

# Application of Plasma-Polymerized *p*-xylene Thin Film to Organic EL Device

Ran ZHAO\* , Kenji TANAKA\*\* ,  
Yoshiharu MAEKAWA\*\*\*, Minoru KUSABIRAKI\*\*\*\*  
and Masao AOZASA\*\*\*\*\*

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## Synopsis

Plasma-polymerized *p*-xylene(PPPX) was deposited and photoluminescent(PL) spectrum was investigated. Effects of the residual radicals in PPPX were examined. Red shift of Alq<sub>3</sub> was observed in a layered sample of Alq<sub>3</sub> and PPPX.

KEYWORDS: Plasma-polymerized film, PL spectrum, *p*-xylene

## 1. Introduction

Since the first report by Tang and Van Slyke in 1987 on organic thin film electroluminescent(EL) device, it has been extensively investigated as a next generation flat panel display of great promise, because of their merit of high luminance, low driving voltage and a variety of emission colors<sup>1)</sup>.

To fabricate organic EL device, several deposition techniques such as spin-casting, vacuum vapor deposition, and plasma polymerization have been used.<sup>2)</sup>

Among them plasma polymerization method has not been used much so far. However it has many advantages. For example, it can prepare uniform film with few pin holes at low substrate temperature. The film thickness can be well controlled and many monomers are available. Therefore, we anticipate its application to fabricate stable EL device. However it has been pointed out that the residual radicals in plasma-polymerized film might cause degradation of organic materials<sup>3)</sup>. Therefore it is necessary to clarify the effects of the residual radical on the performance of the material comprising an EL device.

In this study, PPPX was chosen as a radical source and its effect on Alq<sub>3</sub>, which is popularly used as an emission layer in an organic EL device, was examined by PL emission. Investigated sample configurations were PPPX/Alq<sub>3</sub>, PPPX/Alq<sub>3</sub>/PPPX, PPPX and Alq<sub>3</sub>.

## 2. Experimental

In this study, *p*-xylene monomer of 99 % purity(Wako Pure Chemistry) was used. The molecular structure of *p*-xylene is shown in Fig. 1 (a). Thin films of plasma-polymerized-*p*-xylene were prepared in an capacitively coupled glow discharge reactor shown in Fig. 2. PPPX was deposited on polished quartz or Corning# 7059 glass substrate(MATSUNAMI GLASS IND.), which was cleaned in neutral detergent, tap water, pure water and isopropyl alcohol. In order to exclude the residual oxygen in *p*-xylene monomer and monomer bubbler, we exhausted the gas thawing the monomer after freeze. This process was repeated two or three times. A preliminary Ar discharge was built before polymerization. Firstly, the reactor was exhausted down to the base pressure of  $7 \times 10^{-2}$  Torr using a rotary pump<sup>4)</sup>.

The preliminary discharge of Ar was performed at a pressure of 0.2 Torr with vavle A opened. The discharge was sustained for 15 minutes by an r.f. power generator operating at 13.56 MHz with a matching box. After preliminary discharge vavle A was closed. Then vavle C was opened gently to restrain the monomer boiled and vavle B was opened to bubble the monomer for 3 minutes. Then Ar begins carrying *p*-xylene monomer into the reactor.

