Comparison of Spin and Blade Coating Methods in Solution-process for Organic Light-emitting Devices

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We compared solution-based spin and blade coating methods in fabrication of organic light-emitting devices (OLEDs). The effect of F8BT film morphology, prepared by two different methods, on device performances was studied in detail. The film morphology and molecular packing arrangement of the F8BT films were investigated by atomic force microscopy (AFM), X-ray reflectivity (XRR), and X-ray diffraction (XRD). We found that the device performances are dependent on evaporation condition of solvent during the formation of the organic layer.

Keyword: organic light-emitting device, solution process, blade coating

1. Introduction

Solution-processed organic light-emitting device (OLED) technology is promising for next-generation flat and flexible panel displays and lighting applications [1-3]. The solution-processes such as spin, blade, slot-die, gravure coating, and inkjet printing have attracted attentions as low-cost, and highly productive methods [4-6]. Spin coating has an advantage as simple and fast fabrication process to form thin organic layers. However, spin coating shows high stress caused by spinning motion and non-uniformity of large areas [7].

In this study, we formed organic layers for OLEDs by using blade coating method, which has an advantage to large area process and productivity [8]. Spin and blade coating methods show a large difference in solvent evaporation process. Spin coating shows rapid evaporation of the solvent due to centrifugal forces, whereas blade coating shows slow evaporation in natural drying condition. We found that the device performances are dependent on the evaporation condition of the solvent during the formation of the organic layer. We fabricated solution-processed OLEDs with an emitting layer of poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) by spin and blade coating methods. The film morphology and molecular packing of the F8BT were investigated by atomic force microscopy (AFM), X-ray reflectivity (XRR) and X-ray diffraction (XRD) measurements.

2. Experimental

2.1. General methods

Thermal gravimetric analysis was performed on a SEIKO EXSTAR 6000 TG/DTA 62000. Differential Scanning Calorimetry (DSC) was performed on a Perkin-Elmer Diamond DSC Pyris instrument at a heating rate of 10 °C/min under a nitrogen atmosphere. UV-visible absorption spectra of the films on quartz were recorded with a Shimadzu UV-3150 spectrometer. Photoluminescence (PL) spectra were recorded using a Jobin Yvon Fluoromax-4 fluorometer. Photoluminescence quantum efficiencies (PLQE) were measured on a Hamamatsu C9920-01 integral sphere system under a nitrogen atmosphere.
2.2. Device fabrication and characterization

Devices were fabricated on glass substrates pre-coated with indium-tin-oxide (ITO) with a sheet resistance of 15 $\Omega$ per square. The OLEDs with a configuration of ITO (130 nm)/poly(3,4-ethylene-dioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) (CLEV1OS CH8000) (30 nm)/poly(9,9-dioctyl-fluorene-alt-N-(4-butylphenyl)-diphenylamine) (TFB) (20 nm)/poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) (70 nm)/lithium quinolinolate (Liq) (1 nm)/Al (100 nm) were fabricated. The substrates were successively cleaned in ultrasonic baths containing ultra-purified water, acetone and 2-propanol for 10 min each. The substrates were dried for 20 min by exposure to a UV-ozone atmosphere. A 0.45 µm filtered dispersion of PEDOT:PSS (from Starck) was spin coated on ITO substrates and then the film was annealed at 200 °C in air for 10 min. TFB (from American Dye Source) layer was spin coated from a $p$-xylene solution and annealed at 200 °C in nitrogen environment for 60 min. The emissive layer of the F8BT (from Sumitomo Chemical) layers were spin and blade coated using a $p$-xylene solution in air and annealed at 130 °C in nitrogen environment for 10 min. Liq and Al were deposited by thermal evaporation under $2 \times 10^{-5}$ Pa. The active area was 2 × 2 mm². The film thicknesses were measured using Dektak 8 surface profilometer. The EL spectra were taken by a Hamamatsu photonics PMA-11 multichannel analyzer. The current-voltage (I-V) characteristics and luminance were measured using a Keithley 2400 Source Meter and Konika Minolta CS-200, respectively. The morphology of the films were observed using a Bruker Dimension Icon atomic force microscopy (AFM) in tapping mode with a tip resonance frequency of 330 kHz. X-ray reflectivity (XRR) and X-ray diffraction (XRD) were measured by a Rigaku SmartLab diffractometer equipped with a rotating anode (Cu Kα radiation, $\lambda = 1.5418 \text{Å}$).

