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Effect of geometrical shape of nozzle tip on electrospray deposition of organic thin film

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Abstract

Electrospray deposition (ESD) is an attractive wet fabrication technique of organic thin film. We systematically investigated the effects of geometrical shape of the nozzle tip on the spraying properties of organic solution by ESD. In this study, 5 types of cylindrical metal nozzles with protrusion of 0 (flat end) to 4 at tips were prepared by 45º bevel cut. For spraying a chlorobenzene solution of Alq_3, each protrusion spouted one liquid thread at the nozzle voltage of 4.3 kV and flow rate of 2.0 μL/min. It was clearly confirmed that the diameter of deposited droplets and their size dispersion was reduced with increasing the number of protrusion from 0 to 4. The area occupation ratio of small droplets (< 2 μm) was increased to be 29, 38, 63, 66, and 83 % with increasing protrusion number from 0 to 4. It can consider that reduction of droplet size was caused by reduction of solution flow rate for each liquid thread and concentration of electric field at sharp protrusions. Surface roughness RMS value of Alq_3 films (60 nm in thickness) deposited by ESD using nozzles with 0 and 4 protrusions were significantly improved from 32.5 to 6.8nm.

1. Introduction

Electrospray deposition (ESD) is an attractive candidate for solution-based wet process of organic semiconductor thin film fabrication. In ESD, with increasing the applied voltage, spraying mode changes from Convergent Jet (CJ) mode which has single liquid thread to multi-jet (MJ) mode which has multiple liquid threads. Recently, we reported that MJ mode can generate remarkably smaller droplets with diameter less than 1 μm with smaller size distribution compared with CJ mode, consequently MJ mode can form much smoother (RMS < 2.5 nm) and uniform organic thin film by modified ESD [1]. However, MJ mode has a problem of instability due to a difficulty to fix the position of multiple liquid threads spouted at cylindrical metal nozzle tip. In this study, we investigated the effect of geometrical shape of a cylindrical metal nozzle tip on the spraying characteristics of organic solution by ESD. By forming multiple protrusions at the nozzle tip, we attempted to concentrate the electric field and to fix position of liquid threads for spraying smaller droplets and stabilizing the MJ mode [2]. We also compared the surface morphology of Alq_3 layer deposited by ESD using conventional flat-end metal nozzles and a metal nozzle with 4 protrusions at the tip.

2. Experiments

Conventional metal needles with a gauge number of 22 (O.D. = 0.72 mm, I.D.= 0.41 mm) were used as spraying nozzle. Five types of nozzle tips were prepared by 45 degrees beveling using a diamond cutting disk, to have different number of protrusions at the tip of nozzle as shown in Figure 1. The nozzle types of (a), (b), (c), (d), and (e) corresponds to the protrusion number of 0 (flat-end), and 1, 2, 3, and 4, respectively. Using these nozzles, Alq_3 solution was sprayed for 1 minute by ESD on ITO coated glass substrates (Figure 2). The Alq_3 solution of chlorobenzene (CB) with 20 vol% dimethyl-sulfoxide (DMSO) was prepared at a concentration of 0.5 mg/ml. For the deposition, nozzle voltage (V), distance between nozzle tip and substrate (L), substrate temperature, and solution feed rate was 4.3 kV, 3.0 cm, 25 ºC, and 2.0 μl/min, respectively. After the deposition, sample surfaces were observed with field emission scanning electron microscope (FE-SEM) to evaluate the diameter distribution of Alq_3 deposition marks. To evaluate the effect of nozzle tip geometry on the organic thin film deposition, 60-nm-thick Alq_3 films were deposited by changing L. The films were measured by optical microscope, white light interference microscope, and fluorescence microscope.

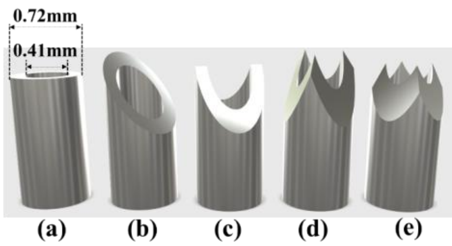

Fig. 1. Schematic of processed nozzle tip (flat-end (a), the number of protrusions 1 (b), 2 (c), 3 (d), 4 (e))