\*Student, Doctor Course of Dept. of Electrical Engineering

\*\*Research Associate, Dept. of Electrical Engineering

\*\*\*Lecturer, Dept. of Electrical Engineering

\*\*\*\*Associate Professor, Dept. of Electrical Engineering

\*\*\*\*\*Professor, Dept. of Electrical Engineering

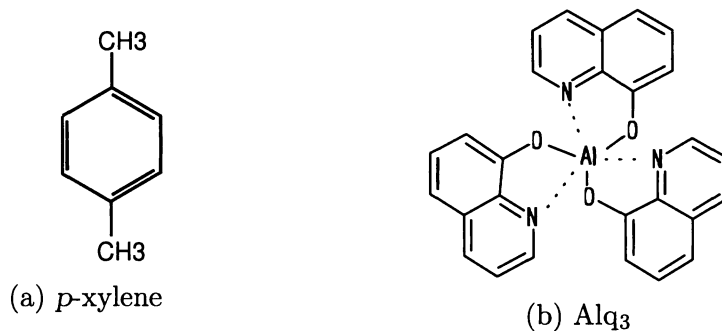


Fig. 1 Molecular Structures

Finally, PPPX deposition was started by sustaining glow discharge under the conditions (power: 15 W, base pressure:  $7 \times 10^{-2}$  Torr, Ar pressure: 0.4 Torr, deposition time: 10 min). The molecular structure of Alq<sub>3</sub> is shown in Fig. 1(b). Alq<sub>3</sub> was deposited by vacuum vapor deposition(Tokuda) at the pressure of  $10^{-6}$  Torr.

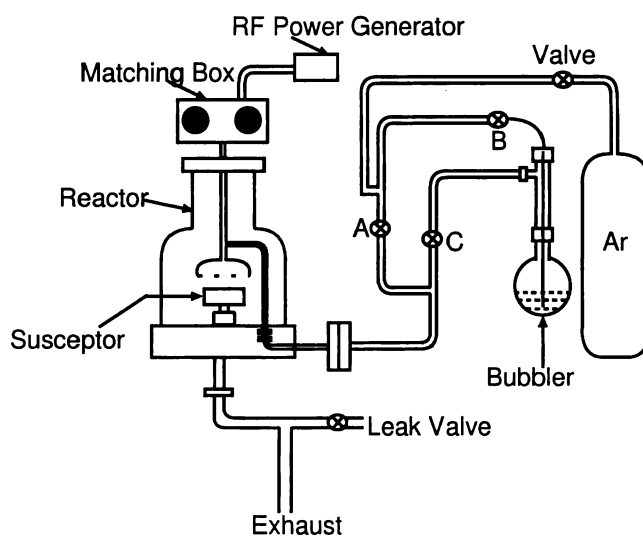


Fig. 2 Capacitively Coupled Glow Discharge System for Plasma Polymerization

Fig. 3 shows a PL measurement system. The PL emission was observed under the excitation of a He-Cd laser(20 mW, 325 nm). This system consisted of He-Cd laser(KIMMON Electric, IK320R), glass filter(HOYA, U-340), interference filter(SIGMA KOKI, 326.0 nm), monochromator(JASCO, CT -25C), optical chopper(SCIENCE INSTRUMENT), lock-in amplifier(NF LT-572B) and personal computer(IBM, Aptiva).

PL spectrum was obtained as follows: The noise of unfavorable light from the equipment was cut by two optical filters. The ultraviolet light was chopped by an optical chopper and irradiated on a sample. PL emission from a sample was monochromized using monochromator and the monochromized emission was transformed into electric signal by a photo-multiplier. Using a lock-in amplifier, the monochromized emission signal was amplified and acquired into a computer with A/D converter.

