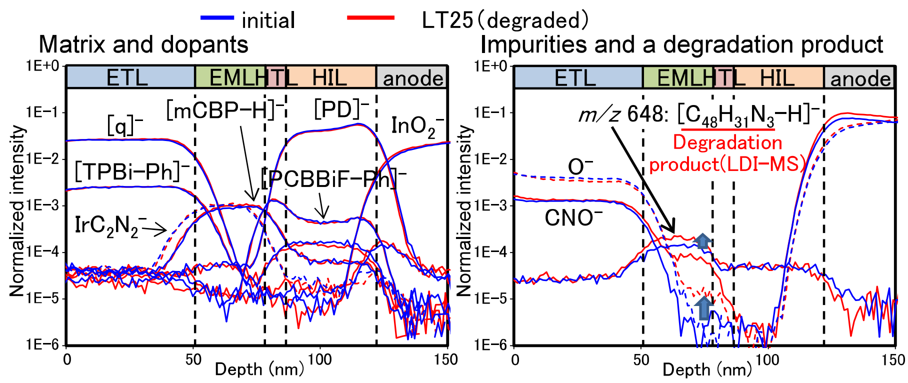
PL line profiles

✓Decrease of emission from EML

➔Degradation in EML

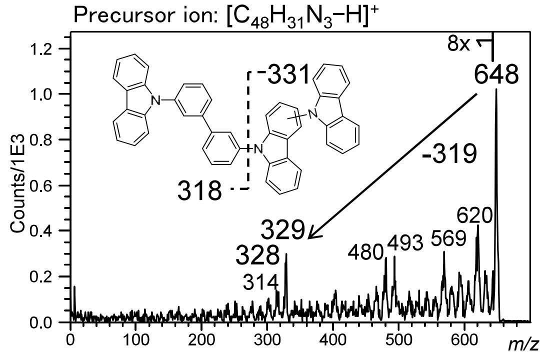
4. GCIB-TOF-SIMS and MS/MS

Features;
High sensitivity, 3D distribution analysis, structural analysis in thin layer (> several nm)



Negative depth profiles of initial and LT25 OLED devices

✓Increase of a degradation product and oxygen in EML



Product ion spectrum of degradation product

✓Structural information of the degradation product

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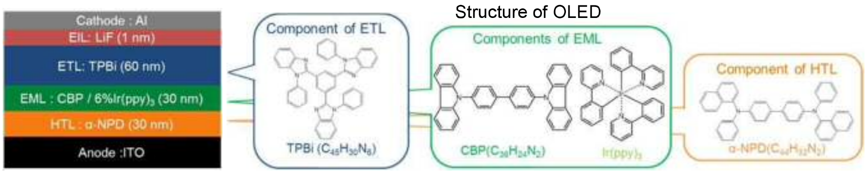
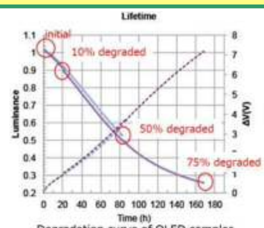
TOF-SIMS MS/MS for analysis of degradation product in OLED driving test

PL line analysis, GCIB-TOF-SIMS, and TOF-SIMS MS/MS were applied to the degradation analysis of OLED in driving test. TOF-SIMS MS/MS revealed the detailed chemical structure of degradation product in the specific depth region in OLED stacks.

■ test pattern size: 2 mmφ ■ driving test: initial, 10%, 50%, and 75% degraded

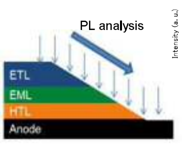
Structure of OLED



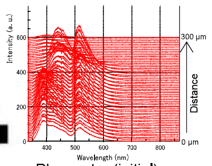


Degradation curve of OLED samples

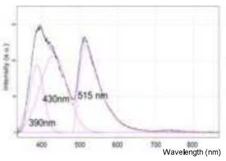
PL analysis of inclined surface



Schematic of analysis



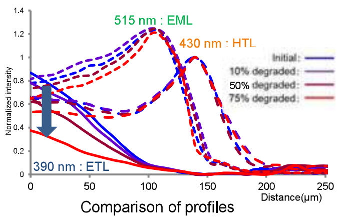
PL spectra (initial)



Peak separation of PL spectrum

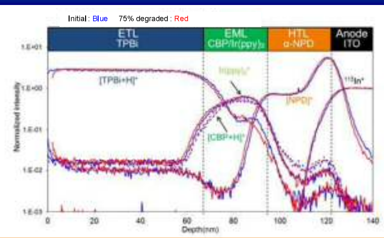
Comparison of profiles of PL intensities

Decrease of peak intensities in ETL
⇒ Degradation of ETL components

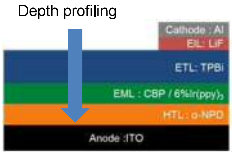


Comparison of profiles

GCIB-TOF-SIMS depth profile of OLED

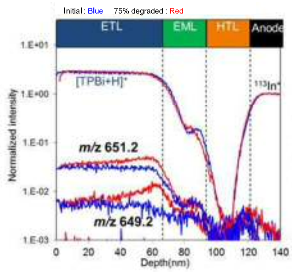


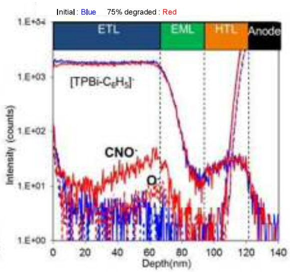
Depth profiling



Intensities of main components and dopant were not changed after degradation.

Difference between the spectra of each layer ⇒ Depth profile



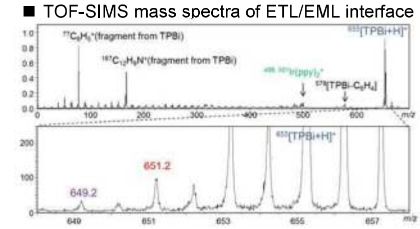


Degradation at EML ~ EML/ETL interface
⇒ Corresponding with PL results, *m/z* 649, 651 peaks were obtained from degradation products

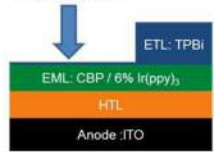
TOF-SIMS MS/MS

Ar-GCIB etching to ETL/EML interface ⇒ TOF-SIMS analysis

■ TOF-SIMS mass spectra of ETL/EML interface

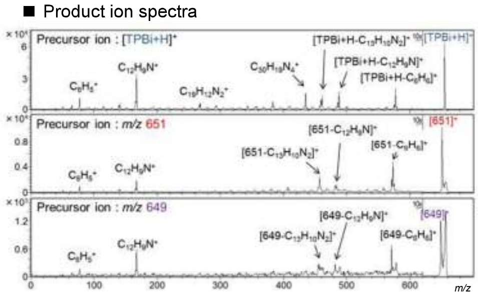


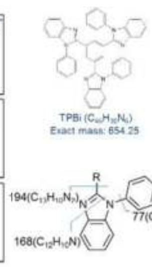
Measurement



Insufficient information in MS spectra ⇒ MS/MS analysis

■ Product ion spectra

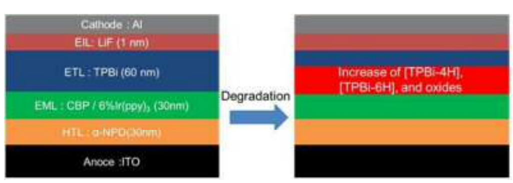




Degradation products can be assigned as derivatives of TPBi, [TPBi-4H] and [TPBi-6H].

