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Fluorene bilayer for polymer organic light-emitting diode using efficient ionization method for atomized droplet

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ABSTRACT

We present a solution-processed planar fluorene bilayer by an ultrasonic atomized deposition method in combination with a needle electrode as an ionization part for an atomized droplet. An important advantage of our method is that the atomized droplet is efficiently charged using a needle electrode, which speeds up the deposition rate of the polymer thin film. The deposition rate increases 2 to 3 times compared to a that obtained with a conventional technique without using the ionization method, and real-time monitoring of landed droplets indicates that the number of droplets increased as the voltage applied to the needle electrode was increased, owing to the highly charged atomized droplets. Furthermore, the TFB/F8BT bilayer was achieved by optimizing the substrate temperature, and the polymer organic light-emitting diode exhibits a luminance value exceeding 12,000 cd/m^2 by insertion of the TFB as an electron blocking layer. The maximum current efficiency of the fluorene bilayer device was 6.64 cd/A, which was a 3.2-fold increase compared to that obtained with the reference device without the TFB electron blocking layer.

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1. Introduction

Polymer organic light-emitting diodes (P-OLEDs) have attracted interest for application in flat panel displays and general lighting owing to their high brightness, usage of large/flexible plastic substrate, very low fabrication cost because a roll-to-toll printing process is used, and tunable emission wavelength. The molecular structure and polymerization degree of polymer materials are important for improving the luminescence characteristics and long-term stability of P-OLEDs; therefore, novel polymers have been produced in previous studies [1–3]. In addition, a device structure is also investigated for achieving high device performance. For example, previous studies demonstrated superior high device performance using multilayer structures, inverted structures [4], and inserted electron/hole blocking layers to restrict the carrier recombination zone to the thin emissive layer [5]. However, the most serious problem of P-OLEDs is that it is difficult to fabricate the multilayer structure with a conventional solution process such as spray coating. This is because the underlying polymer layer is easily dissolved by the solvent during the coating of the upper polymer layer. Therefore, several chemical modification methods for the underlying layer and novel solution processes

have been investigated for fabrication of the multilayer structure [6–9].

Currently, a poly(9,9-dioctylfluorene-*alt*-N-(4-butylphenyl)-diphenylamine)/poly-(9,9-dioctylfluorene-*alt*-benzothiadiazole) (TFB/F8BT) bilayer is being investigated for improvement of the optical characteristics of P-OLED [10–13]. This is because the optimized fluorene polymer shows a high photoluminescence quantum yield of >80% and high hole mobility [14,15]. These papers describe the reason for the improved performance of the bilayer device, namely: (i) reduced exciton quenching by shifting the carrier recombination zone away from the interface; (ii) reduced leakage of electrons from the F8BT emissive layer to the hole transport layer, resulting in efficient carrier confinement in the F8BT emissive layer. The energetic offset of the lowest occupied molecular orbital (LUMO) levels at the TFB/F8BT interface is 1.1 eV [16], and this prevents electron leakage from the F8BT emissive layer to the hole transport layer [17]. As a result, the carrier recombination probability in the emissive layer increases, and this phenomenon is suitable for both high luminance efficiency and superior long-term stability even for P-OLEDs. In general, the TFB and F8BT bilayer are sometimes mixed at a heterojunction, and a mixed layer is formed. In the TFB:F8BT mixed layer, the primary exciton contribution is found to be <2%, which implies that >98% of the excitons undergo charge transfer at the TFB/F8BT interface. Therefore, the relative PL quenching with respect to pure F8BT is only <57% (PL yield of F8BT

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80%, of TFB:F8BT 35%) [18]. For these reasons, the precious coating process for the TFB:F8BT bilayer has been attracting interest for P-OLED applications.

One approach is a transfer technique for fabricating the fluorene bilayer structure [19]. In this technique, the TFB layer is first prepared on the O_2-plasma-treated glass substrate with a poly(styrenesulfonate) (PSS) layer to aid float-off in water. The F8BT-coated substrate is then laminated on the dry side of the aforementioned TFB-coated glass substrate. As a result, the TFB/F8BT bilayer can be formed without dissolving the underlying layer. However, the surface of the F8BT layer is relatively rough after removal of the PSS layer compared to those fabricated by other solution processes, and this will reduce the device performance. In another important technique, the non-orthogonal solvent used against the underlying layer (i.e., TFB) is used as the solvent for the upper layer (i.e., F8BT). In this case, the choices of polymer and solvent are limited, and the TFB/F8BT bilayer cannot be formed by solvent selection alone without modification of the chemical structure of F8BT. The solvent processing route makes scale-up feasible; however, concerns remain over the reproducibility of the entire process used in this method. Currently, a solution process called the electrospray deposition method has been investigated for fabricating the polymer multilayer structure. In this method, the highly charged droplets are continuously divided by Coulomb repulsion, and the small droplet size of <1 μm speeds up solvent evaporation [20]. Therefore, the multilayer structure can be realized [7–9]; however, the deposition rate is low approximately several nm/min, which results in low throughput of the mass production system. These disadvantages of previous studies prevented the practical use of solution-processed polymer-based electronic devices. Therefore, a simple fabrication process for the polymer multilayer has been an attractive research field.

