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◆ 특집 ◆ 인쇄전자 소자 제작을 위한 다양한 인쇄 공정 기술 개발

공압과 정전기력을 이용한 스프레이 박막 코팅 기술 개발

Development of Spray Thin Film Coating Method using an Air Pressure and Electrostatic Force

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In many electro-devices, the vacuum process is used as the manufacturing process. However, the vacuum process has a problem, it is difficult to apply to a continuous process such as a R2R(roll to roll) printing process. In this paper, we propose an ESD (electro static deposition) printing process has been used to apply an organic solar cell of thin film forming. ESD is a method of liquid atomization by electrical forces, an electrostatic atomizer sprays micro-drops from the solution injected into the capillary with electrostatic force generated by electric potential of about several tens kV. The organic solar cell based on a P3HT/PCBM active layer and a PEDOT:PSS electron blocking layer prepared from ESD method shows solar-to-electrical conversion efficiency of 1.42% at AM 1.5G 1sun light illumination, while 1.86% efficiency is observed when the ESD deposition of P3HT/PCBM is performed on a spin-coated PEDOT:PSS layer.

Key Words: Spray Coating (스프레이 코팅), Electrostatic Spray Deposition (정전기 스프레이 증착), Air Pressure (공압) Organic Photovoltaic (유기태양전지), PEDOT:PSS (전도성고분자)

NOMENCLATURE

KV = applying kilo voltage into the nozzle
Ω/□ = dimensionless quantity to obtain sheet resistance
d = distance between capillary and corresponding electrode
r_c = outer diameter of capillary

1. Introduction

The word, “PEMS” stands for “Printed Electro-Mechanical System” which is fabricated by means of various printing technologies. Passive and active components in 2D or 3D such as conducting lines, resistors, capacitors, inductors and TFT, which are printed with functional materials, can be classified in this category. And issue of PEMS is applied to a R2R process in the manufacturing process.

In many electro-devices, vacuum process was used manufacturing process as conventional process. However, Vacuum process is difficult to apply to the continue process such as a R2R printing process. Besides, it causes a very high device manufacturing cost with processing cost. Therefore, many developers have been interest to be applied a continuous process with contact printing or noncontact printing technology. Recently, many researchers proposed a various continuous printing processes instead of conventional batch coating processes. In this paper, we propose an ESD printing process has been used to apply an organic solar cell fabrication process. ESD is a method of liquid atomization by electrical forces. The atomizer nozzle is usually made in the form of metal or glass capillary, which is biased by a high voltage. The shear stress on the liquid surface, due to the established electric field, causes elongation of a jet and its disintegration into droplets. The droplets obtained by this method can be extremely small, in special cases down to nanometers. The advantage of ESD method is that droplets are highly charged, up to a fraction of the Rayleigh limit. The Rayleigh limit[1] is the magnitude of charge on a drop, which overcomes the surface tension force that leads to the drop fission. In Electrostatic deposition process the droplet diameter (for dripping mode) or spray (nano particles) depends on the applied voltage. As the voltage increases the diameter of the droplet decreases which help in fine thickness deposition on the substrate.

2. ESD Printing Method

2.1 Introduce of ESD method

Electrostatic atomizer sprays micro-drops from the solution injected into capillary, with electrostatic force generated by electric potential of about tens of kV. Such devices have been widely used in physics laboratories since 1950s and as the ionizer for mass analyzers, recently.[2] As shown in Fig. 1, the device consists of capillary containing solution, corresponding substrate electrode, and high voltage power source. High electric potential applied to capillary generates extremely strong electric field at the tip of the capillary by the focusing effect of electric field. The electric field strength at the end of the capillary can be calculated using following formula.[1]