Peaks in low *m/z* were common. Shifts of peaks in high *m/z* were common. ⇒ Cyclization of TPBi

Summary



An example of [TPBi-4H]

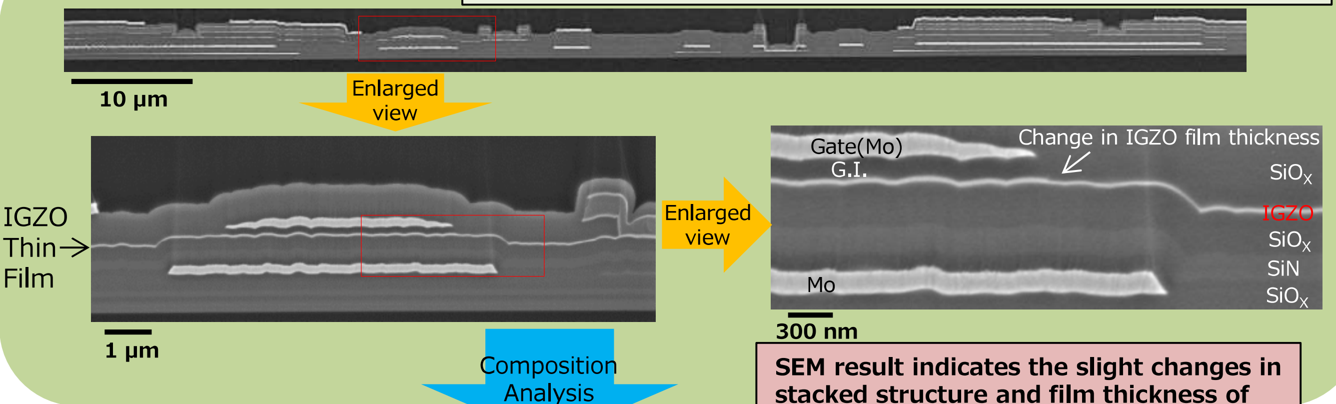
PL line analysis, GCIB-TOF-SIMS, and TOF-SIMS MS/MS were applied to OLED degradation analysis. These techniques revealed the detailed chemical structure of the degradation product in the specific depth region in OLED stacks.

SEM, EDX and SCM evaluation of IGZO-TFT

Amorphous IGZO (In-Ga-Zn-O) semiconductor has been researched and developed as an one of candidates for next-generation TFTs and other electronic devices because of its excellent properties such as high channel mobility and low leakage current. We introduce a case study of the morphological observation and carrier distribution of IGZO-TFT cross sections of commercial products using SEM-EDX and SCM.

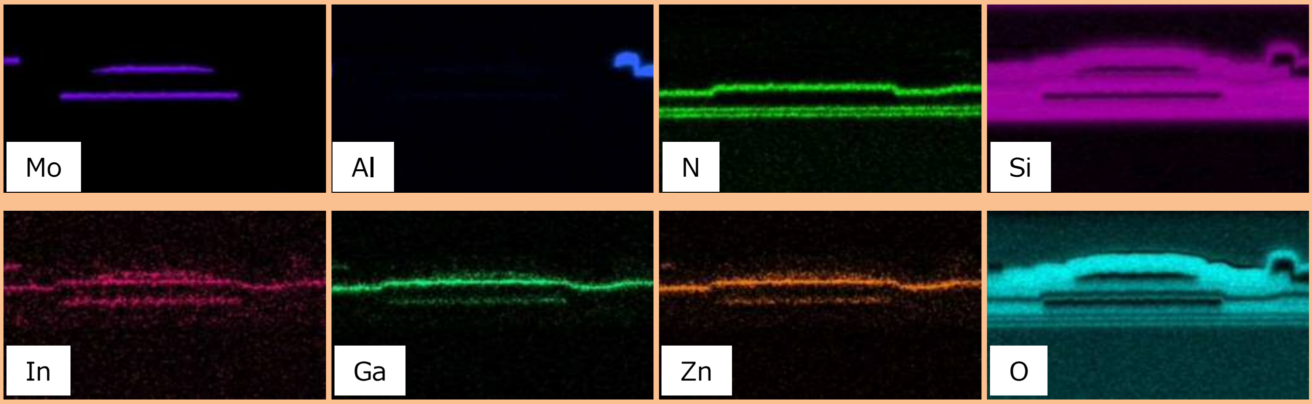
1. Cross-sectional SEM observation

Wide range observation from mm to nm by the optimization of sample preparation.



SEM result indicates the slight changes in stacked structure and film thickness of IGZO film.

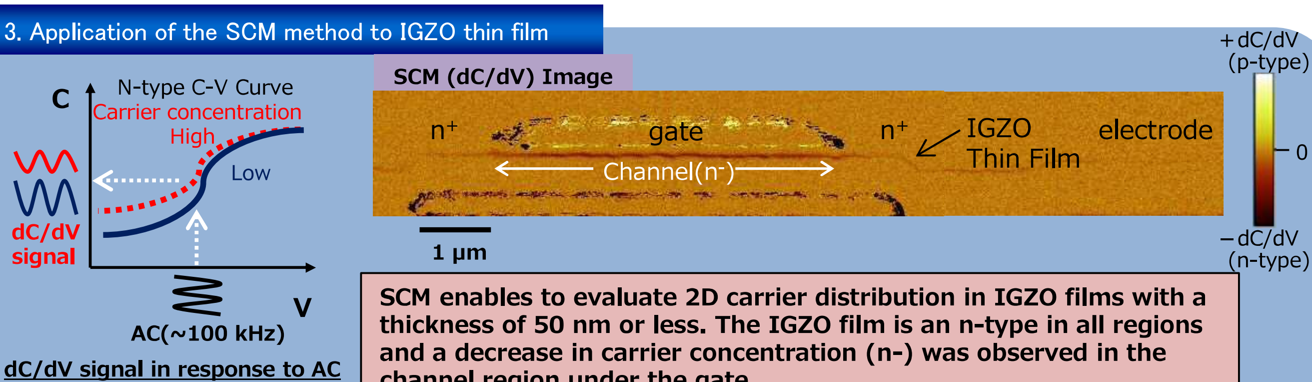
2. SEM-EDX composition analysis



※The In, Ga and Zn signals in the Mo electrode are due to the background effect.

Data measured with optimized sensitivity and spatial resolution

3. Application of the SCM method to IGZO thin film



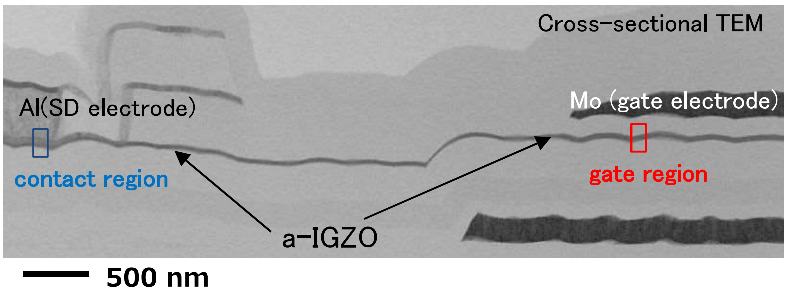
SCM enables to evaluate 2D carrier distribution in IGZO films with a thickness of 50 nm or less. The IGZO film is an n-type in all regions and a decrease in carrier concentration (n-) was observed in the channel region under the gate.

Evaluating the final product is very important for yield improvement, quality check and patent searches.

Electronic structure of a-IGZO and a-IGZO/metal interface structure in a TFT device

IGZO (InGaZnO) with high electron mobility has been used in many kinds of electronic devices. We characterized elemental composition distribution and electronic structure of a-IGZO with nano-spatial resolution to consider the roles of IGZO at different locations in a structured TFT device.