Currently, we are investigating an ultrasonic atomized deposition method for fabricating a planar TFB/F8BT bilayer. Ultrasonic atomization methods have been investigated as a deposition method [21,22]; however, the deposition efficiency is low, resulting in a low deposition rate of several nm/min and low material utilization. Our methodology has advantages for several reasons such as the usage of an arbitrary solvent for the polymer, a simple experimental setup without the necessity of a vacuum chamber, and especially efficient ionization of droplets, which results in an improved deposition rate and lower surface roughness by solvent evaporation optimization [23].

In this study, we investigated an efficient ionization method for flying droplets in the ultrasonic atomized deposition method using the needle electrode. In this method, the corona discharge causes ionization of flying droplets, resulting in a high deposition efficiency corresponding to the high deposition rate. In addition, we demonstrate the TFB/F8BT bilayer structure and improved current efficiency of the multilayer P-OLED with TFB/F8BT.

2. Experimental

Fig. 1 shows a schematic illustration of the ultrasonic atomized deposition method, which employs a needle electrode for ionization of atomized droplets. First, a polymer solution is continuously atomized by applying an ultrasonic wave to a polymer solution. The frequency of the ultrasonic wave was 3 MHz, and nitrogen gas (0.5 L/min) was used as the carrier, which assists atomized droplet flow from the ultrasonic generator to the substrate. The most important part of this deposition method is the needle electrode, which was placed above the substrate. The diameter of the needle electrode was 20 mm, which was larger than that of the glass tube. Therefore, the atomized droplets were not attached to the needle electrode. A high negative voltage of several kilovolts was applied to the needle electrode to ionize the flying droplets from the
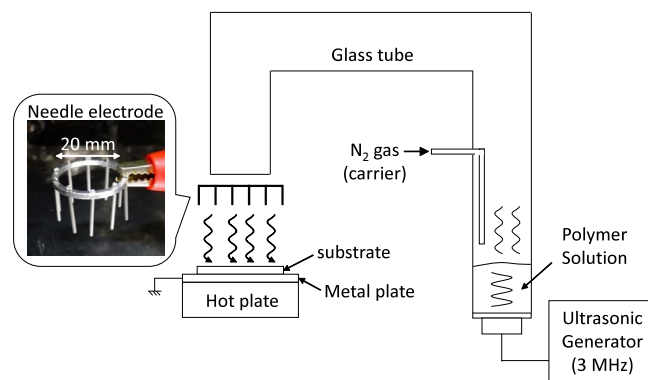

Fig. 1. Experimental setup of ultrasonic atomized deposition method in combination with needle electrode. Inset shows photograph of needle electrode having 20 mm diameter.

ultrasonic generator. As a result, the ionized droplets reach the substrate, resulting in the formation of a polymer thin film. In addition, the substrate temperature was controlled at 50 °C using a hot plate to optimize the speed of evaporation of the solvent [23]. The applied voltage was controlled from −1 to −6 kV at a fixed distance of 3.0 cm between the substrate and the needle electrode.

We investigated a fluorene bilayer, which contains TFB (ADS25913E, Mw = 10,000–200,000) and F8BT (ADS133YE, Mw = 15,000–200,000) purchased from American Dye Source without further purification. Concentrations of TFB and F8BT were 1 and 0.1 wt.% in o-dichlorobenzene (o-DCB), respectively. Because the TFB layer was formed by a spin-coating process, the concentration of the TFB solution is higher than that of the F8BT solution that was used in the ultrasonic atomized deposition method. First, the F8BT neat film was deposited on an indium tin oxide (ITO)-coated glass substrate (R_s = 15 Ω/sq) for 10 min. Then, the deposition rate and the surface roughness of the F8BT thin film were estimated by measuring the thickness and by using an atomic force microscope (AFM) image. In addition, a magnified image of a droplet that landed on a glass substrate was observed using an objective lens and a charge-coupled device camera (AUSB-K, Arms System). Next, the relative deposited area as a function of time was estimated using an image processing software (ImageJ), and the relative deposition area was calculated as the deposited area of the total droplet area divided by the observation area of the microscope image.

The device structure was ITO/PEDOT:PSS (40 nm)/TFB (25 nm)/F8BT (70 nm)/LiF (0.5 nm)/Al (100 nm) for the multilayer structure (device A), and the ITO/PEDOT:PSS (40 nm)/F8BT (70 nm)/LiF (0.5 nm)/Al (100 nm) was used as a reference device (device B) without the electron blocking layer (EBL). The fabrication process for the multilayer OLED was as follows. First, an ITO-patterned glass substrate was cleaned for 20 min with ultrasonic cleaning using acetone, deionized water, and isopropyl alcohol. Next, the substrate was treated in the ultraviolet-ozone for 20 min. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS; AI-4083, Clevious) was then spin-coated at a rotation speed of 2000 rpm for 1 min on the ITO-patterned glass substrate as a hole transport layer. After annealing at 140 °C for 10 min in the atmosphere, TFB was also spin-coated in a nitrogen-purged grove box as an EBL. The rotation speed of the spin-coating process was 3000 rpm for 1 min. The thicknesses of the PEDOT:PSS and TFB layers were 40 and 25 nm, respectively. The sample was then annealed at 130 °C for 20 min, and the F8BT thin film was deposited as an emissive layer with the ultrasonic atomized deposition method. A high voltage of −6 kV was applied to the needle electrode for depositing the F8BT layer, and this deposition condition