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# Solution processed organic light-emitting diodes using the plasma cross-linking technology

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ABSTRACT

Solution processed multilayer organic light-emitting diodes (OLEDs) present challenges, especially regarding dissolution of the first layer during deposition of a second layer. In this work, we first demonstrated a plasma cross-linking technology to produce a solution processed OLED. The surfaces of organic films can be cross-linked after mixed acetylene and Ar plasma treatment for several tens of seconds and resist corrosion of organic solvent. The film thickness and surface morphology of emissive layers (EMLs) with plasma treatment and subsequently spin-rinsed with chlorobenzene are nearly unchanged. The solution processed triple-layer OLED is successfully fabricated and the current efficiency increases 50% than that of the double-layer OLED. Fluorescent characteristics of EMLs are also observed to investigate factors influencing the efficiency of the triple-layer OLED. Plasma cross-linking technology may open up a new pathway towards fabrication of all-solution processed multilayer OLEDs and other soft electronic devices.

## 1. Introduction

Organic light-emitting diodes (OLEDs) have attracted much attention in both scientific and industrial communities as potential candidates for flat-panel displays and solid state lighting [1–4]. OLEDs can be fabricated using a vacuum deposition method or a solution processed method [5–7]. Although vacuum thermal evaporation has been generally used as a fabrication process, the method has several problems such as poor scalability, high cost and complicated color patterning process. For large flat-panel displays and inexpensive lighting applications, solution coating process such as spin-coating, ink-jet printing, or nozzle printing is a preferred choice due to its low fabrication cost and easy scalability [8–11].

The solution printing process is comparable to the vacuum deposition process in terms of film density, film uniformity, and surface roughness if the process condition and ink formulation are properly controlled. However, it is more challenging to obtain multilayer OLEDs in the case of solution processing than in the case of vacuum evaporation. Sequential deposition of multiple layers can potentially lead to partial dissolution of the first layer in the solution processed OLED. Several approaches for realizing solution processed multilayer OLEDs include mainly the cross-linking method [12,13] and the orthogonal solvent method [14–16]. The former approach is to convert a soluble precursor into an insoluble polymer film by thermo- or photo-crosslinking. The latter approach is to find suitable solutions for each function layer so that the successive solution will not redissolve already present layers. However, the two methods are both suitable for partial materials. So far, a universal method has not been reported.

Herein, we demonstrated a plasma approach to produce cross-linked surfaces in organic films for solution processed multilayer OLEDs. We compared differences between the films with and without plasma treatment and checked the solvent resistance. The surfaces of organic films can be cross-linked after mixed gases plasma treatment for several tens of seconds, permitting the sequential solution spin-coating to form another film without intermixing of layers. Based on cross-linking reactions, the triple-layer OLED using the solution processed method was fabricated and the performance was tested.

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## 2. Materials and methods

### 2.1. Materials

Most of the materials used in our experiments are purchased from Luminescence Technology Corp., including 2,9-dimethyl-4,7-diphenylphenanthroline(BCP), fac-tris(2-phenylpyridine)iridium ($Ir(ppy)_3$), 4,4′,4′′-tri(*N*-carbazolyl)triphenylamine (TCTA), poly(*N*-vinylcarbazole) (PVK). 1,3-bis(2-(4-tert -butylphenyl)-1,3,4-oxadiazo-5-yl)benzene (OXD-7) is purchased from the Han Feng Chemical Corp.

### 2.2. Measurements

X-ray photoelectron spectroscopy (XPS) was employed to measure the core level spectra of C1s, N1s and the chemical composition at the surface of emissive layers (EMLs) in a RBD upgraded PHI5300 system with Al Kα X-ray anode source (h$\nu$ 1486.6 eV) at 14.0 kV and 250 W. The scanning step was set to 0.15 eV. The fluorescence of EMLs was explored with the fluorescence optics of an Axio ScopeA1 microscope (Zeiss, Oberkochen, Germany) under 470 nm light excitation. The images were captured using an AxioCam digital camera interfaced with a computer. Surface elements of organic films are analyzed by an Energy Dispersive Spectrometer (EDS) combined with scanning electron microscope (SEM, Phenom Prox, Holland). An atomic force microscopy (AFM, BRUKER Dimension ICON) in tapping mode was used to investigate the surface morphology. The absorption spectra of EMLs were measured by UV–vis absorption spectrometer (Beijing Purkinje TU-1900/TU-1901). The thickness of films was confirmed using a Dektak 8 surface profilometer.

### 2.3. Plasma treatment and solvent-resistance testing

The blended EML materials PVK:OXD-7:$Ir(ppy)_3$ in the ratio 66:32:10 by weight were solved in chlorobenzene at a concentration of 10 mg $ml^{-1}$. The EML solution was spin-coated on ITO surface at 1500 rpm for 15 s and annealed at 100 °C for 60 min resulting in a film thickness of 55 nm. The films were then treated in inductively coupled plasma of mixed gases (Ar: acetylene, 7:1 by flux) with operating pressure of 4 Pa and an rf power of 50 W for 30 s. The base pressure is $10^{-3}$ Pa. To compare the surface variation of plasma-treated EMLs before and after spin-rinsed with several drops of chlorobenzene, the profilometer and UV–vis absorption spectrometer were to monitor the thickness variation and optical microscope was to observe the characteristics of fluorescence and AFM was to investigate the surface morphology. The measurements were conducted in ambient air.