1. TFT structure of the sample

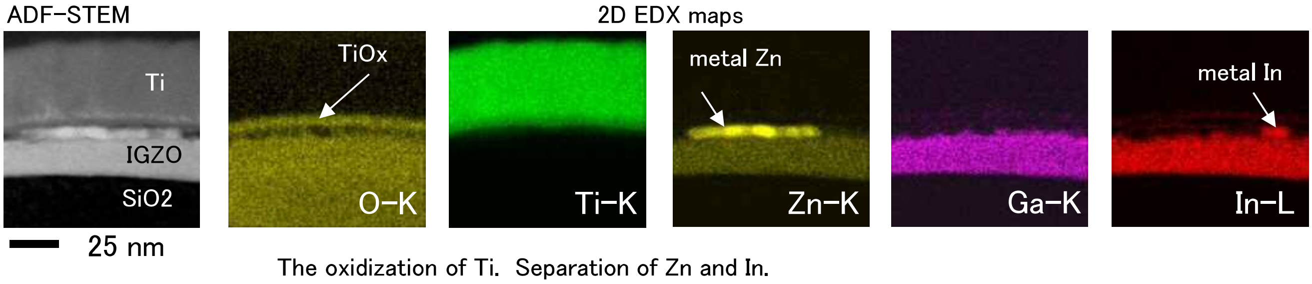


<u>Previous SCM measurement</u>

↓

<u>a-IGZO (50 nm thick) is n-type semiconductor and the carrier density at contact region is higher than that at the gate region.</u>

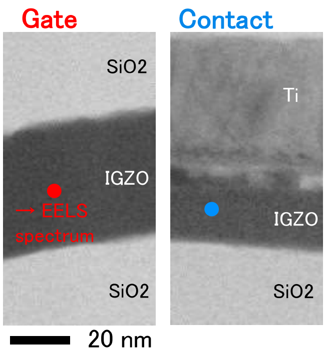
2. Elemental composition at source (drain) metal/a-IGZO contact interface

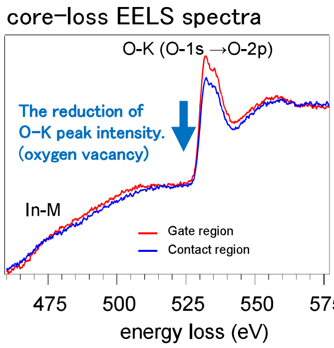


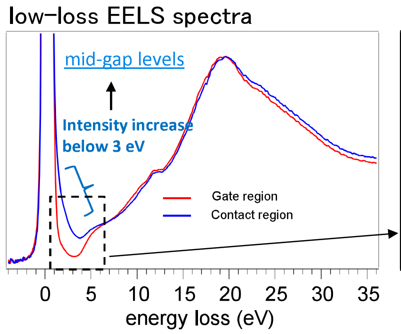
The oxidization of Ti. Separation of Zn and In.

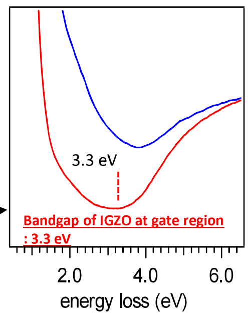
The metallic Zn and In at the interface ⇒ Contact resistance reduction

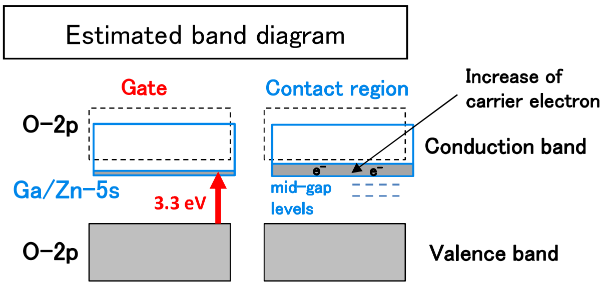
3. The difference of a-IGZO electronic structure between contact and gate region











At the contact region :

- Increase of carrier density by oxygen vacancy,
- Creation of mid-gap levels

→ The reduction of contact resistance between a-IGZO/metal.

<u>The local electronic strucrure and electric property can be considered by STEM-EELS with nm spatial resolution.</u>

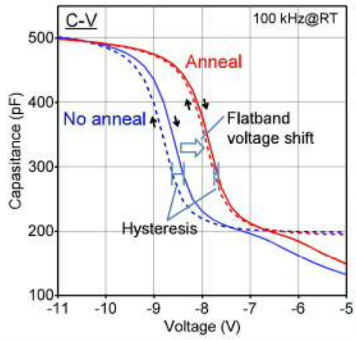
Precise evaluation for SiN films by mercury probe and XPS

Silicon nitride (SiN) films are widely used as various dielectrics due to their versatility. But the electrical properties of SiN films strongly depend on the formation conditions. We characterized the change in the electrical and physical properties of annealed SiN film by mercury probe and XPS. Our comprehensive study enables us to evaluate a relationship between film qualities and electrical properties of SiN films.

1. C–V and I–V properties by mercury probe

Sample: SiN (300 nm)/p-Si
Annealing: 800 °C, 2 hours in N_2

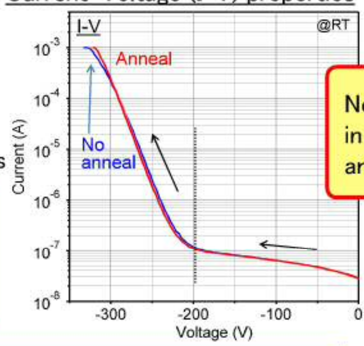
Capacitance-Voltage (C–V) properties



- Decrease in hysteresis width after annealing
  -> Decrease in mobile charges
- Positive flatband voltage shift after annealing
  -> Decrease in positive fixed charges

Decrease in detrimental mobile charges and fixed charges by annealing
-> Improvement of C–V property

Current-Voltage (I–V) properties



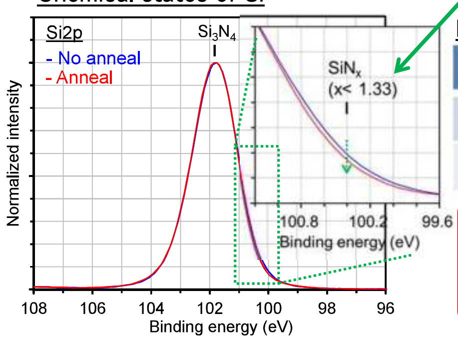
No significant change in I–V property before and after annealing

2. Elemental compositions and chemical states by XPS combined with wet etching

Using wet etching techniques, the states of 1) SiN surface, 2) middle layer and 3) SiN/Si interface were evaluated by XPS.

1) Surface (after removing native oxide)

Chemical states of Si



A very little difference was precisely detected!

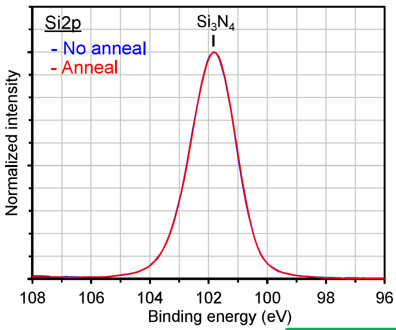
Elemental composition

Surface	N/Si*
No Anneal	1.25
Anneal	1.28

Reduction of Si-rich SiNx on surface by annealing

2) Middle layer (150 nm-depth)

Chemical states of Si



* N/Si ratio was converted using the RBS result of annealed sample to improve an accuracy of quantification by XPS.

Elemental composition

Middle	N/Si*
No Anneal	1.27
Anneal	1.28

No significant change in the middle layer before and after annealing

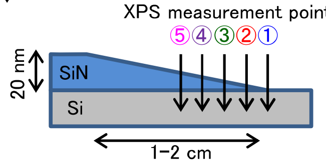
3) SiN/Si interface

Measurement flow

- Thinning SiN films to around 20 nm-thick
- **Graded etching** [1]
  Our **original** technique to create several cm-long slope at thin film on substrate. Detailed interface analysis is available along the slope using XPS.
- XPS for 5 points near SiN/Si interface

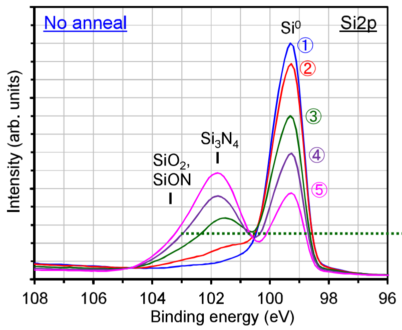
1. Y. Muraji *et al.*, Jpn. J. Appl. Phys. **41**, 805 (2002).

