

Preparation of Plasma-polymerized *p*-xylene Films for Encapsulation of Organic Light-emitting Diodes

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(Received: 1 September 2008 / Accepted: 23 November 2008)

Plasma-polymerized *p*-xylene (PPPX) films were prepared in a triode glow discharge. The formation characteristics, Fourier transform infrared (FTIR), photoluminescence (PL) and electron spin resonance (ESR) spectra of PPPX films, dielectric loss tangent ($\tan D$) of PPPX film condensers and encapsulation of organic light-emitting diodes (OLEDs) with PPPX films were investigated. When the glow discharge polymerization was carried out under monomer vapor pressure of 0.2 Torr and rf voltage was applied to the substrate electrode, the thickness of PPPX films changed almost linearly with polymerization time. The FTIR, PL and ESR spectra of PPPX films, and $\tan D$ of PPPX film condenser, changed with rf voltage. The luminance of encapsulated OLEDs with PPPX film was higher than for non-encapsulated OLEDs after the preparation of PPPX film.

Keywords: plasma-polymerized *p*-xylene film, triode glow discharge, FTIR, PL, OLED

1. Introduction

Thin polymer films can be prepared on any solid surface at low temperature by the glow discharge method. Polymer films produced by this process are pinhole-free and homogeneous, and have excellent electrical properties. For those reasons, they have applications in dielectrics for conversion devices, capacitors, passivation of semiconductors, and as barriers to specific vapors [1].

Films of *p*-xylene have a high melting point and unusually good chemical resistance. In addition, they have excellent electrical properties, including high volume resistivity and dielectric strength, dielectric loss tangent ($\tan D$), and very small change in dielectric constant with frequency [2].

One of the authors has investigated the dielectric breakdown of plasma-polymerized hexamethyldisilazane films [3] and hexamethyldisiloxane coating [4], and plasma treatment of indium-tin oxide (ITO) surfaces to improve luminescence characteristics of organic light-emitting devices [5].

In the present study plasma-polymerized *p*-xylene (PPPX) films were prepared in a triode glow discharge. Effects of rf voltage applied to the substrate electrode on the formation characteristics, Fourier transform infrared (FTIR), photoluminescence (PL) and electron spin resonance (ESR) spectra of PPPX films, and $\tan D$ of PPPX film condensers were investigated and PPPX films were applied to encapsulation of organic light-emitting diodes (OLEDs). The purpose of applying rf voltage is to control the deposition rate and change the FTIR, PL spectra, spin density and $\tan D$.

2. Experimental

2.1 Sample preparation

PPPX films were prepared on three kinds of substrate (Al deposited glass, ITO coated glass and quartz), and on one type of device (OLEDs), for measurements of thickness and $\tan D$, FTIR and PL spectra, and luminous characteristics of encapsulated OLEDs.

A triode glow discharge system [4,6] was used for the preparation of PPPX films. The reaction chamber contained three electrodes. An aluminum anode and cathode, 65 mm in diameter, were connected to a dc power supply. The substrate electrode was placed in the center of the chamber, between the anode and cathode. Either a glass (or quartz) substrate or device was mounted on the substrate electrode.

Prior to polymerization, *p*-xylene monomer was degassed by repeated freezing and pumping. Plasma polymerization was carried out by applying an rf voltage (100 kHz) between the grounded anode and the substrate electrode through a 24 μF capacitor at 15 mA discharge current, with monomer pressure 0.2 Torr.

Poly(*N*-vinylcarbazole) (PVK), 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), and tris(2-phenylpyridine) iridium ($\text{Ir}(\text{ppy})_3$) were dissolved in chloroform. PBD or $\text{Ir}(\text{ppy})_3$ -doped PVK thin films and poly(3,4-ethylenedioxythiophene)-poly(styrene sulphonic acid) (PEDOT-PSS) layers were prepared by spin coating on ITO coated glass substrate. The concentrations of PVK, PBD, and $\text{Ir}(\text{ppy})_3$ were 49.4, 49.4 and 1.2 wt.%, respectively.

Al electrodes of PPPX film condenser and Al-Li (99:1 wt.%) electrodes of OLEDs were formed by vacuum vapor deposition at 10^{-6} Torr. Fig. 1 shows the

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schematic structure of the encapsulated OLEDs with PPPX film.