$$E_C = \frac{2V_c}{r_c \ln(4d/r_c)} \tag{1}$$

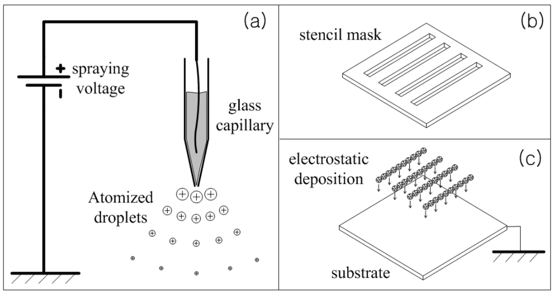


Fig. 1 Schematic of ESD configuration

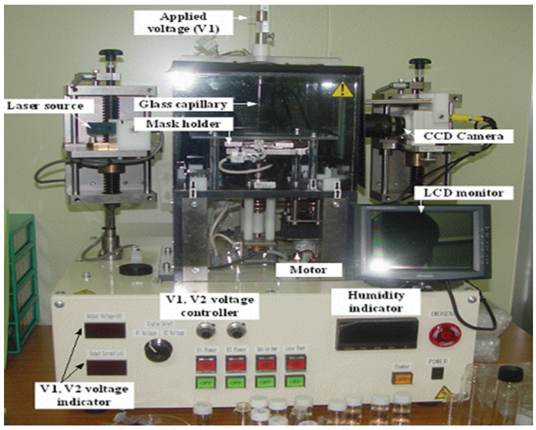


Fig. 2 A small area coating ESD system

where, Vc is a input high voltage, rc is outer diameter of capillary and d is distance between capillary and corresponding electrode. The field strength becomes larger when the applied voltage is higher and the outer diameter of capillary tip is smaller.

Fig. 2 shows a small area coating ESD system. ESD de-vice incorporates a capillary holder, a guide ring, guiding gauze, Teflon shield, and sample substrate in acryl chamber. High voltage applied inside the capillary generates focused electrostatic force which ejects the charged particles in micron sized drops. Charged particles are divided sequentially by repulsion force of the charge and guided towards the mask by electrostatic field. Fine particles passed through the mask deposit on the substrate below.

2.2 A thin film coating method using ESD

Fig. 3 shows a conductive coating process using ESD method. If applying voltage is low voltage of under the 3KV, ESD is ejected a dripping mode. That is possible to

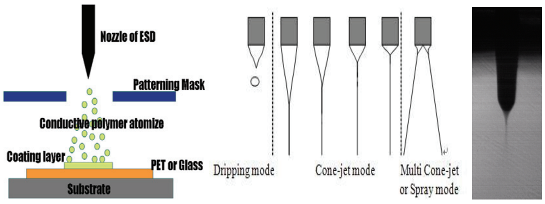
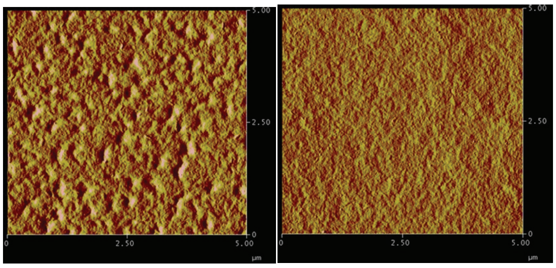


Fig. 3 Thin film coating method using ESD spray



(a) Spray time of 1hr (b) Spray time of 2hr

Fig. 4 AFM image of transparent electrode

change a DoD ejection using applying voltage of pulse type. And this kind of ejection mode is possible to use a instead of ink-jet ejection. Otherwise, ESD have a cone-jet or spray mode. And these mode is used the other application. Example, cone-jet mode is possible to use a direct line patterning process. Spray mode is used to be coating process with a nano thin film. These methods are possible to apply on continuous coating process such as R2R process. Especially, ESD spray coating process will be possible to use on the continuous manufacturing process for organic electronic device with thin film layers. At another point, this method has the advantage of hydrophobic surface coating method. Because an ejected small drops using ESD spray method evenly are filled in film or glass substrate. Generally, organic materials have occurred cohesion phenomenon on the hydrophobic surface when spin coating method was used in the multi layer coating. Therefore, we experiment that ESD spray method is suited for thin film coating method which a transparent electrode is fabricated by conductive polymer. PET film was coated a conductive polymer using ESD method and conductive polymer is used by PH500 (Baytron corp.) and glycerol as an additive solution. Applied voltage was 5KV and spray time were 1hr or 2hr in the case of small single nozzle system. Thin film thickness of ESD coating is formed by only applying

