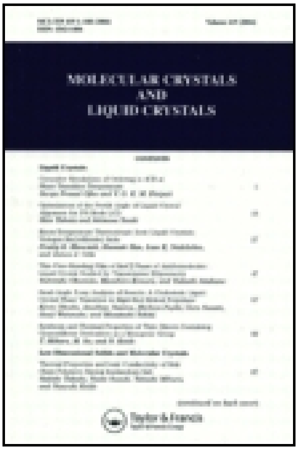

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

SEPARATE-COATING AND LAYER-BY-LAYER DEPOSITION OF POLYMER EMITTING MATERIALS BY THE SPRAY DEPOSITION

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To cite this article: Katsuhiko Fujita, Takamasa Ishikawa & Tetsuo Tsutsui (2003): SEPARATE-COATING AND LAYER-BY-LAYER DEPOSITION OF POLYMER EMITTING MATERIALS BY THE SPRAY DEPOSITION, Molecular Crystals and Liquid Crystals, 405:1, 83-88

To link to this article: http://dx.doi.org/10.1080/15421400390264180

Mol. Cryst. Liq. Cryst., Vol. 405, pp. 83–88, 2003
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390264180

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SEPARATE-COATING AND LAYER-BY-LAYER DEPOSITION OF POLYMER EMITTING MATERIALS BY THE SPRAY DEPOSITION

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The spray deposition method has been developed as a new way of polymer ultra-thin film preparation for organic optoelectronic devices such as an organic light emitting diode (OLED). In this method, a highly diluted solution of an organic material is nebulized into air and concentrated under a controlled evaporation condition. The resulting aerosol is transported by a carrier gas and deposited onto a solid substrate. This method has substantial advantages that an almost insoluble and non-evaporative material can be fabricated into a thin film, and that a separate-coating and layer-by-layer deposition of polymer materials can be performed. An OLED was prepared from highly diluted THF solutions (10^{-4} wt%) of two poly-phenylenevinylene derivatives. One shows red emission and the other green. The red polymer was deposited on an ITO electrode through a shadow mask with round holes and 0.1 mm line width to result a fine separate-coating and the green one was laminated onto the patterned film. An Al anode was deposited on the polymer film in a vacuum evaporator. The fabricated OLED showed a patterned emission at around 10 V.

Keywords: organic light-emitting diode; organic semiconductor; polymer thin film; spray deposition; π-conjugated polymer

INTRODUCTION

Organic semiconductors are nowadays applied to optoelectronic devices, such as electroluminescent (EL) dysplays [1,2], thin film transistors (TFT) [3] and photovoltaic cells [4]. The substantial advantages of organic semiconductors are flexibility and wide variation of the molecular structure. By utilizing the advantages, flexible displays are being developed and the optical or electronic properties of the organic semiconductors are tuned by

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*Corresponding author. E-mail: katsuf@asem.kyushu-u.ac.jp the molecular design based on quantum chemical predictions. Many synthetic chemists struggle to prepare the promising molecules. However, those prepared materials have to clear another high hurdle, processability into amorphous thin films. Especially π-conjugated polymers, which are expected to have broad applicability due to the durability, are made into thin films by wet processes such as spin-coating and ink-jet printing. Those methods require a certain extent of solubility in a volatile solvent for the materials; for example, a concentration of around 1 wt% is needed for the spin-coating method. If the concentration restriction is alleviated, many materials left without investigation of optoelectronic properties could be applied to actual devices and widen the range of organic semiconductors.

We have reported the new organic thin film preparation method, spray deposition [5]. This method can provide an amorphous thin film from highly diluted solution of π-conjugated polymers. Here we describe other features of this method, a separate-coating and a layer-by-layer deposition of polymer materials. Those features are fundamental to produce sophisticated devices from polymer materials, for example, a high resolution electroluminescence display, an element driving thin film transistor and an integrated circuit.

EXPERIMENTAL

Spray deposition apparatus is shown in Figure 1. The solution is nebulized into air and made into an aerosol with the particle size of around 10 µm. The aerosol is transported by nitrogen carrier gas from the first chamber to a nozzle facing a substrate in the second chamber. During the transportation, the solution particles shrink with the evaporation of the solvent. The evaporation rate can be varied by controlling the spraying rate of the solution and the temperature of the chamber walls and the substrate. The substrate is held on a ceramic heater with a thermocouple settled on a computer-controlled x-y positioner stage. The particles containing the appropriate amount of the solvent are deposited onto the substrate which is moved at a speed of 1–10 mm/min by the positioner while keeping the distance from the nozzle constant.