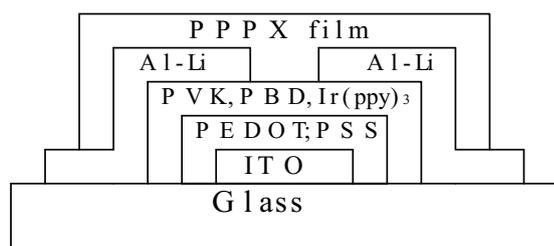


Fig.1 Schematic diagram of encapsulated OLEDs with PPPX film.

2.2 Measurements

The thickness of PPPX films was measured by means of multiple beam interferometry. Measurements of the capacitance, C , and the equivalent parallel conductance, G , of the PPPX condenser were carried out at 1 kHz using an Ando TR-IB bridge. $\tan D$ was calculated from $\tan D = G/\omega C$, where ω is angular frequency.

Applied rf voltage and substrate potential in the triode glow discharge system were measured using an Iwatsu DS-5110 digital oscilloscope. FTIR spectra were acquired using a Shimadzu FTIR-8600PC spectrophotometer with an RAS-8000 reflectance attachment. 100 scans were accumulated for each spectrum.

The luminance versus applied voltage characteristics of OLEDs, and PL spectra of PPPX films were measured using a homemade system [7]. The thickness of PPPX films for measurements of FTIR and PL was 800 nm. All measurements were performed at room temperature in air.

3. Results and Discussion

3.1 Formation characteristics of PPPX films

Fig.2 shows the relationship between the thickness of PPPX films and polymerization time. The thickness changed almost linearly with time, and increased with increasing rf voltage.

Fig.3 shows the changes in the surface potential of the substrate electrode when rf voltage was applied through a capacitor between the substrate electrode and the grounded anode. The substrate potential was negatively biased so that the average current could be zero in one cycle [8]. It becomes more pronounced as the applied rf voltage increases.

Positive ions in the *p*-xylene plasma are accelerated by the voltage $|V_r - V_s|$ to enter the substrate electrode, where V_r is the dc potential of the substrate electrode and V_s is the plasma space potential around the substrate [9]. Application of rf voltage increases the number of positive ions and the amount of energy entering the surface of PPPX film. As a result, the thickness of PPPX film increases with increasing rf

voltage.

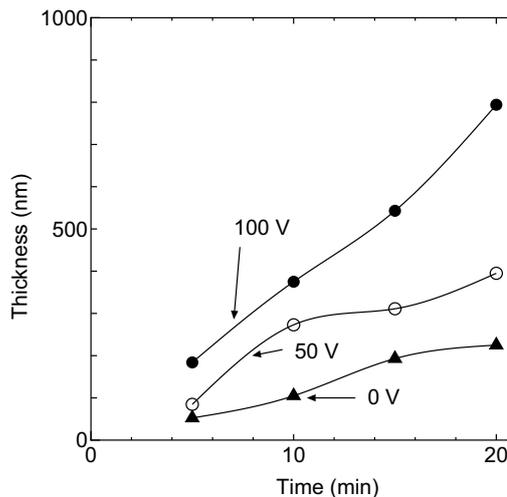


Fig.2 Relationship between thickness of PPPX films and polymerization time.

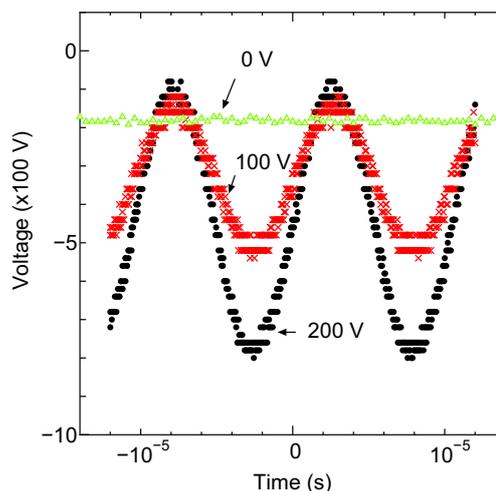


Fig.3 Changes in substrate potential with time.

3.2 FTIR, PL, and ESR spectra of PPPX films

Fig.4 shows FTIR spectra of PPPX films. The characteristic absorptions of $-\text{CH}_2$ and $-\text{CH}_3$ stretch vibrations and benzene ring vibration are observed at $3000\text{--}2800$ and 1500 cm^{-1} , respectively. Bands at 1380 and $900\text{--}700\text{ cm}^{-1}$ are assigned to CH_3 and benzene ring substituents, respectively [10-12].