3. Results and Discussion

We fabricated and compared the two devices with different emitting layer (EML) prepared by spin or blade coating methods. The spin coating condition was 2500 rpm for 30 sec. The device structures of the OLEDs are following: ITO (130 nm)/PEDOT:PSS (30 nm)/TFB (20 nm)/F8BT (70 nm)/Liq (1 nm)/Al (100 nm). PEDOT:PSS and TFB layers were formed by spin coating method, and Liq and Al were evaporated. At 1000 cd/m², the device from blade coating method showed driving voltage of 4.5 V, external quantum efficiency (EQE) of 5.0% and current efficiency of 18.1 cd/A, while the device from spin coating method showed 5.1 V, 4.5% and 16.0 cd/A, respectively (Fig. 1). The driving voltage and EQE of the device with blade coating method were improved compared with those of the device with spin coating method.

We investigated the film morphology of the F8BT films obtained from different coating methods. UV-vis absorption spectra, photoluminescence (PL) spectra, and AFM images of the F8BT films were measured (Fig. 2 and Fig. 3). The two films showed almost...
similar optical characteristic and no difference in surface roughness. PL quantum yields of the films were also almost same, 66% in case of spin coated film and 68% in case of blade coated film. These results indicate that the difference of the coating method does not give the difference to make dense molecular packing affecting the PL quenching and spectra. On the other hand, XRR and XRD measurements showed slightly different molecular packing arrangement of the F8BT films. Figure 4 showed XRR profiles of F8BT film with 70 nm thickness prepared by spin and blade coating methods. The fringe amplitude of the blade coated F8BT was very smaller than that of the spin coated F8BT. Factors affecting the fringe amplitude are surface roughnesses of substrate and F8BT film and molecular packing arrangement of F8BT film. Using of same substrates and similar roughnesses of the F8BT films confirmed by AFM measurement suggest that the difference of roughness does not relate with the difference of fringe amplitudes. If the XRR profiles can be fitted with one-organic layer model, the fringe amplitude determines the density of F8BT film. In this case, the densities of spin and blade coated F8BT films were fitted to be about 1.0 g/cm³ and 0.6 g/cm³, respectively. The value of 1.0 g/cm³ is reasonable for common organic polymer, while the value of 0.6 g/cm³ is abnormally low and this number does not represent actual density. This result suggests that the spin coated F8BT film can be fitted with one-organic layer model, but the blade coated F8BT film cannot be fitted with one-organic layer model. Unfortunately, we could not fit the XRR profile of the blade coated F8BT film using any models. It is assumed that X-ray was scattered by microcrystals or a peculiar structure in the blade coated F8BT film. This scattering effectively decreases coherency of X-ray, which results in decrease of the fringe amplitude. These results suggest that the blade coated F8BT has different molecular packing arrangement from the spin coated F8BT.

Then, we investigated XRD profiles for spin and blade coated film of F8BT. Unfortunately, any peaks of the XRD profiles were not obtained in the F8BT films prepared with the same condition (130 °C annealing for 10 min) of the device fabrication, due to the weak scattering intensities. To enhance the scattering intensities, the F8BT films were annealed at 250 °C higher than crystallization temperature (ca. 210 °C from DSC measurement), for 5 min in air. Figure 5 shows out-of plane and in-plane XRD profiles for those spin and blade coated F8BT films. The XRD profile of the blade coated F8BT film
was different from that of the spin coated F8BT film. These results show that the annealing process at high temperature cannot eliminate the morphology hysteresis, and indicate that the molecular packing arrangement of blade coated F8BT is different from that of spin coated F8BT. Structure of the partially crystallized polymer after annealing is considered largely influenced on the initial structure before annealing.

