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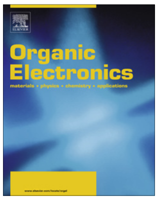

Fabrication of high-efficiency multilayered organic light-emitting diodes by a film transfer method

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ABSTRACT

In this paper, we report the fabrication of small-molecule-based thin-film layers with a thickness of several tens of nanometers on a release layer by bar coating and subsequent stacking onto other organic layers by the developed film transfer method using driving belts and rollers as a prototype roll-to-roll technique. We use novel thermally activated delayed fluorescence (TADF) materials in this process, achieving multilayered organic light-emitting diodes (OLEDs) with high external quantum efficiency (EQE), which is comparable to those of OLEDs prepared by conventional vacuum deposition. The developed film transfer method shows great potential to realize OLEDs with high efficiency at low cost.

1. Introduction

Even though organic light-emitting diode (OLED) technology has been steadily developed and commercialized because of its important advantages of high visibility and low power consumption, a novel approach from the aspects of both materials and device fabrication processes is necessary for OLEDs to further their use in display and solid-state lighting applications. From the viewpoint of materials, we have recently developed a new category of high-performance compounds that emit based on thermally activated delayed fluorescence (TADF) [1–4]. TADF technology shows considerable potential to be central in reducing material cost and achieving full color emissions including pure blue emission. Concerning OLED fabrication, solution-based processes are a focus because of their possibility to reduce fabrication cost and allow large-area production compared with dry processes such as vacuum deposition [5,6]. Currently, numerous researchers are devoted to producing OLEDs containing small molecules by solution-based processes to take full advantage of the merits of both, i.e., functionalized small-molecule materials with high electroluminescence (EL) efficiency and capability to prepare large-area devices at low cost [7].

Solution-based processes such as spin-coating [7], ink-jet methods [8–12] and blade coating [13] have been used to fabricate multilayered OLEDs. In both cases, to prevent underlying organic layers from being dissolved by organic solvents during the formation of upper layers, use of cross-linking curing agents or orthogonal solvents is required [14–18]. However, introduction of cross-linking moieties onto OLED materials unfavorably influences device characteristics and orthogonal solvents limit the materials that can be used in multilayered OLEDs [19,20]. In addition, materials need to be tailored to the requirements of a

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particular solution-based process. To overcome these limitations, the fabrication of multilayered OLEDs by an electrospray method [21] and transfer method using a mold [22] has been attempted. Although these techniques produce multilayered OLEDs without damaging underlying layers, device performance equivalent to that of dry-process devices has not been accomplished. Moreover, these methods are not suitable for mass production of OLEDs from the viewpoint of tact time during fabrication, because layer stacking requires a certain amount of time.

In this study, we develop a film transfer method using driving belts and rollers as a prototype roll-to-roll technique to fabricate OLEDs. In this transfer technique, because organic layers are not directly fabricated on underlying organic layers, there is no dissolution or mixing of existing layers. Moreover, film transfer is conducted during belt rotation, which reduces the operating time to fabricate OLEDs. We report here the fabrication of small-molecule-based thin-film layers with a thickness of several tens of nanometers on a release layer by bar coating and subsequent stacking onto other organic layers by the developed film transfer method. We used novel TADF materials in this process, achieving multilayered OLEDs with a high EQE of more than 19%.

2. Experimental

2.1. Materials

N,N′-bis(4-diphenylamino-4′-biphenyl)-N,N′-diphenyl(1,1′-biphenyl)-4,4′-diamine (TPT1) provided by Hodogaya Chemical Co., Ltd., was used as a hole transport material. bis-4-(N-carbazolyl)phenyl)phenylphosphine oxide (BCPO) was synthesized as a host material for the light-emitting layer (EML) [23]. Green dopant (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) was also synthesized [4]. 1,3,5-tris(1-phenyl-1H-benzo[d]imidazole-2-yl)benzene (TPBi) was used as an electron transport material. The glass transition temperature (T_g) of TPT1, BCPO and TPBi were 144, 137 and 124 °C, respectively. Fig. 1 shows the chemical structures of materials used in this experiment.

