

Investigation of initial deposition stage of small molecule Alq₃ on α -NPD layer by modified electro-spray deposition (ESD) technique (nano-mist deposition: NMD)

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Abstract

Development of solution based multi-layer deposition technique is one of an attractive step for further prevalent of organic devices. In this study, we investigated initial deposition stage of small molecule bilayer structure by modified electrospray deposition (ESD) technique named nano-mist deposition (NMD). A typical light emitting small molecule of Alq₃ was deposited on hole transparent small molecule of α -NPD layer using common solvent of dichloromethane (DCM) with dimethyl sulfoxide (DMSO) as an additive solvent. It was found that α -NPD layer was dissolved by DCM droplet and many pits were formed on the surface at the DMSO concentration of 10% or less, however the surface erosion was suppressed at the DMSO concentration over 20%. This result suggests that appropriate additive solvent enables small molecule thin-multilayer structure by solution based ESD (NMD) technique.

1. Introduction

Since a report of high intensity electroluminescence with a low-operation voltage of organic light-emitting diode (OLED) using Alq₃ (60 nm)/diamine (75 nm) structure by Tang et al. [1], small molecule thin-multilayer deposited by vacuum evaporation has been used as a standard for high-efficiency OLEDs. However the vacuum evaporation has difficulty in fabricating large-scale devices, makes in efficient use of expensive raw materials, and has high manufacturing cost. On the other hand, many of solution processes have advantages of low cost, large scale manufacturability, and efficient use of materials, but also have drawbacks of difficulty to use with low-solubility small molecules and fabricating multilayers due to dissolution of the underlying layers.

We focused on electrospray deposition (ESD) as a candidate of solution based deposition technique enable to form small molecule thin-multilayer. Using ESD, micro/nano-sized charged droplets are generated from solution by electrospray phenomenon and the droplets are deposited on a substrate. The ESD is expected to have many attractive qualities, including multilayer deposition,

large-area deposition, ability to use small-molecules etc. These features arise from the wet-dry controllability of the fine droplets, Coulomb repulsion of the droplets, and use of a dilute solution. Recently, ESD has begun to be used for OLEDs fabrication [2-6].

In this study, we observed the initial deposition stage of small molecule Alq₃ by ESD on α -NPD layer using common solvent to investigate the interface morphology and effect of additive solvent on the formation of high quality small molecule thin-multilayer by ESD technique.

2. Experimental Method

In this study, we employed a three-electrode ESD system called nano-mist deposition (NMD) [6, 7] with an extraction electrode near the nozzle tip to improve the controllability of ESD. A schematic view of the NMD system used in this study is shown in Fig. 1. The system consisted of a glass syringe equipped with a metal nozzle (1st electrode), a syringe pump, an extraction ring electrode (2nd electrode), a ground plate (3rd electrode), and two high-voltage power supplies. The ground plate was maintained at 25 °C. The nozzle and extractor voltage were set to 4.9 and 3.0 kV, respectively.

Indium-tin-oxide (ITO) coated glass was used as substrate. After cleaning of ITO surface by organic solvent and UV irradiation, tetrahydrofuran (THF) solution of 3.0 mg/mL α -NPD was spin coated on it (30 nm). A dichloromethane (DCM) with 0-30 vol% dimethyl-sulfoxide (DMSO) solution of 0.5 mg/mL Alq₃ was used for NMD. To evaluate the initial deposition stage of Alq₃ by NMD, the solution was sprayed for 2~3 seconds toward the substrate and the surface morphology was observed by white light interferometer.

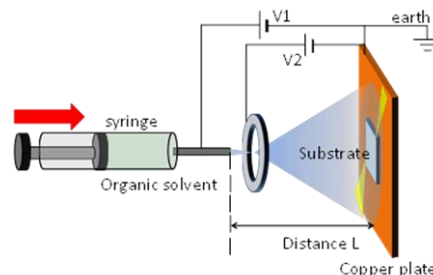


Fig. 1. Schematic of the nano-mist deposition (NMD) system.

3. Results and Discussion

Figure 2-4 shows the white light interferometer images of α -NPD surfaces and cross-sectional profiles (corresponds to broken red line position of upper image). The surface of as prepared α -NPD was smooth as shown in Fig. 2 (a).

On the other hand, many small pits with $\sim 2\ \mu\text{m}$ in diameter and $\sim 27\ \text{nm}$ in depth were observed on the surface after Alq_3 deposition using DCM solvent without DMSO (Fig. 2 (b)). It can be considered that these pits are formed by dissolving of α -NPD by DCM droplets. This surface erosion makes interface quality poor. For the case of solvents with DMSO concentration of 5 and 10 vol%, in addition to the small pits formed by DCM larger circular deposits ($\sim 10\ \mu\text{m}$ in diameter) were formed as shown in fig. 3 (a) and (b). These deposits are considered to be Alq_3 contained in DMSO droplets. It can be note that erosion of α -NPD surface was not observed.