XPS measurement point

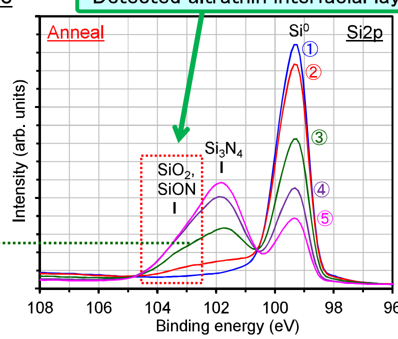


SiN Thickness
①: 0.2 nm
②: 0.4 nm
③: 1.1 nm
④: 1.5–2.0 nm
⑤: 2.3–2.6 nm

Chemical states of SiN/Si interface



Detected ultrathin interfacial layer!



Increase in oxide component after annealing due to residual oxygen in annealing atmosphere → Reduction of fixed charges by interfacial oxidation

Mercury probe and XPS enable us to detect a very little difference of samples. To combine mercury probe with other analyses, electrical properties are related to impurity, defects and chemical states etc.

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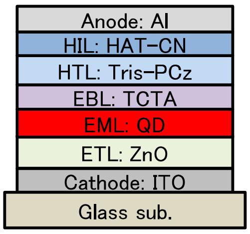
Degradation analysis of QLED devices

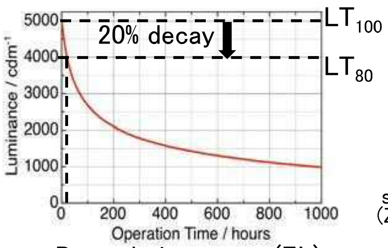
QD-LED (QLED) devices have emissive layer of quantum dots (QDs), and are one of the most promising next-generation electroluminescent devices. We analyzed fresh and degraded QLED devices and attempted to reveal the cause of the luminance decay for the degraded device.

1. QLED device sample

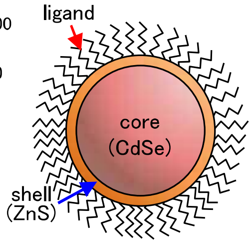
Samples: fresh (LT_{100}) and degraded (LT_{80}) QLED devices ＊QLED devices were provided by i[3]-opera.



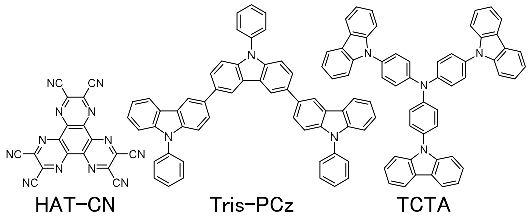
QLED stack



Degradation curve (EL)

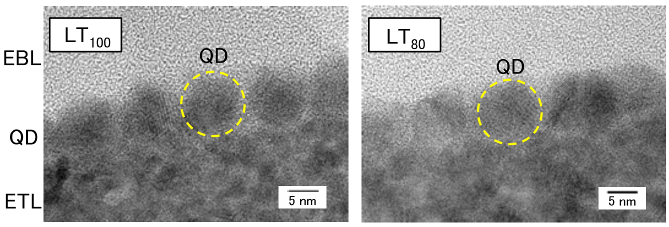


QD structure



Structures of organic materials

2. Cross-sectional TEM

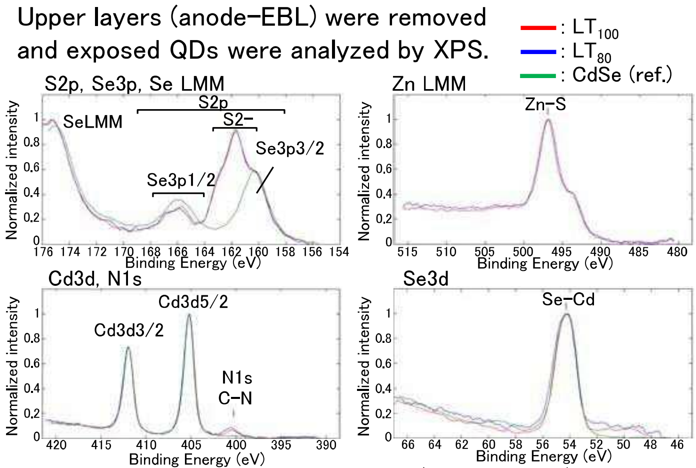


Comparison of TEM images around QDs

✓ No change of QD shape and size
✓ No aggregation of QDs

3. Chemical states of QDs by XPS

Upper layers (anode-EBL) were removed and exposed QDs were analyzed by XPS.



Comparison of XPS spectra (narrow scan)

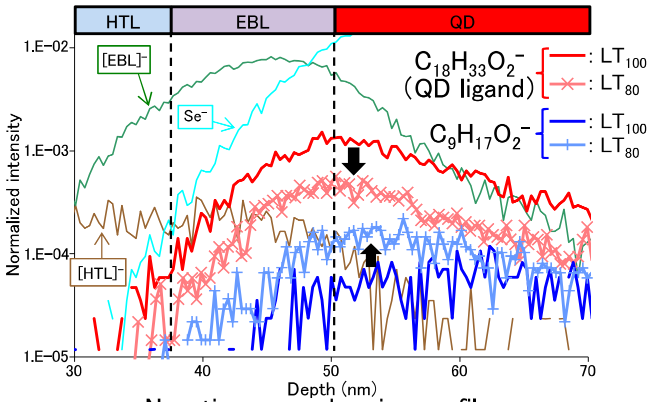
Elemental composition ratio

	S/Cd	Zn/Cd	Se/Cd
LT_{100}	0.87	1.37	0.79
LT_{80}	0.97	1.35	0.86

✓ No significant change of chemical states of the elements in QD core and shell

4. Depth profiles of organics by GCIB-TOF-SIMS

The anodes were pealed off and residual stacks were analyzed by GCIB-TOF-SIMS.



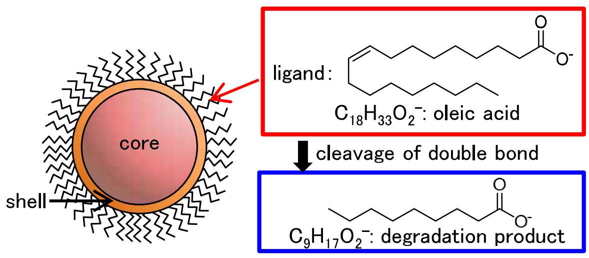
Negative secondary ion profiles

✓ Decrease of QD ligand
✓ Increase of degradation product ($C_9H_{17}O_2^-$)

5. Summary

Decomposition of QD ligand shown below possibly changes the carrier balance and coordination state of QD.

Replacement to more stable ligand would contribute to improve the device lifetime.



