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Slot-die coating of organic thin films for active-matrix organic light-emitting diode displays

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ABSTRACT

We investigate solution coating of organic thin films for the fabrication of active-matrix organic light-emitting diode (AMOLED) displays. For blanket layers, an aqueous polymer-based hole injection layer (HIL) and non-aqueous polymer-based hole transport layer (HTL) are fabricated by slot-die coating and also by spin coating for comparison. Thin organic films coated on a substrate with a pixel-defining layer (bank) exhibit the concave profile due to capillary rise. With an attempt to suppress it and thus obtain thin films with high conformity, we carry out solution coating by varying the pixel size, solvent, and drying condition. As the pixel size increases, the overall film thickness increases by an enhancement in the filling of a solution into the cells. We have found that spin coating provides more conformal thin films for the aqueous polymer HIL. When a high-boiling-point solvent and vacuum drying are used for the non-aqueous polymer HTL, however, the film conformity by slot-die coating is higher than that by spin coating. It is attributed that an evaporation-induced convective flow (microflow) occurs from the pixel edge to the center. It also enables the formation of homogeneous light distribution over the emission area of OLED pixels.

1. Introduction

High-performance and reliability active-matrix organic light-emitting diode (AMOLED) displays have been fabricated using thermal evaporation in a vacuum and a fine metal mask (FMM). As an alternative, solution printing and coating of organic thin films offer great potential for achieving low-cost manufacturing of large-area display panels. Printing technologies (e.g., inkjet, nozzle, gravure, and offset) are suitable for the fabrication of patterned emission layers [1]. Meanwhile, coating methods (e.g., slot, spin, spray, and blad) are preferred for the fabrication of blanket layers [2–8]. Of those, pre-metered slot-die coating provides large scale roll-to-roll production and coating of thin films with the thickness as low as 20 nm and a wide range of process materials [4–6]. Slot coating was also used to fabricate polymer solar cells [7], OLED devices under ambient air [8], and homogeneous small-molecule OLED layers [9]. For an electrowetting display panel, it also enabled the filling of oil into the cells in the presence of the ribs [10]. Recently, there have been some attempts to fabricate AMOLED display panels using slot-die coating and nozzle printing [11]. It was demonstrated that the intra-pixel thickness uniformity by slot coating was better than that by spin coating.

During slot coating, we encounter step height (about 1 μm) in a substrate for AMOLED, which is induced by bus lines, bank (pixel-defining layer), etc. Due to the different material type (e.g., indium-tin-oxide (ITO) for anode and photoresist (PR) for bank) and surface tension gradient, the thickness uniformity of films coated in the presence of the patterned PR bank is inevitably degraded [11]. Namely, the coated films have the concave profile due to capillary rise, which occurs because of surface tension and adhesive forces between a solvent and the bank layer. It results in the inhomogeneous light distribution over the emission area of each pixel. As such, organic thin films with high conformity are required for the application of commercial displays. The morphology of inkjet droplets was shown to be controlled by the aspect ratio of the sidewall height to width [12]. It was demonstrated by dispensing nanoliter droplets using pipettes that the higher hydrophobicity (higher contact angle) on the sidewall surface yielded a flatter profile of films [13]. In addition, the film conformity would vary depending sensitively on the pixel size, coating method, solvent, and drying condition. If slot coating is used to fabricate thin organic films on the substrate with small pixels, the time interval for the upstream meniscus to move from one bank to the next one becomes smaller, the pinning effect by which occurs and thus coating bead breaks up [10]. The use of a proper solvent is also one of important factors that determine the film conformity because capillary action and film drying are directly related with the solvent property (e.g., surface tension, and boiling point (BP)) [14]. The surface tension gradient by dual solvent system was shown to

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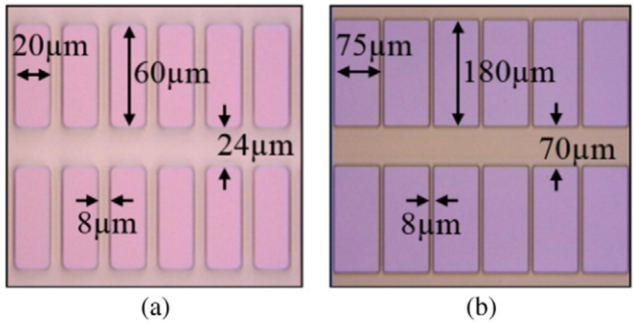

Fig. 1. Image of patterned PR bank structures with the size of (a) 20 μm × 60 μm and (b) 75 μm × 180 μm captured by optical microscope.

remove ring-like stains in an aqueous solution drop [15]. If the time scale for flow induced by surface tension gradients was well matched to the evaporation time scale, coating defects in corners were mitigated [16]. Furthermore, a drying method would be crucial because OLEDs require extremely thin organic layers. There are several drying methods such as drying by convection (hot air), vacuum drying, dielectric drying, natural air drying, etc. Drying by hot air may be unsuitable for such thin organic films. In this case, vacuum drying would be preferred, which is usually used to increase the drying rate. To our best knowledge, however, much information of capillary rise and film conformity in slot-die coating of organic thin films for AMOLED displays is not available in open literature.