Following solutions were prepared. Solution A: a polystyrene (MW: 500,000) was dissolved in a tetrahydrofuran (THF) at the concentration of 1×10^{-4} wt% and a coumarin152A was mixed at the concentration of 2×10^{-5} wt%. Solution B: the polystyrene THF solution at the concentration of 0.5 wt% and a rubrene was mixed at the concentration of 2×10^{-2} wt%. Solution C: the polystyrene THF solution at the concentration of 1 wt% and the rubrene and cumarine152A were mixed at the concentration of 5×10^{-2} wt%. Solution B was spin-coated on a glass substrate

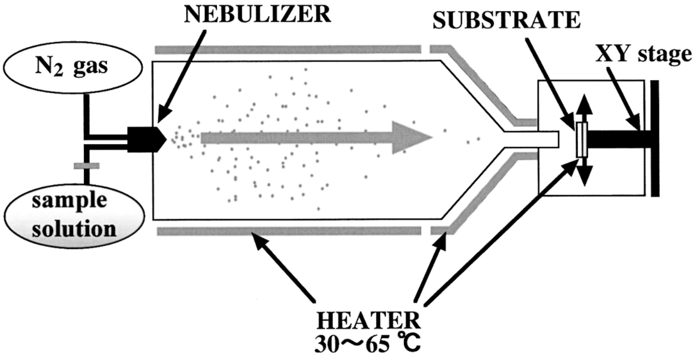

FIGURE 1 Schematic illustration of the spray deposition apparatus.

and solution A was spray-deposited onto the film to prepare a layer-by-layer film. For a mixed layer film as a reference, solution C was spin-coated on a glass substrate. The absorption spectra of the films were measured to confirm the composition ratio of the dyes in the films. The photoluminescence was observed by fluorescence spectrometer.

Two kinds of poly-*p*-phenylenevinylene derivatives, MEH-PPV and DHF-PPV (Fig. 2), were dissolved in a THF at the concentration of 1×10^{-4} wt%. The MEH-PPV solution was spray-deposited onto a glass substrate with an indium-tin oxide transparent electrode through a shadow mask having holes with a 500 μm diameter in 100 μm separation followed by the deposition of DHF-PPV onto the patterned MEH-PPV film without the shadow mask. The film thickness was measured at each step by atomic force microscope. The film was observed by fluorescent microscopy. A buffer layer of LiF and an Al cathode were deposited on the polymer film in a vacuum deposition apparatus to fabricate an EL device.

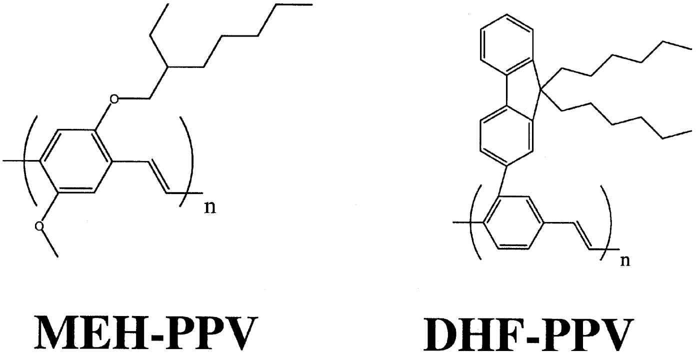

FIGURE 2 Molecular structure of MEH-PPV and DHF-PPV.

RESULTS AND DISCUSSION

Layer-by-layer Deposition

The absorption maximum and the fluorescence maximum of the coumarin-containing film were observed at 390 nm and 480 nm, respectively. The absorption band of the rubrene overlaped well with the fluorescence band of coumarin. The combination of the dyes is wellknown to show a high efficiency of an excitation energy transfer from the coumarin to the rubrene.

The absorbance of the mixed film of the polystyrene containing both dyes at 390 nm and 490 nm corresponding to the absorption peak of each dye were 0.025 and 0.035, respectively. The ratio of the absorbance was 1.4. The layer-by-layer film gave the absorption at the same wavelengths were 0.070 and 0.090, respectively. The ratio was almost comparable value of 1.3. Both films contain the two kinds of dyes in almost same ratio. Figure 3 shows the fluorescence spectra of the mixed film and the layer-by-layer film with an excitation wavelength at 390 nm. In the fluorescence spectrum of the mixed film the fluorescence band ascribed to the coumarin was banished due to the energy transfer from the coumarin to the rubrene. On the other hand, the fluorescence from the coumarin was observed in the spectrum of the layer-by-layer film. This suggests that the two dyes were