Estimated degradation scheme

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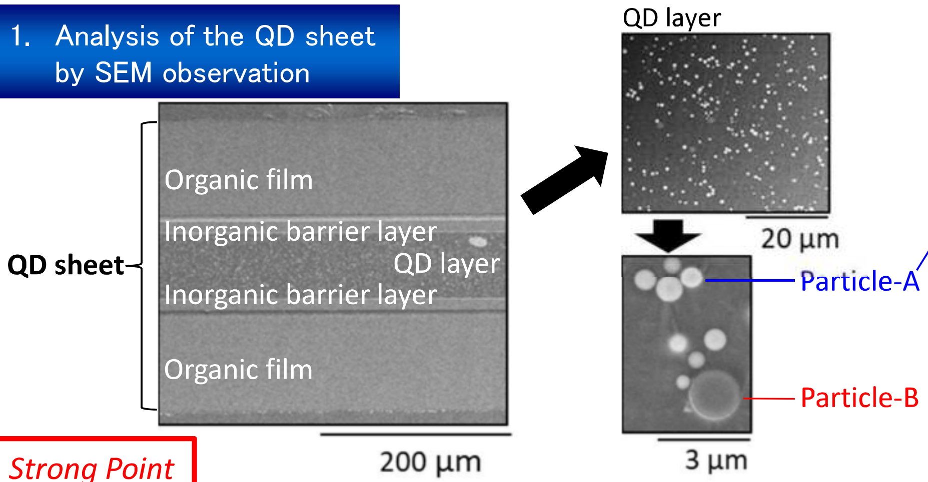
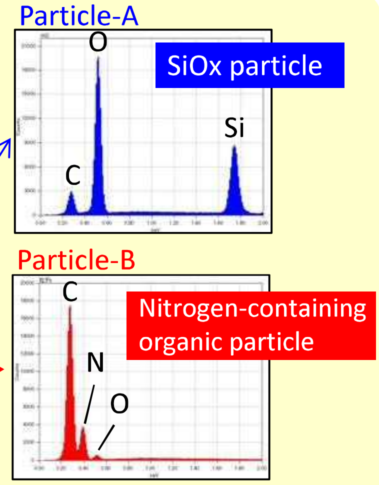
Evaluation of the QD sheet by SEM-EDX analysis and quantitative image analysis

About QD (quantum dot) sheet used for the backlight of the liquid crystal display, we developed technique to get the layer structure and the elemental information by SEM-EDX analysis.
By special cross-section processing technique and the high efficiency EDX detector, we are able to ofer the various quantitative information such as the particle diameter and the distribution.

1. Analysis of the QD sheet by SEM observation



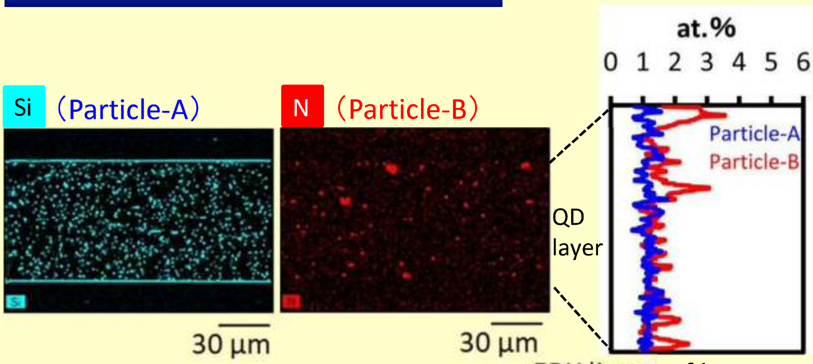


EDX spectra of each particle

Strong Point

Accurately confirm *elemental information of micro particles* and *layer structure in a wide range*.

2. Evaluation of the QD layer using the high efficiency EDX detector



EDX line profile of Silicon and Nitrogen

Strong Point

★EDX analysis by low accelerating voltage
_***Higher*** efficiency and ***Higher*** spatial resolution

Particle-A is uniformly distributed
Particle-B is unevenly distributed

3. Image analysis

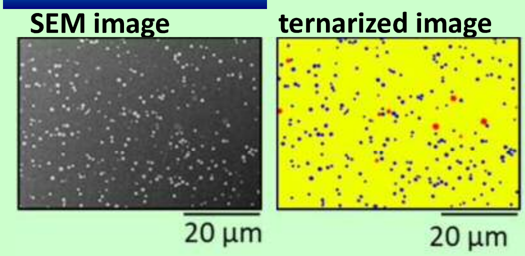


Table. Area ratio and particle diameter

	Particle area/ QD layer area	Average particle diameter
A	4.3%	0.8 µm
B	0.4%	1.2 µm

Strong Point

★Image analysis under the optimum conditions at any situation

Various quantitative information such as diameter, area ratio, site distribution …

Various Information

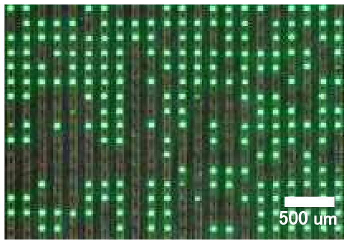
SEM image	⇒	**Layer composition, Thickness**
SEM-EDX analysis	⇒	**Elemental information, Distribution**
Image analysis	⇒	**Diameter, Area ratio, Histogram, etc.**

Toray Research Center, Inc.

Defect analysis of micro-LED with sub-μm level

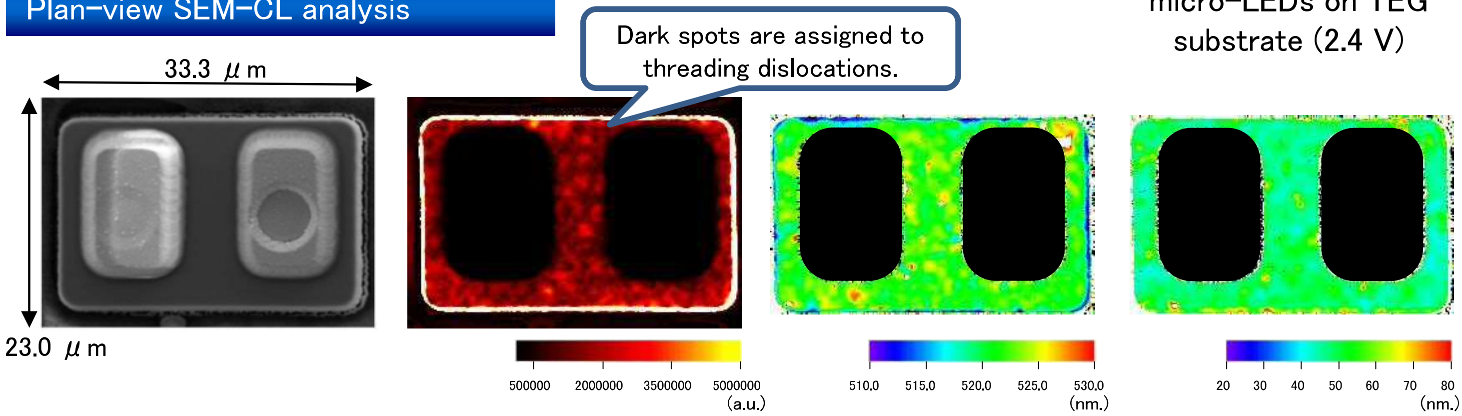
Cathodoluminescence (CL) is a unique technique that combines electron microscopy and spectroscopic analysis. CL can evaluate point defects of semiconductor chips with high sensitivity and high spatial resolution. CL is a very effective method for evaluating micro-sized LEDs.