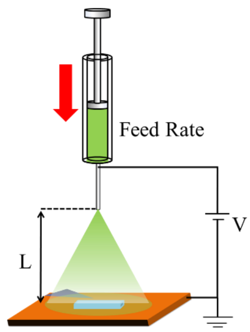

Fig. 2. Schematic of the electrospray deposition method

3. Results and discussions

It was confirmed that number of liquid thread were 1, 1, 2, 3, and 4 for nozzles (a), (b), (c), (d) and (e). That is for the nozzle (a), solution was sprayed in CJ-mode and for the nozzles (b), (c), (d) and (e), each protrusion spouted one liquid thread. That is nozzles (c), (d), (e) realized MJ mode under relatively low applied voltage. Figure 3 shows FE-SEM images of Alq_3 deposition marks using nozzles (a)-(e). For the case of single liquid thread, relatively large droplet marks with a diameter around 16 nm was observed for nozzle (a), but the maximum diameter was remarkably reduced to 5.3 μm for nozzle (b) suggesting the effect of concentration of electric field at the sharp protrusion. For the case of MJ-modes of (c), (d), and (e), further reduction of droplet mark size was observed. Figure 4 (a)-(e) shows histograms of diameter of deposited Alq_3 droplet marks. Area occupation ratio of deposition marks as a function of diameter ranges are also plotted in each histogram with open circles. It can be note that all of nozzles generate small size particles with diameters smaller than 1 μm but the maximum size was monotonically reduced with increasing number of protrusions (liquid threads). As a result, the size distribution became smaller for large number of protrusions (liquid threads). The area occupation ratio of smaller droplets (with diameters smaller than 2 μm) was increased to be 29, 38, 63, 66, and 83 % with increasing protrusion number from 0 to 4. It can consider that reduction of droplet size was caused by reduction of solution flow rate for each liquid thread and concentration of electric field at sharp protrusions.

Figures 5 and 6 shows fluorescence images and height profiles of the Alq_3 films deposited using the nozzle (a) and (e). The uniformity of fluorescence image was much improved by use of nozzle (e) and surface roughness RMS value of films using nozzles (a) and (e) were 32.5 and 6.8 nm, respectively. In spite of almost same deposition condition (L was optimized for each nozzles), the features of films were completely different.

4. Conclusions

The effects of geometrical shape of nozzle tip on ESD of organic thin film was systematically investigated. By using of multiple protrusion nozzle, stable MJ mode was easily realized and deposited droplet size and distribution of large droplets was reduced with increasing number of protrusion that is number of liquid threads. The surface morphology of deposited Alq_3 organic film was remarkably improved by use of the nozzles with multiple protrusions.

Acknowledgements

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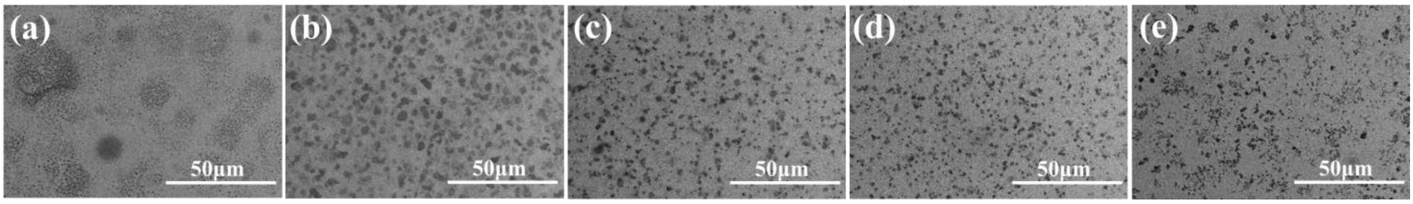

Fig. 3. SEM images of deposition marks of Alq_3 solution on ITO substrate

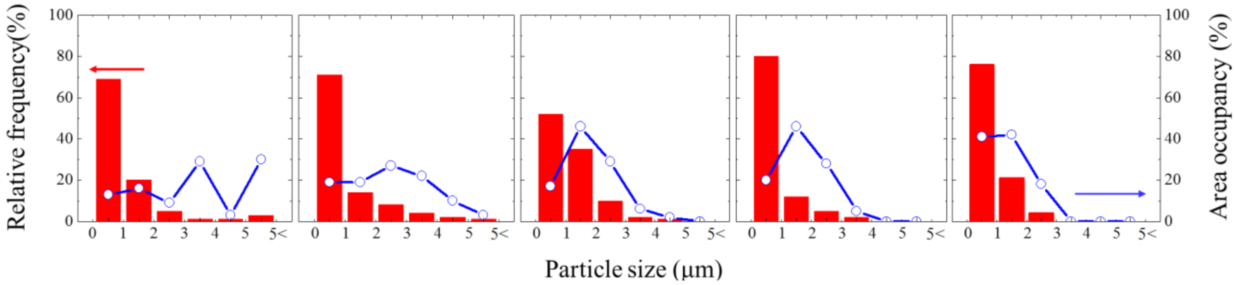

Fig. 4. Ratio of diameters of deposition marks (left axis) and ratio of area occupancy of each diameter for entire (right axis)

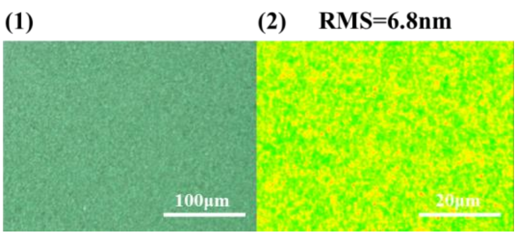

Fig. 5. A fluorescent image (1) and height profile (2) of Alq_3 film formed with nozzle (a)

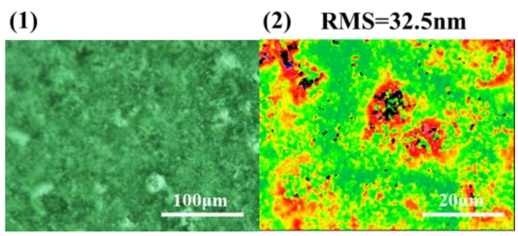

Fig. 6. A fluorescent image (1) and height profile (2) of Alq_3 film formed with nozzle (e)