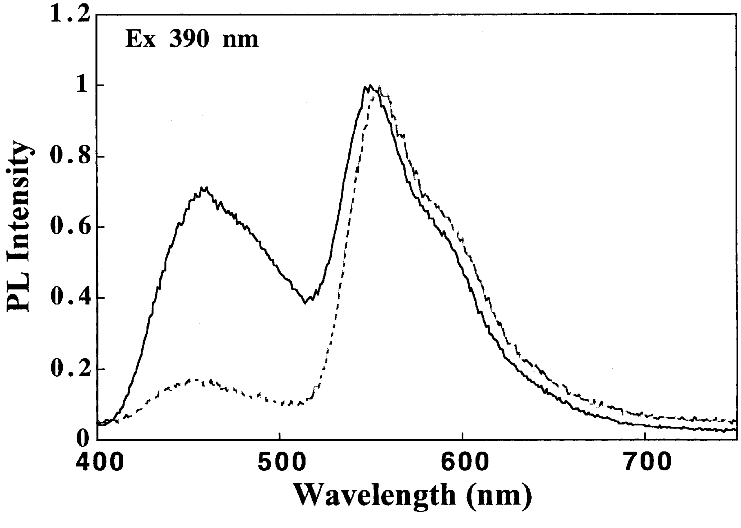

FIGURE 3 Fluorescence spectra of the mixed polystyrene film of the coumarin and the rubrene (---) and the layer-by-layer deposited film of polystyrene containing each dye (——).

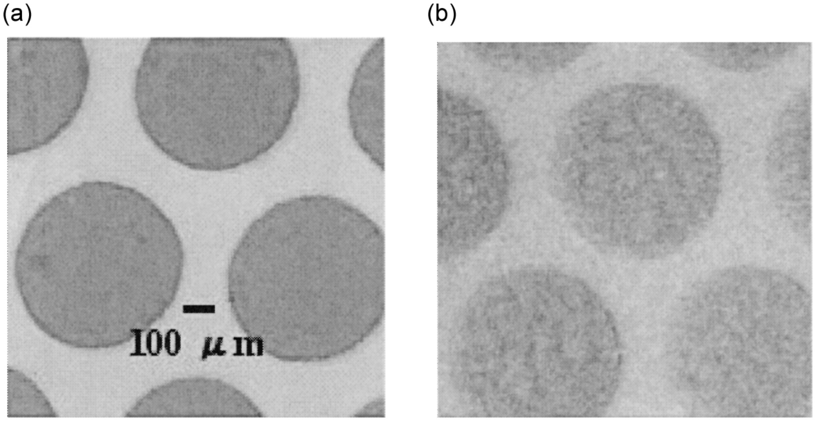

FIGURE 4 Fluorescence micrograph of (a) the patterned MEH-PPV and (b) the layer-by-layer deposited film of DHF-PPV onto the patterned MEH-PPV.

separated in the layer-by-layer film. Therefore, the upper layer should be spray-deposited without mixed up with the lower layer.

Separate-coating

Figure 4a exhibits the patterned MEH-PPV film prepared spray-deposition with a shadow mask. The distinct orange round shape pattern was observed. This clearly shows that the separate-coating by use of a shadow

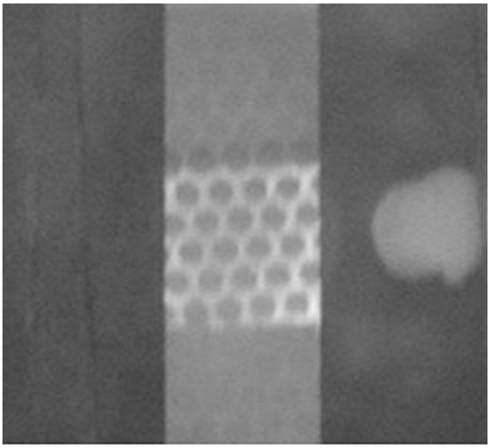

FIGURE 5 Photograph of the emitting EL device consist of the layer-by-layer patterned film of two PPV derivatives.

mask is possible with a 100 μm resolution. Even after the upper layer of DHF-PPV onto the patterned film (Fig. 4b) was spray-deposited, the pattern exhibited no change. The diffusion of the material during the upper layer deposition is negligible at least μm scale. This patterned film was applicable to the EL device (Fig. 5). The EL was observed only in the single layer region among the round region because it is thinner than the layer-by-layer round region. A layer-by-layer film of MEH-PPV and DHF-PPV without the masked pattern also showed the EL. The layer-by-layer region has also applicability to optoelectronic devices.

CONCLUSION

It is shown that the spray deposition has three remarkable features, preparation of a thin film applicable to an actual device from highly diluted solutions, a mask-patterned separate-coating film and a layer-by-layer film. This method will be a powerful tool for optoelectronic studies of materials of very low solubility or pyrolytic organic materials.

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