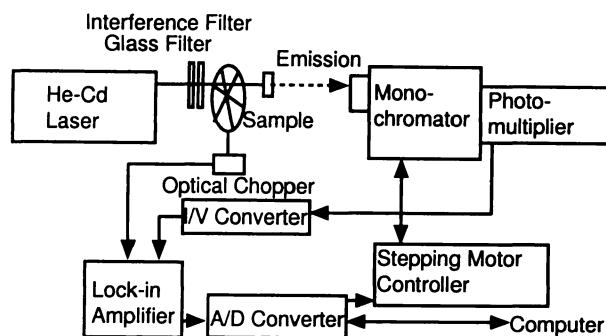


Fig. 3 Measurement System of PL Spectrum

### 3. Experimental Results and discussions

#### 3.1 PL spectrum of PPPX film deposited on glass substrate

The PL spectrum of PPPX excited by 325 nm light is shown in Fig.4. The emission spectrum shows a peak at 438 nm. As this peak is not symmetric, peak separation into Gaussian peaks were performed. In the separation, we used a least squares method. ASNOP(Application System for Non-linear Optimization Problems) is utilized to solve the least squares problem. ASNOP is an application which generates FORTRAN program. The curve fitting with four Gaussian peaks was satisfactory while that with three Gaussian peaks was not. The result of the peak separation into four Gaussian peaks is shown in Fig.4. The peak wavelengths were 394 nm, 421 nm, 453 nm and 497 nm respectively, where the maximum peak was at 453 nm.

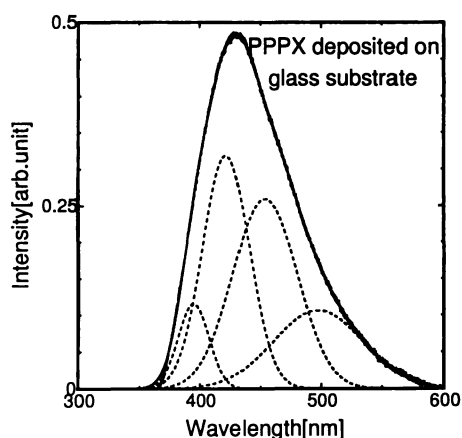


Fig. 4 PL Spectrum of PPPX Deposited on Glass Substrate

#### 3.2 PL spectrum of PPPX film deposited on quartz substrate

As the PL spectrum shown in Fig. 4 might include the emission due to the glass substrate, we deposited the PPPX on a quartz substrate and the PL spectra were compared.

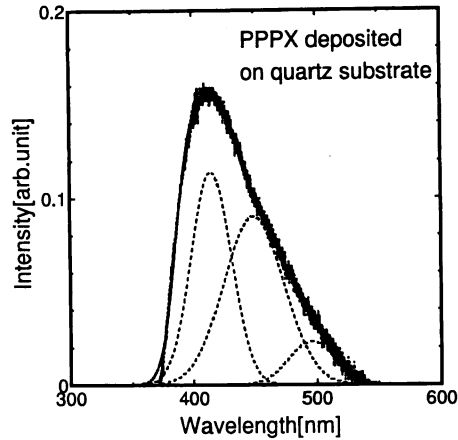


Fig. 5 PL Spectrum of PPPX Deposited on Quartz Substrate

Using ASNOP, peak separation into four Gaussian peaks was performed. However just three Gaussian peaks at 414 nm, 450 nm and 495 nm were obtained. Comparison between Fig.4 and Fig.5 shows that a peak at 394 nm in Fig.4 would be due to the glass substrate. So hereafter we examined a sample on quartz substrate.

### 3.3 PL spectra of samples deposited on quartz substrate

PL emission spectrum of  $\text{Alq}_3$  was examined first. We fabricated three kinds of samples  $\text{Alq}_3$ ,  $\text{PPPX}/\text{Alq}_3$  and  $\text{PPPX}/\text{Alq}_3/\text{PPPX}$  on quartz substrate as shown in Fig. 6(a) PL spectrum of  $\text{Alq}_3$  consists of three peaks at 499 nm, 531 nm and 574 nm. Therefore in order to investigate the change of PL spectra of PPPX and  $\text{Alq}_3$  in  $\text{PPPX}/\text{Alq}_3$  and  $\text{PPPX}/\text{Alq}_3/\text{PPPX}$  samples, we divided the PL spectrum into six Gaussian peaks that is three for PPPX and three for  $\text{Alq}_3$ . The results of peak separation are shown in Fig. 6(b) and Fig. 6(c). Fig. 6(b) shows that six peaks of  $\text{PPPX}/\text{Alq}_3$  sample are at 395 nm, 421 nm, 493 nm, 512 nm, 552 nm and 610 nm respectively. Fig. 6(c) shows that six peaks of  $\text{PPPX}/\text{Alq}_3/\text{PPPX}$  are at 394 nm, 420 nm, 487 nm, 504 nm, 542 nm and 596 nm.