Micro-LED display is a self-emitting display technology where each subpixel is an individual LED chip, and it plays an increasingly important role in the new generation of display technology. Although micro-LEDs are small in size and analysis methods are limited, CL analysis is a very useful method that can provide a lot of information about properties.



micro-LEDs on TEG substrate (2.4 V)

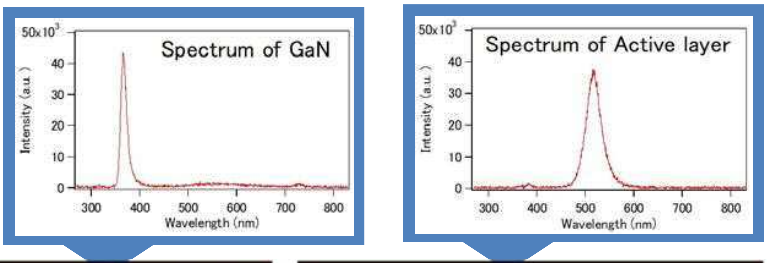
Plan-view SEM-CL analysis

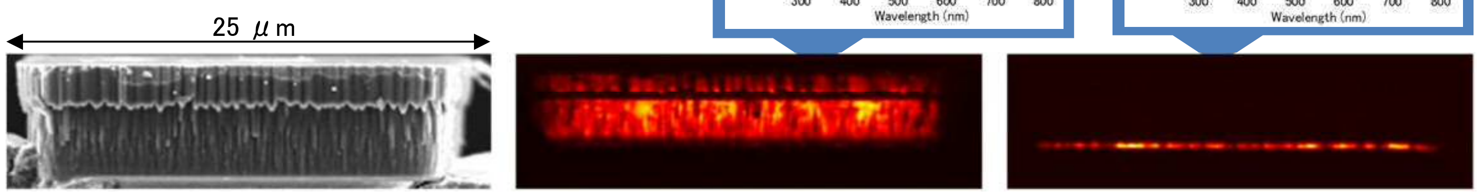


(a) SEM image (b) CL intensity image of active layer (c) CL peak wavelength image of active layer (d) CL width image of active layer

✔ CL intensity is related to defects.
✔ CL peak wavelength is mainly related to stress.
✔ CL width is related to crystallinity.

Cross-sectional SEM-CL analysis





(a) SEM image (b) CL intensity image of GaN band-edge (c) CL intensity image of active layer

✔ CL has the feature of high spatial resolution, which enables to obtain information such as defects in each layer.

CL analysis can contribute to improving your R&D, reliability, and productivity.

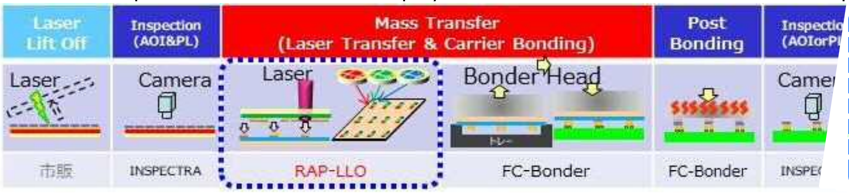
Toray Research Center, Inc.

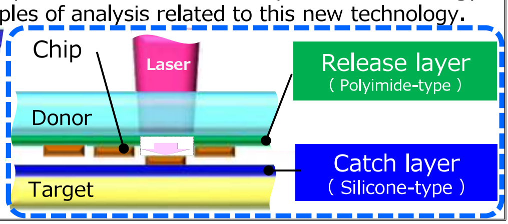
Analysis for manufacturing technology of micro LED – Optimization of laser transfer conditions –

In the manufacturing process of micro LED displays, the laser process is very effective for accurate and fast transfer of micro chips. However, it is necessary to select the appropriate laser wavelength and energy for high-precision transfer. We introduce analysis methods that can evaluate surface contaminations and damage in order to select optimal process conditions.

RAP-LLO Toray Engineering Co., Ltd.

Toray Engineering Co., Ltd. supplies a wide variety of equipment related to the micro LED manufacturing process, and has developed a new technology, RAP-LLO (Random Access Patterned - Laser Lift Off). The new technology, RAP-LLO is capable of transferring only selected chips at a high speed of 10,000 chips per second, and is expected to become an indispensable technology for the widespread use of micro LED displays in the market. We will introduce examples of analysis related to this new technology.





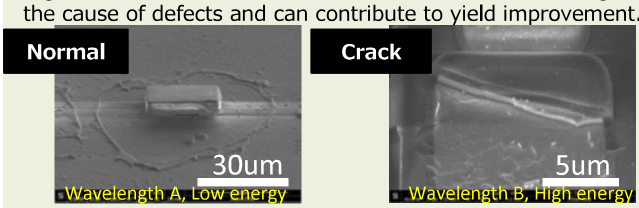
Condition of laser transfer

Daring to experiment under inappropriate condition

Laser	Wavelength A	Wavelength B
Low energy	Transferred	Not released
High energy	Transferred	Cracking

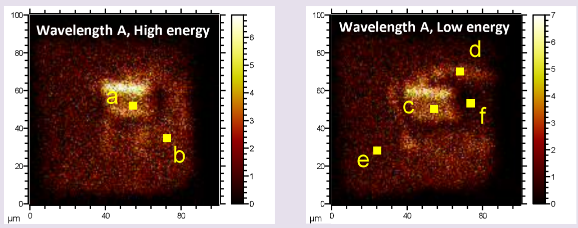
Morphological observation (SEM)

Chip cracks are observed under inappropriate condition. High resolution SEM observation is effective in determining the cause of defects and can contribute to yield improvement.

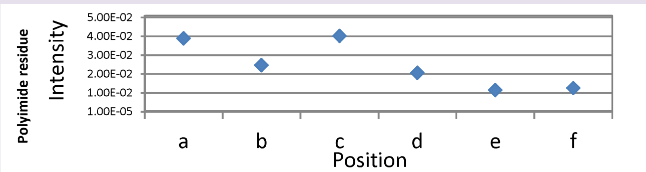


Surface-contamination evaluation (TOF-SIMS)

TOF-SIMS can obtain chemical structure of organic materials with high sensitivity and high spatial resolution. It is an ideal method to evaluate the matching of laser conditions with release materials and catch materials.



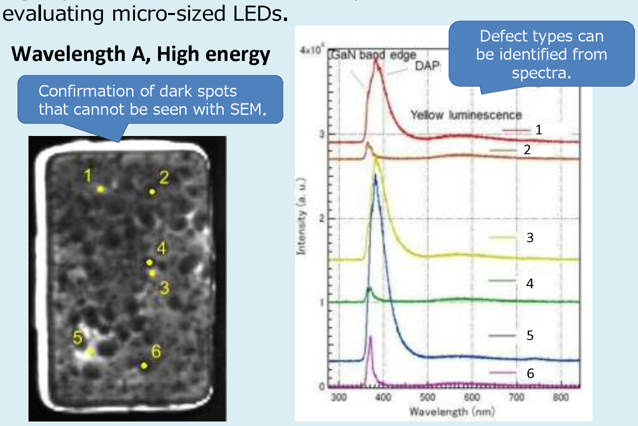
Distribution of polyimide residue



Contamination were found on the top surface of the chip even in the normal transfer process, and the distribution of the contamination varied among the conditions. TOF-SIMS is an important method for selecting appropriate laser conditions.

Damage evaluation (Cathodoluminescence)

Cathodoluminescence (CL) can evaluate damage (defects) on the surface of semiconductor chips with high sensitivity and high spatial resolution, and is a very effective method for evaluating micro-sized LEDs.



CL image   CL spectrum

Many dark spots were observed under all the normal transfer conditions. It is conceivable that these could have occurred during the lift-off process of the LED chip from the sapphire substrate. CL method can evaluate residual defects in chips with high sensitivity, it can be used for process improvement.

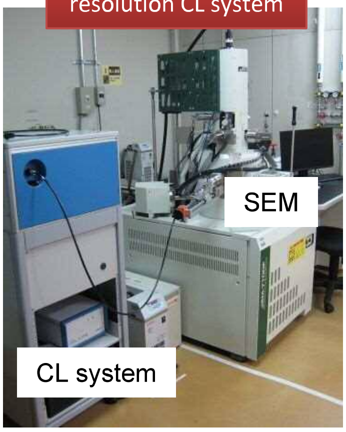
Toray Research Center will contribute to accelerate the development of micro-LEDs by utilizing the latest analysis techniques and the more than 40 years of experience we have accumulated.

Toray Research Center, Inc.