Further increase in DMSO concentration to 20 and 30 vol% brought about dissipation of small pits (figs. 4 (a) and (b)). The surface erosion by DCM droplets was clearly suppressed by increase of DMSO concentration. This phenomenon is attractive for fabricating high quality small molecule multilayer.

4. Conclusions

We investigated the initial deposition stage of Alq_3 on α -NPD by modified ESD technique named NMD using common solvent of DCM with additive solvent of DMSO. Short time deposition clearly showed the surface morphology of initial stage of deposition. The surface erosion by DCM droplets was observed for DMSO concentration at 10 vol% or less, but was suppressed by increase of DMSO concentration over 20 vol%. These results may give a route to form high quality small molecule thin-multilayer structure by a solution based ESD (NMD) technique.

Acknowledgements

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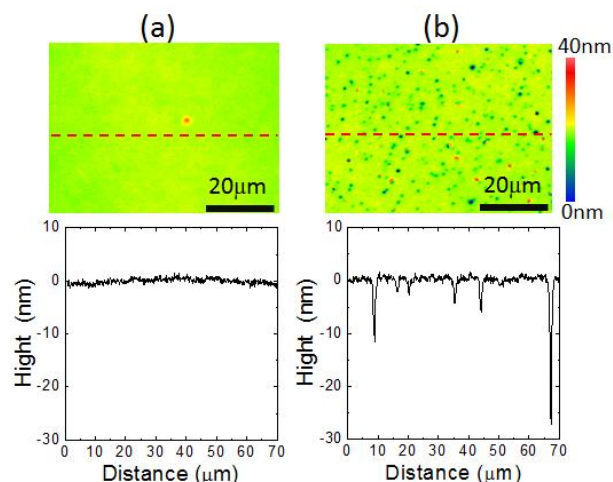


Fig. 2. White light interferometer images and cross-section of α -NPD layers. As prepared (a) and after Alq_3 deposition using DMC with 0 vol% DMSO (b).

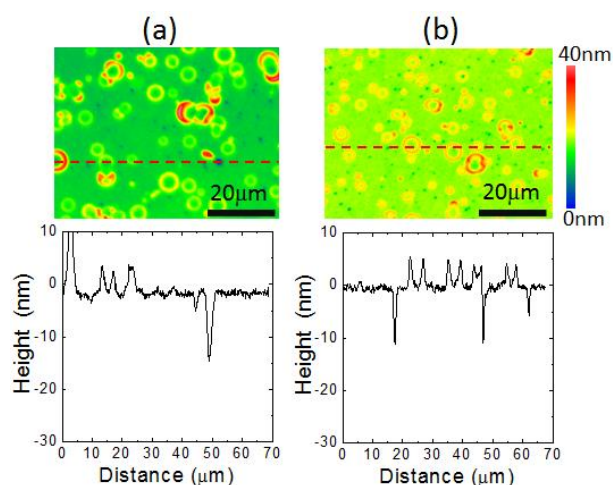


Fig. 3. White light interferometer images and cross-sections of α -NPD layers. After Alq_3 deposition using DCM with 5 vol% (a) and 10 vol% (b) of DMSO.

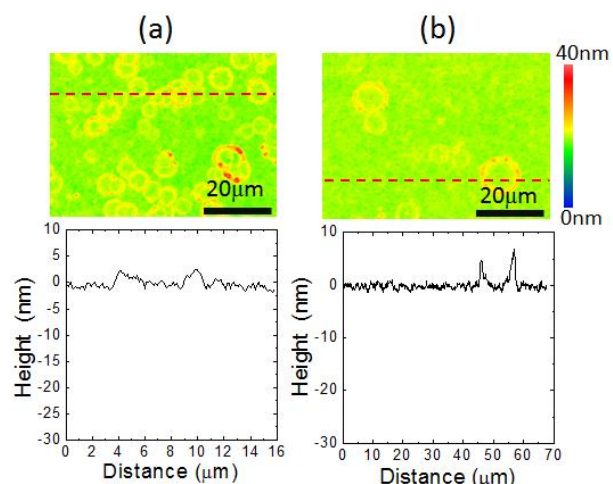


Fig. 4. White light interferometer images and cross-sections of α -NPD layers. After Alq_3 deposition using DCM with 20 (a) and 30 (b) vol % of DMSO.