A very large band in the region $3500\text{--}2800\text{ cm}^{-1}$ and a very small band at 1500 cm^{-1} from the benzene ring appeared in PPPX film prepared at 0 V. It has been reported that the benzene ring was destroyed by glow discharge polymerization and functional groups, such as $-\text{CH}_2\text{--CH}_2\text{--CH}_2\text{--}$ and $-\text{C}=\text{C}=\text{C}\text{--}$ appeared [12]. The application of rf voltage to the substrate electrode is accompanied by disappearance of the absorption bands, which indicates the occurrence of diamond-like structures in the polymerization.

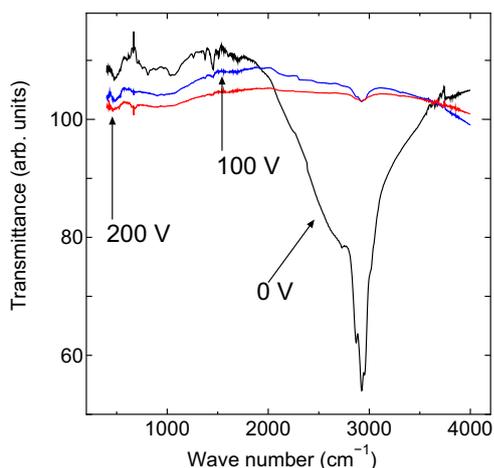


Fig.4 FTIR spectra of PPPX films.

Fig.5 shows the changes with elapsed time, in PL spectra of PPPX film prepared at 0 V. The PL spectrum has a peak at 470 nm which decreased after 1 week. Consequently, the subsequent spectra were measured immediately after the preparation of PPPX film. Fig.6 shows the changes in PL spectra of PPPX films with applied rf voltage. The peak at 470 nm decreased with increasing rf voltage, which might be due to the disappearance of benzen rings as suggested by the FTIR spectra.

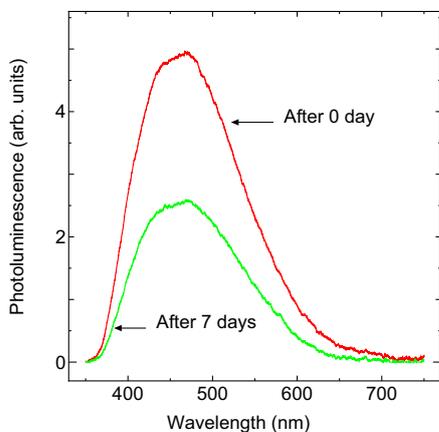


Fig.5 Changes with elapsed time in PL spectra of PPPX films prepared at 0 V.

Table I shows the line width of ESR spectra and the concentration of spin density of PPPX films, which increased with increasing rf voltage, V_3 . In addition, line width of ESR spectra increased with discharge current, I . The ESR signal may be due to carbon radicals introduced in the polymerization of *p*-xylene, suggesting that cross-linking of the PPPX film is progressive with increasing rf voltage and discharge current.

3.3 Tan D of PPPX film condensers

Fig.7 shows the changes in tan D of PPPX film condensers with polymerization time. Tan D of PPPX

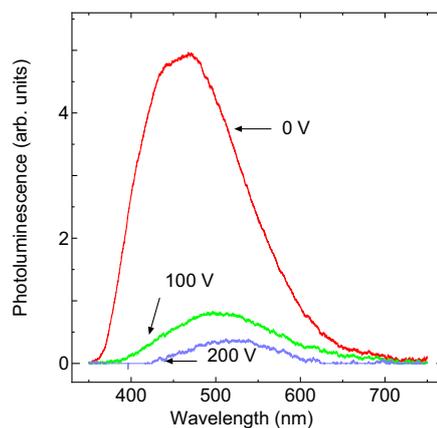


Fig.6 Changes in PL spectra of PPPX films with rf voltage.

Table I. Line width of ESR spectra and concentration of spin density of PPPX films.

V_3 (V)	I (mA)	line width (Gauss)	spin density (spins/cm ³)
0	15	2	-
0	23	7	4×10^{17}
100	15	13	-
300	15	14	2×10^{18}

film condensers is larger than that of conventional poly(*p*-xylene) film condenser 0.011 % [2]. Tan D of the sample prepared at 0 V, which increases with time, is smaller than that of the sample prepared at 100V, for which tan D decreases with polymerization time.