In this paper, we have investigated the feasibility of slot-die coating of the blanket layers in the presence of the bank layer and the film conformity by varying the pixel size, solvent, coating scheme, and drying condition. To this end, we have employed glass substrates with different pixel configurations, solvents with different BP and surface tension, and three different drying conditions (i.e., under atmospheric pressure, medium vacuum, and high vacuum). To analyze the film quality, we have calculated the conformity and intra-pixel thickness uniformity from the measured concave profile of coated films. It is demonstrated that the film conformity can be raised by a factor of 2 and the emission uniformity of OLED pixels can be enhanced to a great extent using a high-boiling-point solvent in combination with vacuum drying.

2. Experiment

As a pixel-defining layer, we fabricated the bank layer using a photoresistor (PR, zpp 1700 pf-30, ZEON). It was patterned into two different pixel configurations of 20 μm × 60 μm and 75 μm × 180 μm. Fig. 1 exhibits the optical images of those pixel structures. The height of bank is about 1.5 μm. The resolution of the 20 μm × 60 μm pixel structure is about 300 pixel per inch (ppi) and the other one 100 ppi. The bank layer was formed on a 150-nm-thick ITO pre-coated on a glass substrate (370 mm × 470 mm, purchased from Geomatech Co., Ltd.). The total number of unit cells on the glass substrate is 48 and each cell is as large as 50 mm × 50 mm, the active area of which is 43 mm × 29 mm. ITO was treated with UV/O_3 for 90s at a power of 150 W. For a hole injection layer (HIL), aqueous poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS, Clevios AI 4083) was employed, which has the solid content of 1.3–1.7% and the work function of 5.2 eV. Before coating, we used a cellulose acetate disposable syringe filter (0.2 μm, DISMIC-25CS) to filter out aggregated particles existing in the PEDOT:PSS solution. For a hole transport layer (HTL), we used poly(*N*-vinylcarbazole) (PVK, purchased from Sigma Aldrich), which has also been used as a host for phosphorescent dyes [17–19]. As a solvent for the HTL, we used ethyl benzoate (purchased from Sigma-Aldrich) with the BP of 213 °C. To filter out aggregated particles existing in the HTL solution, we used PTFE syringe filter (0.5 μm, 25JP050AN).

Table 1
Fixed values of coating process variables.

Variables	Value	
	HIL	HTL
Die shim thickness	50 μm	
Coating gap	150 μm	
Coating speed	4 mm/s	3 mm/s
Flow rate	0.1 ml/min	
Plate temperature	22 °C	
Ambient temperature	24 °C	

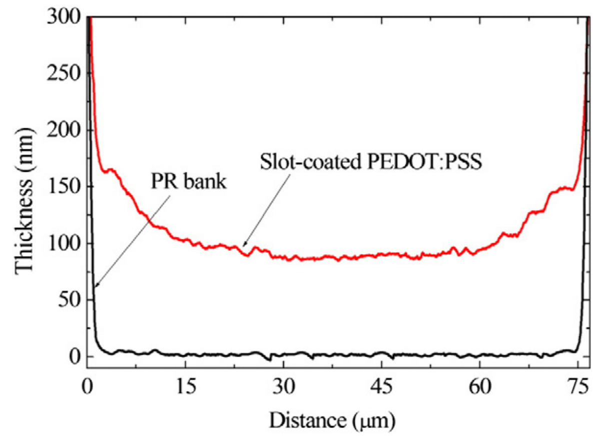

Fig. 2. Measured thickness profile of PEDOT:PSS film slot-coated on a substrate with the pixel size of 75 μm × 180 μm and dried under atmospheric pressure.

We have slot-coated the blanket layers using a table slot coater that consists of a moving plate (400 mm × 500 mm) with a plate heater (up to 150 °C), dry unit (NIR lamp up to 400 °C), syringe pump system (flow rate 0.1–10 ml/min), and slot head module (head size: 240 mm × 30 mm × 56.5 mm, surface flatness: ±3 μm, coating gap: 3–2000 μm with a resolution of 1 μm). The effective coating width is as wide as 150 mm. Since slot-die coating involves many process variables, we fixed their values, as presented in Table 1. In fact, they were fixed based on our previous work regarding slot coating for the fabrication of large-area OLED lighting panels [20]. For comparison, the HIL and HTL films were also fabricated by spin coating. The spin coating speed at the first stage was set to be 100 rpm for 10 s and 2500 rpm for HIL (2000 rpm for HTL) at the final stage for 40 s. The mass fraction of PVK was chosen to be 3.2 wt% for spin coating and 2.5 wt% for slot coating in order to obtain a target film thickness, which was also tuned with the fixed coating process variables. Slot coating was performed on 370 mm × 470 mm glass substrates, whereas spin coating was carried

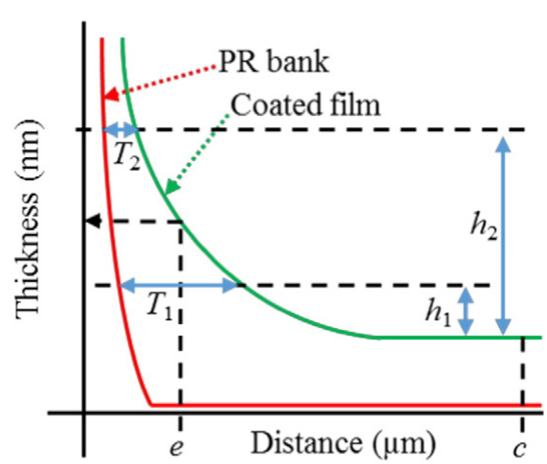

Fig. 3. Schematic view of thickness measurement and conformity calculation from the concave profile of coated thin films.