Thin Solid Films 550 (2014) 395–403

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Morphology characterization of phenyl-C61-butyric acid methyl ester films via an electrohydrodynamic spraying route

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ARTICLE INFO

Article history:
Received 10 April 2013
Received in revised form 3 November 2013
Accepted 6 November 2013
Available online 15 November 2013

Keywords:
Electrohydrodynamic spray
Phenyl-C61-butyric acid methyl ester
Nanoparticles
Size distribution
Scanning mobility particle sizer

ABSTRACT

In this study, we fabricated a thin film layer of phenyl-C61-butyric acid methyl ester (PCBM) fine particles using electrohydrodynamic (EHD) spray and evaluated the effects of the process parameters on the film morphology. After the PCBM was dissolved in dichloromethane, the solution was sprayed onto a substrate using the stable cone-jet mode of EHD spraying at various flow rates ranging from 5 to 15 μl/min and electric potentials ranging from 3 to 5 kV. The effects of the liquid flow rate, nozzle-plate distance, solute fraction, and electrical conductivity on the spray characteristics were investigated. The sizes of the PCBM particles deposited on the substrate were calculated using a scaling law and a mass balance equation, the results of which were in agreement with those obtained by scanning electron microscopy. A thin film was obtained with the structure of PCBM particles deposited without any void or agglomeration from the EHD spraying technique. The electrical conductivity of the PCBM solution was the dominant parameter in controlling the size of the PCBM particles. As the conductivity was increased to 2.4×10^{-3} S/m from 4.3×10^{-9} S/m, the particle size decreased from 6.7 μm to 320 nm. The size distribution measured using a scanning mobility particle sizer also supported the generation of nano-scale PCBM particles. The decrease of the particle size with increasing electrical conductivity may lead to a better morphology of PCBM films.

1. Introduction

Phenyl-C61-butyric acid methyl ester (PCBM) has received tremendous attention as an effective n-type organic semiconductor and is widely used to fabricate various thin film organic electronic devices. When blended with p-type conjugated polymers such as poly-3-hexylthiophene (P3HT), PCBM acts as an excellent electron acceptor at the photoactive layer of an organic solar cell (OSC) [1–3]. The high electron affinity of PCBM results in efficient photo-induced electron transfer from p-type polymers as well as from metal electrodes for use in biased thin film organic field effect transistors [4–6]. PCBM also has high potential for use in photodetectors [7,8].

The fabrication process of PCBM thin film devices typically utilizes solution processes due to its high solubility in organic solvents. While spin coating, the most widely used solution process, produces high quality thin films, it is a time-consuming batch process and is not scalable to a large area process. To realize large area coverage, various fabrication methods including the spray deposition method have been demonstrated. The spray deposition method has advantages in that the process is continuous, easily scalable, and therefore, is one of the cheapest processes for the coating of organic solutions, allowing for cost-effective mass production of thin film devices [1–3,7,8].

Electrohydrodynamic (EHD) spray, also referred to as electrospray, is one of the most recently developed approaches to deposit thin films composed of fine particles [9–18]. In EHD spray, a metal nozzle containing liquid is biased by a high electric potential which elongates the liquid into the direction of the electric field. If the electric field is strong enough, a so-called Taylor cone appears from which a multitude of relatively monodispersed fine droplets are emitted. The droplets obtained by the EHD spray method can be extremely small, with sizes in the nanometer range in special cases, and relatively monodispersed [19–25]. The electrostatic repulsive forces disperse the droplets homogeneously in the space between the nozzle and a substrate. The film thickness can be easily controlled by varying the concentration and flow rate of the solution and the voltage applied to the nozzle. Recently, EHD spray has been used to prepare organic thin films for their application in electronic devices. Uematsu et al. [14] prepared protein thin films by EHD spray from aqueous solutions of α-lactalbumin and characterized their surface morphologies. Kim et al. [15] fabricated a thin film OSC by EHD spray from P3HT:PCBM dissolved in a mixture of 1,1,2,2-tetrachloroethane and chlorobenzene. Park et al. [16] observed the jetting aspects of EHD spray during the production of P3HT:PCBM thin film OSCs. Park et al. [17] used EHD spraying to deposit a PCBM layer onto a patterned P3HT layer to generate so-called patterned OSCs. Ju et al. [18] demonstrated an organic light emitting diode pixel using EHD spraying of poly(2-methoxy-5-(2-ethylhexoxy)-1,4-phenylenevinylenea) (MEH-PPV).