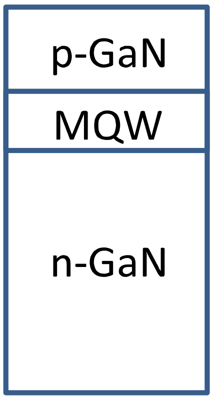
Process optimization and failure analysis of Micro-LEDs and Mini-LEDs

Analysis technologies such as cathodoluminescence (CL) and Raman spectroscopy are useful for Micro-LEDs and Mini-LEDs, which will be adopted in the next generation displays. Especially, our technologies are effective for process optimization and failure analysis.

Overview of high-resolution CL system

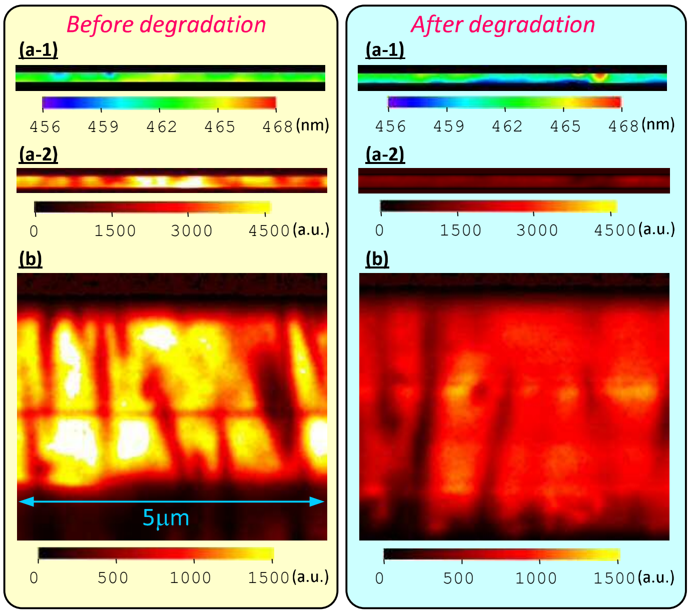


Micro-LED structure



Cross-sectional CL analysis of MQW and GaN layers

Cross-sectional samples were prepared before and after degradation.



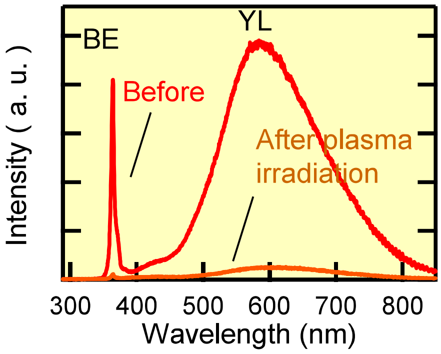
CL spectral mapping
InGaN MQW : (a-1) Wavelength, (a-2) Intensity GaN : (b) Intensity

Consideration of Cross-sectional CL analysis

Decreased luminescence intensity of GaN and InGaN → Decreased crystallinity, resulting in an increase in non-luminescent centers. Wavelength shifts caused by composition, stress, and other factors are also observed with high precision (the average emission wavelength shift for InGaN layers is about 2 nm).

Evaluation of plasma damage (GaN on sapphire)

After plasma treatment of GaN film, damage at the extreme surface (acceleration voltage: 0.5 kV, penetration length: 4.3 nm) was evaluated by CL.

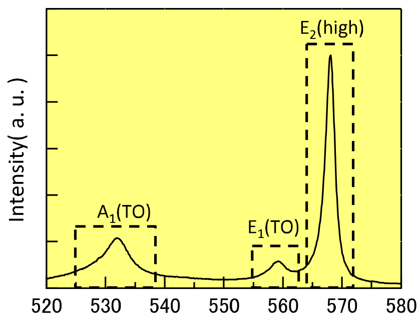


CL spectra (surface measurement)

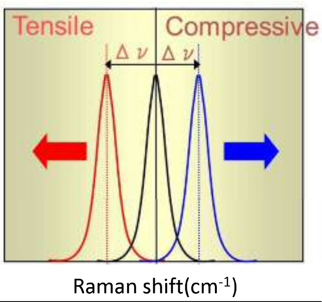
Consideration of surface CL analysis

The band edge emission (BE) intensity of the GaN layer is greatly reduced due to plasma damage. It is possible to evaluate the process damage at the extreme surface layer with high sensitivity.

Stress evaluation of GaN by Raman Spectroscopy



An example of Raman spectrum of GaN (a-plane)



Raman shift(cm^{-1})

$$\Delta\nu\ (cm^{-1}) = C\cdot\sigma\ (MPa)$$

$\Delta\nu$ is proportionate to stress σ

Raman scattering in GaN

GaN has anisotropy because of its hexagonal crystal structure.
⇒Multiple Raman line can be observed. Understanding the nature of vibration modes is important.

Temperature-dependent stress in GaN

Raman can be used for the optimization of packaging

Our features

- High precision measurement
  Stress can be determined within ± several MPa.
  (Wavenumber precision : ± 0.02cm^{-1})
- Temperature-dependent stress measurement
  A temperature of the sample can be changed from -150 to 300°C.
  Stress analysis can be performed at any temperatures.

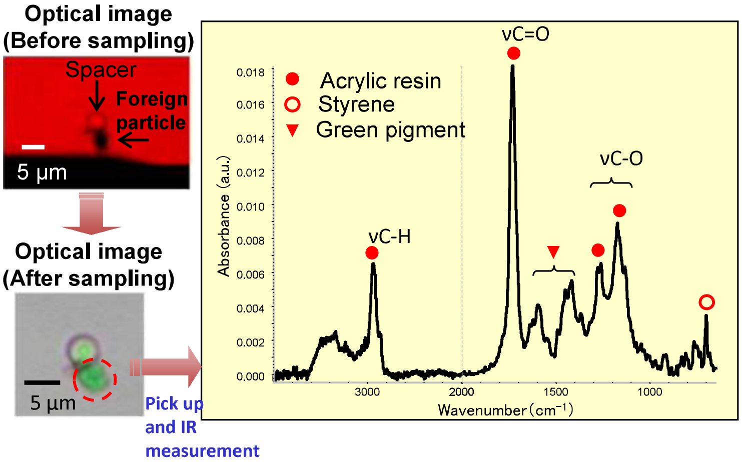
P02292海外営業部(滋賀)20210707

Toray Research Center, Inc.

DO YOU HAVE ANY TROUBLE IN LCD PANEL ?

You can count on us, Toray research center, Inc.

FOREIGN PARTICLE IN LCD PANEL



Foreign particle is styrene acrylate resin with green pigment

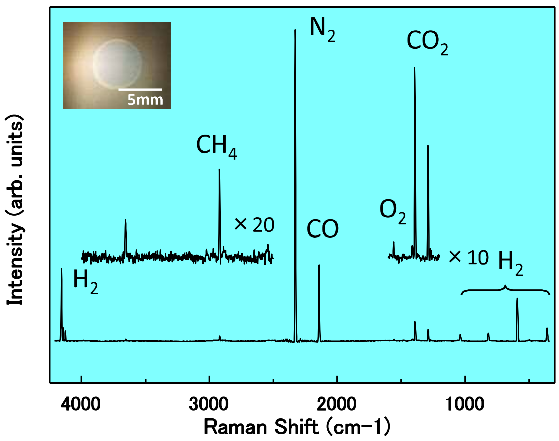
- ✓ **Precise analysis data for trouble shooting**
- ✓ **Micro FTIR and Raman analysis is applicable from 1 µm foreign particle**
- ✓ **E mail data in 1-2 weeks**

Price

110,000 YEN /SAMPLE

(Price will change depending on measurement points, measurement condition)

GAS ANALYSIS IN LCD PANEL



N_2 is process gas in LCD manufacturing, and CH_4, CO, CO_2, H_2 are decomposition of organic compounds in LCD panel

- ✓ **Effective analysis data for process improvement**
- ✓ **No size limitation of panel size**
- ✓ **Raman analysis is available for Inorganic gas except rare gases, organic gas （C＜3）**
- ✓ **E mail data in 1-2 weeks**

Price

200,000 YEN/ SAMPLE

(Price will change depending on measurement points, measurement condition)

000042構造化学第2研究室20160120−3

For Further details, please contact us !