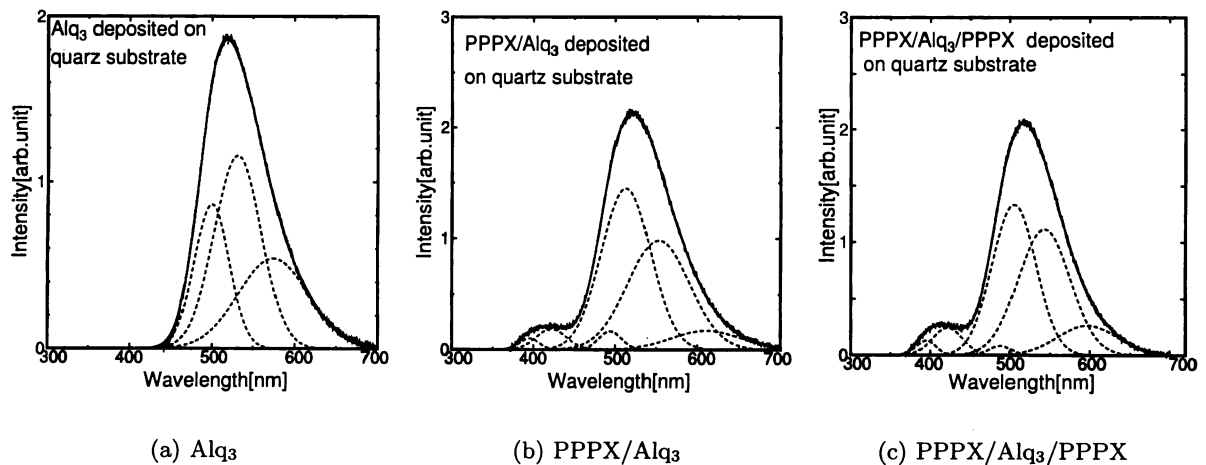


Fig. 6 PL Spectra of Samples Deposited on Quartz Substrate

The results of peak separation ( $\text{PPPX}$ ,  $\text{Alq}_3$ ,  $\text{PPPX}/\text{Alq}_3$ ,  $\text{PPPX}/\text{Alq}_3/\text{PPPX}$ ) is summarized in Table 1.

Table 1 Peak separation

PPPX (nm)	Alq <sub>3</sub> (nm)	Alq <sub>3</sub> /PPPX (nm)	PPPX/Alq <sub>3</sub> /PPPX (nm)
414	-	395	394
450	-	421	420
495	-	493	487
-	499	512	504
-	531	552	542
-	574	610	596

The table shows that the corresponding peaks to PPPX in PPPX/Alq<sub>3</sub> and PPPX/Alq<sub>3</sub>/PPPX thin films shifts to the shorter wavelength while that corresponding to Alq<sub>3</sub> in PPPX/Alq<sub>3</sub> and PPPX/Alq<sub>3</sub>/PPPX thin films shifts to the longer wavelength.

#### 4. Conclusions

The conclusions can be summarized as follows :

1. PPPX spectrum has a peak around 438 nm under the 325 nm excitation.
2. PL spectra of PPPX in PPPX/Alq<sub>3</sub> and PPPX/Alq<sub>3</sub>/PPPX thin films showed blue shift and that of Alq<sub>3</sub> in PPPX/Alq<sub>3</sub> and PPPX/Alq<sub>3</sub>/PPPX showed red shift.
3. Alq<sub>3</sub> still showed a pretty good emission in PPPX/Alq<sub>3</sub> and PPPX/Alq<sub>3</sub>/PPPX sample though some color shift was observed.

#### 5. References

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