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0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.11.009

According to previous reports [9,10,13,26,27], it is important to control the size of the droplets and particles obtained after solvent evaporation, as these characteristics strongly affect the quality of thin films. Jaworek reported that smaller particles need to be generated in order to reduce the number and size of voids, flaws, and cracks in thin films [13]. Choy and Su showed that the average droplet size clearly affected the surface morphology in the preparation of dense and adherent CdS films using the EHD spray process [10]. Xue et al. reported that a significant decrease of the film roughness was observed in a stochastic model simulation of a zirconia thin film [26]. Rietveld et al. investigated the effects of particle size on the roughness of polymer thin films prepared using electrospray deposition of a poly(vinylidene fluoride) (PVDF):acetone solution [27]. PVDF particles were deposited on the substrate and the roughness decreased with decreasing polymer particle size. Therefore, in order to produce uniform thin film, the correlation between the PCBM particle size and the processing parameters of the EHD spray is required.

In this study, we applied the EHD spray method to produce PCBM thin films consisting of PCBM fine particles and evaluated the morphology characteristics of the PCBM particles. The scanning electron microscope (SEM) images and X-ray diffraction (XRD) results showed that the PCBM films with an amorphous crystal structure were uniformly deposited onto the substrate. In order to obtain PCBM particles with a reduced size, the processing parameters of the EHD spray including liquid flow rate, nozzle-plate distance, solution solute fraction, and liquid electrical conductivity were controlled. The size and morphology characteristics of the PCBM particles were observed by SEM. By using a PCBM solution with an increased electrical conductivity, PCBM nanoparticles were produced and the size distribution of the nanoparticles was evaluated using a scanning mobility particle sizer (SMPS) instrument.

2. Materials and methods

2.1. Materials

PCBM powder was purchased from Nanocraft (Renton, WA, USA) and the dichloromethane (DCM) solvent was purchased from Sigma-Aldrich (St. Louis, MO, USA). Various amounts of PCBM powders were dissolved in DCM resulting in 0.12–1.2 wt.% PCBM solutions. The electrical conductivity was controlled by adding electrically conducting additive. For this purpose, dodecyl trimethyl ammonium bromide (DTAB) was purchased from Sigma-Aldrich as an electrical conducting agent. DTAB was added to the pre-mixed PCBM:DCM solutions in 1.54×10^{-3}–6.17×10^{-2} wt.% (0.05–2.0 mM), which resulted in different electrical conductivities.

The properties of the PCBM solutions with and without DTAB were analyzed and the results are summarized in Table 1. The density of each solution was determined using the relationship between the volume and mass of the solution in a bottle using a micro balance. The viscosity and electrical conductivity were measured using a vibration viscometer (SV-10, A&D Co. Ltd., Tokyo, Japan) and a conductivity meter (Model 3200, YSI Inc., Yellow Springs, OH, USA), respectively.

Table 1
Physical properties of the PCBM:DCM solutions.

	Density (kg/m^3)	Viscosity (mPa·s)	Surface tension (mN/m)	Electrical conductivity (S/m)
Without DTAB	1326	0.44	31.5	4.3×10^{-9}[a]
DTAB 0.05 mM	1321	0.43	31.0	7.3×10^{-5}
DTAB 0.2 mM	1325	0.44	31.4	2.3×10^{-4}
DTAB 1.0 mM	1324	0.44	31.2	4.7×10^{-4}
DTAB 2.0 mM	1326	0.44	31.5	2.4×10^{-3}

[a] I. Smallwood, Handbook of organic solvent properties, John Wiley & Sons Inc., New-York NY, 1996.