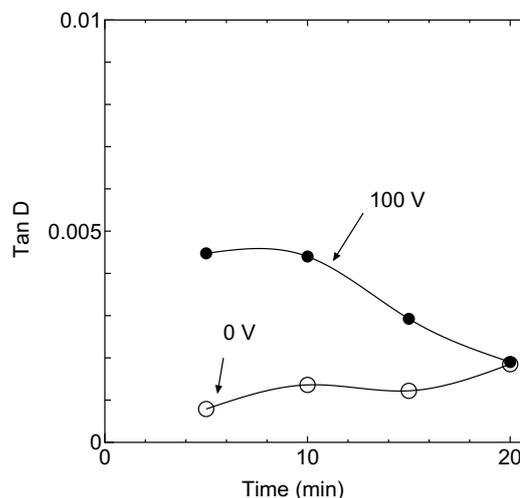


Fig.7 Changes in tan D of PPPX film condensers with polymerization time.

3.4 Characteristics of OLEDs

In order to realize the passivation layers of OLEDs, it is very important to prepare thin, uniform and pinhole-free PPPX films which have chemically and physically stable properties. Films of *p*-

xylene have good passivation properties as stated in 1.Introduction. However, PPPX films have large PL, spin density and tan D. FTIR results suggest that the PPPX films prepared at 200 V show highly cross-linked structure which has good chemical and thermal resistance.

Because positive ions in the *p*-xylene plasma are accelerated by the voltage IV_r - V_{sl} as stated in 3.1 and the OLEDs are damaged by the ion bombardment, at first 300 nm PPPX film was prepared on OLEDs at 0 V and next 1,700 nm film was prepared at 200 V.

Fig.8 shows the relationship between luminance of the non-encapsulated OLED and voltage. The luminance increased from zero at 10 V to 9000 cd/m^2 at 15 V, immediately after preparation of the device. However, it decreased to 1000 cd/m^2 at 15 V after 20 h.

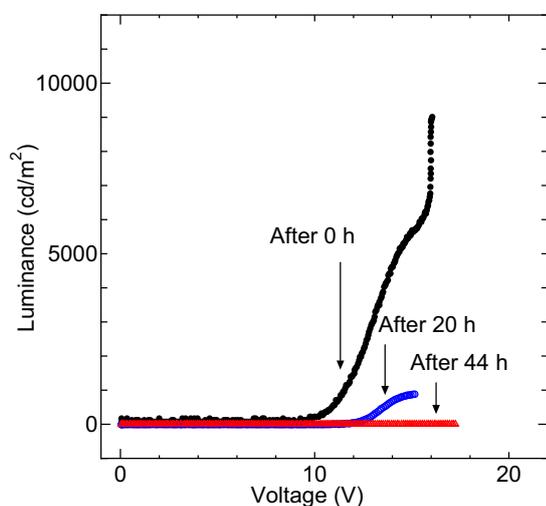


Fig. 8 Relationship between luminance of the non-encapsulated OLED and voltage.

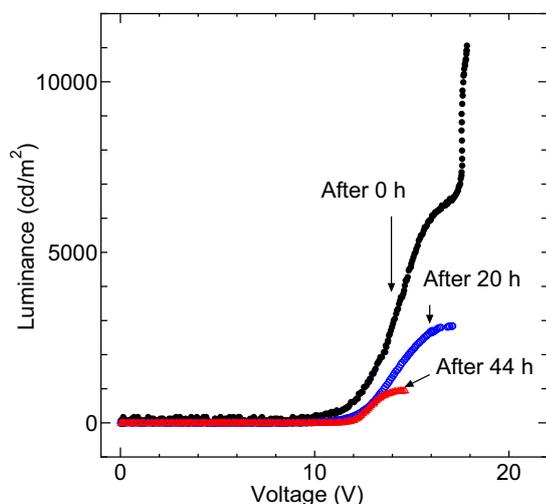


Fig. 9 Relationship between luminance of the encapsulated OLED and voltage.

Fig. 9 shows the relationship between luminance of the encapsulated OLED and voltage. The luminance decreased to 3000 cd/m^2 at 15 V after 20 h. The luminance of encapsulated OLED was higher than that of non-encapsulated OLED, after the preparation of PPPX film.

4. Conclusion

PPPX films were prepared in a triode glow discharge. The effects of rf voltage on the formation characteristics, FTIR, PL and ESR spectra of PPPX films, and tan D of PPPX film condensers were investigated and the PPPX films were applied to the encapsulation of OLEDs.

The thickness of PPPX films changed almost linearly with polymerization time and increased with rf voltage. The FTIR, PL and ESR spectra of PPPX films, and tan D of PPPX film condensers changed with rf voltage. The luminance of encapsulated OLEDs with combined PPPX film prepared at 0 and 200 V was higher than for non-encapsulated OLED after the preparation of PPPX film.

Acknowledgements

The authors would like to thank Mr. A. Tamura and Mr. K. Matsushita for their contributions to this work.

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