Plasma Polymer Films Prepared in a Triode Glow Discharge*

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Plasma-polymerized p-xylene (PPPX) and hexamethyldisiloxane (PPHMDS) films were prepared in a triode glow discharge. Formation characteristic, Fourier transform infrared spectroscopy (FTIR), photoluminescence (PL), relative dielectric constant (εr) of PPPX films, and application to the encapsulation of organic light-emitting diodes (OLEDs) were investigated. The thickness and εr of PPPX films increased and the FTIR and PL spectra decreased with increasing discharge current. The luminance of encapsulated OLEDs with PPPX and PPHMDS films was higher than that of non-encapsulated OLED after the preparation of PPPX and PPHMDS films.

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I. INTRODUCTION

Since plasma polymer films prepared in a electric discharge are pinhole-free and have superior thermal stability, widespread applications of them have been found such as dielectrics in the electronic devices and protective coating for metal and reactive surfaces [1].

One of the authors has investigated the dielectric breakdown of plasma-polymerized hexamethyldisilazane films [2] and hexamethyldisiloxane (PPHMDS) coating [3], and plasma treatment of indium-tin oxide (ITO) surfaces to improve luminescence characteristics of organic light-emitting devices (OLEDs) [4, 5].

In this paper plasma-polymerized p-xylene (PPPX) and PPHMDS films were prepared in a triode glow discharge. The formation characteristic, Fourier transform infrared spectroscopy (FTIR), photoluminescence (PL), relative dielectric constant (εr) of PPPX films, and application to the encapsulation of OLEDs were investigated.

II. EXPERIMENTAL

A. Sample preparation

PPPX and PPHMDS 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 capacitance, FTIR and PL spectra, and luminous characteristics of encapsulated OLEDs.

Prior to polymerization, p-xylene or hexamethyldisiloxane 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 [3, 5].

Poly(N-vinylcarbazole) (PVK), 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), and tris(2-phenylpyridine) iridium (Ir(ppy)3) were dissolved in chloroform. PBD or Ir(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 Ir(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. Figure 1 shows the schematic structure of the encapsulated OLEDs with plasma-polymerized film.

B. Measurements

The thickness (d) of plasma-polymerized films was measured by means of multiple beam interferometry. Measurements of the capacitance (C) of the PPPX condenser which has two parallel electrodes were carried out at 1 kHz using an Ando TR-IB bridge. Relative dielectric constant (εr) was calculated from C = ϵr ε0 S/d, where ϵ0 and S are dielectric constant of vacuum and electrode area, respectively.

FTIR spectra of PPPX films were acquired using a Shimadzu FTIR-8600PC spectrophotometer with an RAS-8000 reflectance attachment. 100 scans were accumulated for each spectrum. The luminance and current of OLEDs, and PL spectra of PPPX films were measured using a homemade system [6]. All measurements were performed at room temperature in air.

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FIG. 2: Relationship between thickness of PPPX films and polymerization time.

![Graph showing the relationship between thickness and time for PPPX films with discharge currents of 8 mA and 15 mA.](image)

FIG. 3: FTIR spectra of p-xylene monomer and PPPX films.

![FTIR spectra of p-xylene monomer and PPPX films, showing characteristic absorption peaks.](image)

FIG. 4: Changes in PL spectra of PPPX films with discharge current.

![Graph showing changes in photoluminescence of PPPX films with discharge current.](image)

FIG. 5: Change in relative dielectric constant of PPPX films with discharge current.

![Graph showing the change in relative dielectric constant of PPPX films with discharge current.](image)

### III. RESULTS AND DISCUSSION

#### A. Formation characteristic

Figure 2 shows the relationship between the thickness of PPPX films and polymerization time. The thickness changed almost linearly with time, and increased with increasing discharge current. The increase of the thickness of PPPX films is considered to be due to the increases of the decomposition rates of the p-xylene molecules.

#### B. FTIR and PL spectra and relative dielectric constant

Figure 3 shows FTIR spectra of p-xylene monomer and PPPX films. The characteristic absorption peaks of sp³ C-H stretching (CH₂ stretching: 2850, 2930 cm⁻¹) and sp² C-H stretching (aromatic stretching: 3020, 3050 cm⁻¹) are observed for monomer [7]. Large band in the region 2800-3000 cm⁻¹ and very small band in the region 3000-3010 cm⁻¹ appeared in PPPX film prepared at 8 mA. However, very small band in the region 2800-3000 cm⁻¹ appeared in PPPX film prepared at 23 mA and band in the region 3000-3010 cm⁻¹ disappeared. It has been reported that the benzene ring was destroyed by glow discharge polymerization and functional groups, such as -CH₂-CH₂-CH₂- and -C=C=C-appeared [8]. The increase of discharge current is accompanied by disappearance of the absorption peaks, suggesting that the PPPX film shows highly cross-linked structure.

Figure 4 shows the changes in PL spectra of PPPX films with discharge current. The peak at 470 nm decreased with increasing discharge current, which might be due to the disappearance of benzene rings as suggested by the FTIR spectra.

Figure 5 shows the change in relative dielectric constant of PPPX films with discharge current. εᵣ of PPPX films...
increased to 2.2 from 1.9 with increasing discharge current, since the density of PPPX film increased with increasing cross-linked structure. $\epsilon_r$ of PPPX films is smaller than that of conventional poly($p$-xylene) films 2.6 [9].

C. Characteristics of OLEDs

Figure 6 shows the relationship between luminance of the uncoated OLED and current density. The luminance decreased with elapsed time. The luminance and current density of OLEDs at constant voltage were measured and decreased with elapsed time. Therefore, the reduction of luminance could be considered to be due to the reduction of current density of OLED, which was affected by oxygen and moisture in air. Figure 7 shows the relationship between luminance of the uncoated and coated OLEDs with PPPX or PPHMDS film and current density after 20 h. The luminance of coated OLED with PPPX or PPHMDS film was higher than that of uncoated OLED.

IV. CONCLUSION

PPPX and PPHMDS films were prepared in a triode glow discharge. Formation characteristic, FTIR and PL spectra, $\epsilon_r$, and application to the encapsulation of OLEDs were investigated.

The thickness and $\epsilon_r$ of PPPX films increased and the FTIR and PL spectra of PPPX films decreased with increasing discharge current. The luminance of encapsulated OLEDs with PPPX and PPHMDS films was higher than non-encapsulated OLED after the preparation of PPPX and PPHMDS films.

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