The relative permittivity was measured using a commercial liquid dielectric constant meter (Model 871, Rufuto Co. Ltd., Tokyo, Japan). The surface tension was measured by the well-known Du Nouy ring method using a surface tensiometer (Model 21, Fisher Scientific Inc., Pittsburgh, PA, USA).

2.2. Experimental set-up

The EHD spray to atomize the PCBM was operated using the experimental setup shown in Fig. 1, which consists of a liquid supply system, an electrical system, and a visualization system. The liquid supply system includes a syringe pump (KDS 200, KD Scientific Inc., Holliston, MA, USA), a feeding tube, and a stainless steel nozzle (inner diameter: 150 μm, outer diameter: 320 μm, Iretech Co. Ltd., Seoul, Korea). The liquid flow rate was varied between 5 and 15 μl/min. The electrical system consisted of two high voltage power supplies (DC — 10–15 kV) and two electrodes. The pin-type nozzle used for the liquid supply system was also used as the anode. The substrate (silicon wafer: 8 mm width × 8 mm length × 0.5 mm thickness) was placed below the nozzle. The distance between the nozzle and the substrate was varied from 30 to 90 mm. The substrate was positioned on a copper electrode (60 mm width × 80 mm length × 0.1 mm thickness), which was used as the ground electrode. A stable cone-jet mode was sustained within a range of the applied electric potential (~3.7–4.6 kV). The visualization system consisted of a high speed camera (FASTCAM SA1.1 model 1000 K-C2, Photron Ltd., Tokyo, Japan) and a 400 W peak power metal halide light source (MHB-400/DOL, Inflidge Industrial Ltd., Yokohama, Japan). The camera used is capable of capturing continuous images with a resolution of 512 × 512 pixels at a recording rate of 60,000 frames per second (fps) and with an exposure time of 400 ns. The exposure time used for all capturing processes was less than 1 μs.

The morphologies of the PCBM films on the Si wafer substrates were observed using a field emission scanning electron microscope (FE-SEM, JSM-6500 F, JEOL, Tokyo, Japan). Prior to SEM analysis, each substrate deposited by PCBM was coated with Pt for 60 s. The absorbance for visible light and the film crystallinity of the PCBM film on the glass substrate were also analyzed using a UV–visible spectrophotometer (Libra S12, Biochrom, Cambridge, UK) and X-ray diffraction (XRD) measurements (DMAX 2200, Rigaku Co., Tokyo, Japan) with Cu Kα radiation ($\lambda = 0.15405$ nm), respectively.

The size distribution of the PCBM particles during the flight was measured using both an aerodynamic particle sizer (APS, model 3321, TSI, Shoreview, MN, USA) and a scanning mobility particle sizer (SMPS, model 3936, TSI). The SMPS consisted of a classifier controller (model 3080, TSI), a differential mobility analyzer (DMA, model 3081, TSI), a condensation particle counter (CPC, model 3375, TSI), and an aerosol charge neutralizer (Soft X-ray charger 4530, HCT Co., Ltd, Icheon, Korea) with a sampling air flow rate of 0.3 l/min. The APS measures the size of particles with an aerodynamic diameter in the range of 0.5 to 20 μm and the SMPS measures particles with a mobility-equivalent diameter ranging from 15 to 723 nm. The PCBM particles during the flight were carried into the APS and SMPS instruments through a sampling hole at the center of the copper plate located 5–70 mm below the nozzle tip.

The size and morphology of the PCBM particles were also analyzed in the obtained SEM images. Both the sizes of the PCBM droplets captured during flight by the visualization system and the PCBM particles after deposition imaged by SEM were measured using ACDSee (version 3.1, ACD Systems) image viewer software. In almost all cases, more than 100 particles were included in the analysis and their average diameter was obtained.

To minimize the penetration of ambient aerosol particles in the PCBM atomization and deposition process, all experiments were conducted in a class 100 (at 0.5 μm) clean room, repeated three times, and the results of these measurements were averaged.