In the out-of plane measurement, the both spin and blade coated F8BT showed weaker peaks at $2\theta = 11.5^\circ$ ($d = 7.7 \text{ Å}$), $2\theta = 8.2^\circ$ ($d = 10.7 \text{ Å}$) and $2\theta = 5.6^\circ$ ($d = 15.6 \text{ Å}$). The three equally space distance diffraction peaks are reported that the peaks arise from different reflections of a π-stacked lamellar phase [9-11]. The blade coated film has much more microcrystalline part of π-π stacked structure than spin coated films. In the in-plane measurement, the blade coated F8BT showed broad peaks around $2\theta = 15.1^\circ$ ($d = 5.9 \text{ Å}$) and $19.6^\circ$ ($d = 4.5 \text{ Å}$), while the spin coated F8BT showed no peaks. These peaks are considered to be attributed to interchain spacing of the alkyl chains [12]. Only the blade coated F8BT showed the peaks derived from the ordered state both in the in-plane and out-of plane measurement, supporting the more scattering microcrystalline structure in the blade coated film.

We assumed that the blade coated F8BT have nucleation even before annealing, and it increased by annealing at 250 ºC. Thus, the XRR profile of blade coated F8BT showed decrease of the fringe amplitude due to propagated nucleation. The generated microcrystal structure from slow solvent evaporation condition shoul d result in the low driving voltage (Fig. 1).

We fabricated to reproduce the molecular packing arrangement of the blade coated F8BT by using spin coating method. Differences of film formation mechanism between spin and blade coating are existence of centrifugal force and solvent evaporation speed. In order to approximate evaporation speed in spin coating method to that in blade coating method, we varied the spin coating condition from 2500 rpm for 30 sec to 950 rpm for 1 sec, 10 sec and 30 sec. In short spin-rotation time for 1 sec and 10 sec, solvent was not dried completely during spin-rotation, and then was naturally dried. The spin-coated F8BT films were also annealed at 130 ºC in nitrogen environment for 10 min. The surface roughnesses of the F8BT films were investigated by AFM (Fig. 3). Spin coating condition did not influence on the surface roughness. Then, we measured XRR profiles of these F8BT films (Fig. 4). Nevertheless, solvent was almost naturally dried in the spin
condition of 950 rpm for 1 sec, the XRR profile showed large fringe amplitude. These results show that reproduction of the molecular packing arrangement of blade coated F8BT by spin coating method is difficult. The spin rotation in only 1 second made the molecular packing arrangement of F8BT film largely different from that of the blade coated film. Shorter spin-rotation time gave slight decrease of fringe amplitude in the wide-angle region. This result suggests that the slower solvent evaporation in the spin coating generated more nucleation.

On the contrary to the result that the OLED with the blade coated F8BT showed lower driving voltage than that of the OLEDs with the spin coated F8BT, the device from slower spin coating showed higher driving voltage. This result suggests that drying and nucleation time scales are totally different between the two coating methods. Understanding the effect of the spin coating condition on the film morphology and the device performance requires further investigation.

4. Conclusion
We compared the solution-processed OLEDs fabricated by spin and blade coating method. The two F8BT films prepared by the two method exhibited similar photophysical properties (UV-vis, PL, PLEQ) and film roughness (AFM images). However, their molecular packing arrangements were different each other, investigated by XRR and XRD. The device with blade coated F8BT exhibited a lower driving voltage and a higher efficiency than that of the device with spin coated F8BT, because the slow solvent evaporation in near-natural dry condition made more ordered $\pi-\pi$ stacked microcrystalline state. We tried to reproduce the molecular packing arrangement of the blade coated F8BT by using spin coating method. Slowest spin coating condition did not reproduce the morphology of the blade coated F8BT film.

References