2.2. Fabrication and evaluation of organic layers on a release layer

A Kapton film (Kapton 200EN, DuPont-Toray Co., Ltd.) coated with a release layer composed of polysiloxane derivatives (Frescera, Panasonic Co.) by bar coating method was used as a donor film. The thicknesses of the Kapton film and the release layer were 50 μm and approximately 2 μm, respectively. Organic materials were dissolved in a mixture of tetrahydrofuran (THF), dichloromethane and acetone. Using organic solutions with a concentration of 5 mg/ml, approximately 50-nm-thick organic layers were formed on the release layer by a bar-coating method. For the EML, an approximately 30-nm-thick organic layer was formed on the release layer using an organic solution with a concentration of 3 mg/ml. The critical surface tension of each layer was derived from contact angles measured by a contact angle meter (Kyowa Interface Science Co., Ltd., Drop Master DM-CE1). Photoluminescence (PL) images of each organic layer were obtained under irradiation with a UV lamp (excitation wavelength of 254 nm). The surface condition and morphologies of organic layers were observed by a laser microscope (Olympus Co., LEXT OLS4000 3D Measuring Laser Microscope) and atomic force microscope (AFM) (JEOL, JSPM-5400) in tapping mode.

2.3. Film transfer and device fabrication processes

Fig. 2 shows a schematic diagram of the film transfer apparatus. The film transfer process is as follows. Both a donor film attached to the donor belt and an acceptor film attached to the acceptor belt were synchronously carried at a speed ranging from 1 to 100 mm/s. Both the upper and lower rollers can be fixed at desired temperatures in the range from room temperature to 160 °C. Film transfer was conducted under an inert atmosphere inside a glove box. OLEDs with transferred layers were fabricated as follows. After the sequential transfer of a 50-nm-thick TPT1 film as a hole transport layer (HTL) and 30-nm-thick BCPO film doped with 12 wt% 4CzIPN (BCPO:4CzIPN) as an EML on top of an indium-tin-oxide (ITO) substrate by the film transfer method, we deposited an additional 10-nm-thick EML, 50-nm-thick TPBi layer as an electron transport layer (ETL) and 0.8-nm-thick lithium fluoride (LiF) as an electron injection layer (EIL), and 100-nm-thick aluminum (Al) cathode under a vacuum of less than 4×10^{-4} Pa. Control devices with the equivalent layers formed by vacuum deposition were also fabricated. We measured the light-emission characteristics, i.e., current density–applied voltage–luminance (J–V–L) characteristics, of the devices using a semiconductor parameter analyzer (Agilent E5273A) and optical power meter (Newport 1930C), and measured EL spectra using a multichannel spectrometer (Ocean Optics UBS2000) at atmospheric pressure.

3. Results and discussion

We tried to dissolve small-molecule materials mainly used for vacuum deposition in conventional organic solvents to fabricate thin layers on a release layer by a bar-coating method. Fig. 3 shows the surface morphologies of BCPO layers observed by a laser microscope. During formation of films of materials with low molecular weight, such as BCPO, on a release layer, we observed numerous tiny circular defects, which resulted in defect formation on the surface of the release layer (Fig. 3(a)). To make a defect-free layer, we used three steps to improve the film quality from the viewpoints of roughness of the release layer and coating condition by controlling the surface tension of organic solutions.

First, we investigated the critical surface tension of the release layer derived from a Zisman plot [24]. We found that the critical surface tension of the release layer was 22.8 ± 0.7 mN/m, which is rather low compared with those of other materials. This is why layers composed of polysiloxane derivatives can be used as release layers. The critical surface tension is an index for wettability, i.e., how readily a drop of the solution added onto a