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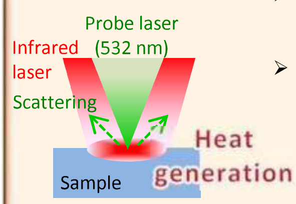
Composition analysis of foreign substances by optical-photothermal IR spectroscopy (O-PTIR)

Optical-photothermal IR spectroscopy (O-PTIR) enables to obtain infrared spectra in non-contact manner with about 1 μm spatial resolution. We applied O-PTIR to analyze small foreign substances which were impossible to be analyzed with conventional micro FT-IR because of their position and mechanical properties.

Principle and characteristics of O-PTIR

◇Principle



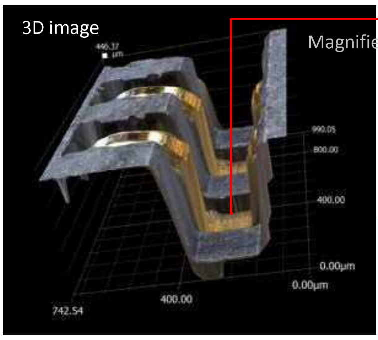
- Sample absorbs infrared laser and diffuses its energy as heat, which cause sample deformation.
- Collimated visible laser (532 nm) detects the sample deformation, which can be converted as IR spectrum.

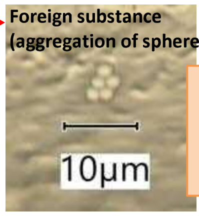
Detected sensitivity depends on IR absorptivity and thermal expansivity of sample itself.

◇Characteristics

- IR measurement with about 1 μm spatial resolution (conventional micro FT-IR is at most 10 μm)
- Acquisition of the same spectra as FT-IR
- Non-contact measurement using probe laser, which enables IR measurement for small foreign substances if they can be observed with optical microscope
- Combination with other analysis available (e.g. SEM-EDX, TOF-SIMS, Raman)

Analysis of foreign substances on a circuit

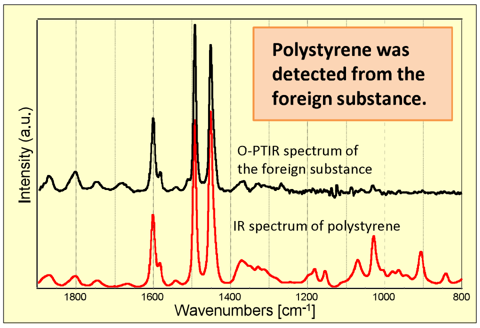




The foreign substance was located on a circuit of 450 μm in depth from top of the sample.

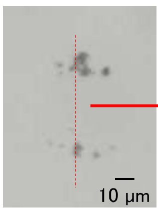
・Impossible to pick up the foreign substances
・Other sample preparation is also impossible due to its size (too small) and sample shape
→O-PTIR measurement was conducted.

■O-PTIR analysis result

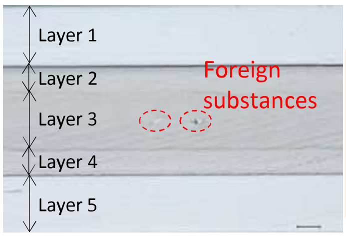


Analysis of foreign substances inside a multi-layered film

OM image



Sample cross section

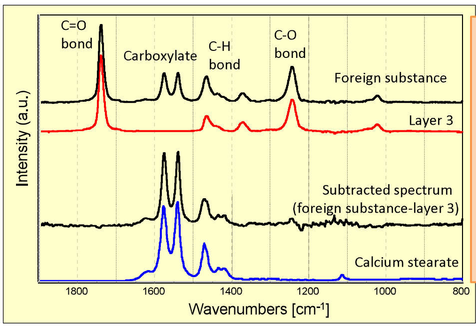


20 μm

The foreign substances in 6-10 μm size were inside layer 3.

・Impossible to measure the foreign substances from sample surface
・Difficult to collect the foreign substances due to sample size and location
→O-PTIR measurement was conducted with sample cross section.

■O-PTIR analysis result



Rich aliphatic carboxylate (e.g. solid lubricant) was detected from the foreign substance.

O-PTIR analysis is effective to analyze small foreign substances in various samples (e.g. on intricate shape sample such as semiconductor, on adhesive, inside polymer material such as film), and we can acquire many information of chemical structure with high spatial resolution and non-contact measurement.

Effective and new solutions for R & D of organic electronics

TRC, as a partner for deeper understanding and continuous evolution

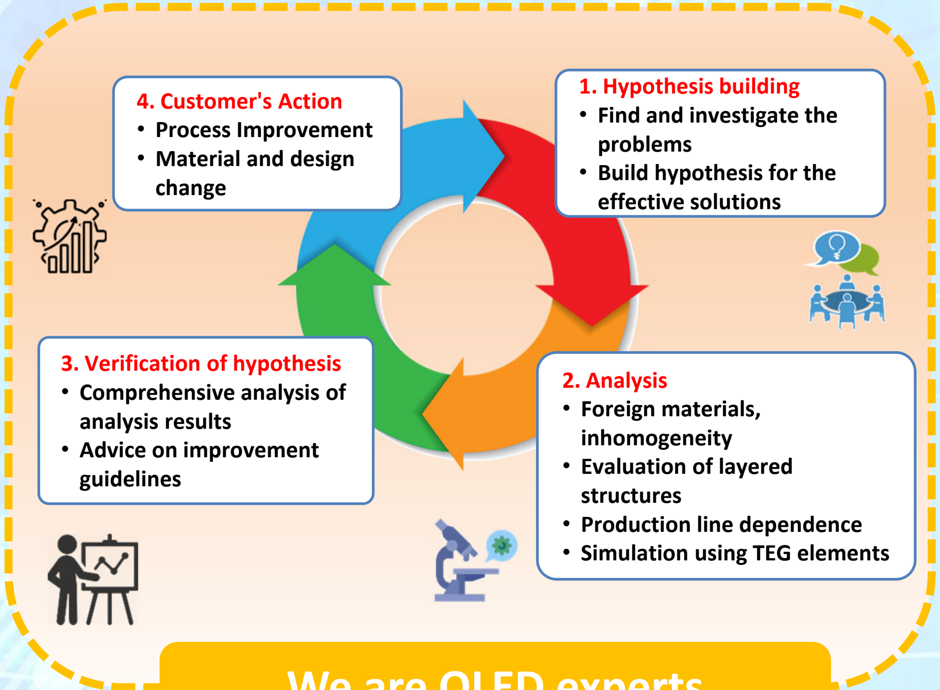
Toray Research Center (TRC) has built the business alliance with OPERA Solutions Inc. to provide a wide range of solutions for R & D in organic electronics. TRC and ORERA solutions can help our customers solve their problem, with our expertise in OLED material / device physics / manufacturing equipment / instrumental analysis.

Do you have any problems in the R&D of organic electronic devices?

- ✓ Check the performance of our own materials in practical use.
  ⇒ **We can fabricate OLED devices on your request and evaluate its performance with high precision.**
- ✓ Examine the stability of our OLED materials during deposition process.
  ⇒ **We can utilize the Continuous Deposition Test for prototyping to simulate a production machine.**
- ✓ Replace the components / materials of production machine.
  ⇒ **We can provide the generated gas and impurity analysis.**
- ✓ Apply new processes and materials.
  ⇒ **We can offer the solution from prototyping to verification.**

You can stimulate your R&D with our highly specialized outsourcing capability.

Please contact us !



We are OLED experts