### 2.4. OLED fabrication and characterization

OLEDs were fabricated on glass substrates coated with a 150 nm layer of indium tin oxide (ITO) with a sheet resistance of 15 Ω $sq^{-1}$. The substrates were ultrasonically cleaned using deionized water, acetone and alcohol sequentially and dried under a stream of nitrogen. Solution of poly(ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) (CLEVIOSTM P VP AI 4083) was spin-coated on the ITO substrates as a hole injection layer (HIL) and then it was transferred into glove box (Mikrouna Co.) in a Ar environment with low moisture and oxygen content (<10 ppm) and dried on a hot plate at 120 °C for 60 min. After that, the chlorobenzene solution consisting of PVK: OXD-7: $Ir(ppy)_3$ (66:32:10 by weight) was spin-coated on the HIL to form a 55 nm film. Then the substrates were annealed at 100 °C for 60 min and transferred into the plasma reaction chamber in protection of Ar. The substrates were treated with plasma for different time. After plasma treatment, 150 nm Al were deposited through a shadow mask (active area of 8 $mm^2$) by thermal evaporation at a base pressure $10^{-3}$ Pa. The double-layer OLEDs have structures of ITO/PEDOT:PSS (25 nm)/PVK: OXD-7: $Ir(ppy)_3$ (55 nm)/Al with plasma treatment for 0 s, 30 s, 60 s, 180 s, labeled as P-0, P-30, P-60, P-180, respetively. Similar to P-30 OLED, the triple-layer OLED was fabricated by spin-coating BCP solution in chlorobenzene to yield a 20-nm-thick film between the EML and Al cathode,with the structure of ITO/PEDOT:PSS (25 nm)/PVK:OXD-7:$Ir(ppy)_3$ (55 nm)/BCP (20 nm)/Al. The triple-layer OLED was labeled as P-30-BCP. The current density-voltage-luminance (J-V-L) curves were measured with a Keithley 2400 source meter and a silicon photodetector calibrated by luminance colorrimeter (CBM-8, Everfine Photo-E-Info Co.). The measurements were conducted in glove box.

## 3. Results and discussion

To find the suitable time of plasma treatment on the EMLs, we compared the current density-voltage, luminance-voltage characteristics of the double-layer OLEDs with the architecture: ITO/PEDOT:PSS (25 nm)/PVK: OXD-7: $Ir(ppy)_3$ (55 nm)/Al. As shown in Fig. 1a, with the decrease of plasma treatment time, the current density increases and the curve of P-30 is barely the same as that of P-0. In Fig. 1b, the turn-on voltage of the OLED with the treatment for 30s is also close to that without treatment. It suggests the plasma treatment for 30 s does not change the whole characteristics of EMLs or influence the performance of P-30. However, the treatment time more than 60s increases the turn-on voltage considerably. It is speculated the surface of EMLs after plasma treatment becomes more insulating, which raises the barrier between the Al cathode and the EML. It is reported some active chemical groups can be easily generated in the plasma of acetylene and Ar mixed gases and they are grafted to the surface of organic films resulting in polymerizing and cross-linking [17–19] because of the high chemical activity of triple bond of acetylene molecules. Kang et al. used a ethynyl group as the thermal cross-linker and synthesized a new cross-linkable hole transporting polymer [20]. The cross-linked film such as undoped polyacetylene and polyethylene mainly made up of C and H elements is commonly insulating. Aizawa et al. synthesized ultrathin polymer insulating layers by initiated chemical vapor deposition with a large energy gap (>8 eV) chiefly owing to its high cross-linking density [21]. The plasma treatment on EMLs produces cross-linking structures in the film surface. The insulating feature of cross-linked films increases the barrier between layers and decreases the current density of devices, which can explain the phenomena of the double-layer OLED characteristics.

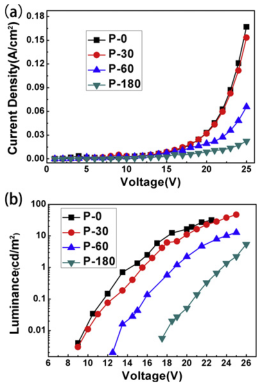

**Fig. 1.** (a) J–V and (b) L-V characteristics of OLEDs with the following device structures: ITO/PEDOT:PSS (25 nm)/PVK:OXD-7:Ir(ppy)3 (55 nm) (plasma treatment)/Al. The plasma treatment time is 0 s, 30 s, 60 s, and 180 s for P-0, P-30, P-60, and P-180, respectively.