Table 1 Performance and condition of small area transparent electrode

Printing System	ESD system with nozzle dia. of 80um
Spray Material	Conductive Polymer(PH500)
Additive Material	Glycerol, DMSO(5%)
Substrate	3M PET film
Apply Voltage	5KV
Spray Time	2hr
Curing Time	30min at 120℃
Layer Thickness	650~700nm
Transparent	70%
Surface Resistance	150Ω/□

voltage and coating time. If we can form into the thickness of 1~10um, we expected a thin film forming of nano thickness using ESD coating method because of general organic material of solid content of below 10%.

2.3 Result of small area system experiment

In the result of experiment, conductive polymer was formed a very high density thin film as show as an AFM image of fabricated transparent electrode in Fig. 4. Its transparent electrode has a roughness of about 5~6nm in the case of 2hr and it has a high conductivity and high density of surface compare with a 1hr and then a thickness was about 650 to 700nm. Table 1 presents a performance of small area transparent electrode. Conductive polymer electrode had a surface resistance of 150Ω/□ at the transparent of about 70% at wavelength of 550nm. We can expect to apply on the applications of touch panel in the result. However, we target in the larger coating process as apply to OPV or PLED fabrication process. In these applications, small area spray process has a problem with long time coating process time because of small capillary size for more small particles spray. Besides, small capillary is occurred a nozzle clog so as to avoid this problem, we used an additive material of glycerol. Therefore, in this paper, we proposed a large area ESD coating process with dual spray coating method using large area coating ESD system with air pressure. Large area coating ESD system has a dual nozzle consists of small size internal nozzle and large size external nozzle. The spray force is applies to electrical force and air pressure force in the large area coating ESD system. Firstly, air pressure is supply to gap in between internal

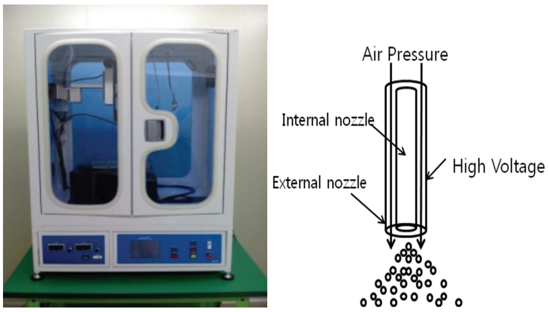


Fig. 5 Large area coating ESD system and dual nozzle schematic

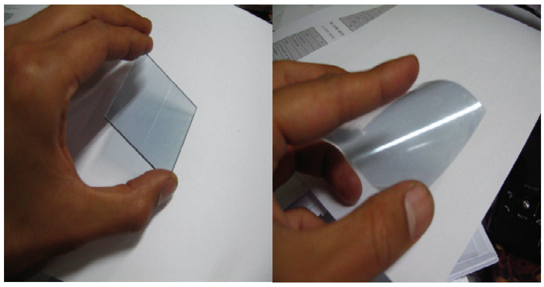
nozzle and external nozzle as general air spray. Secondly, we do apply to charge of high voltage in the external nozzle. In this case, we can have smaller particles and faster deposition time compare with small area ESD system base on the single nozzle. Besides, dual nozzle is possible to avoid nozzle clogging problem with a large internal nozzle size.

2.4 Large area coating ESD system

In the small area coating experiment, we known that ESD method needs a more shortly manufacturing time and higher conductivity. Therefore, we developed a large area coating ESD system and dual nozzle. Fig. 5 shows a large area coating ESD system with a substrate size of 200mm x 200mm. And we applied a dual nozzle that the effect is higher conductivity as a generated smaller micro-drop. Also, we applied a more high voltage for a shortly manufacturing time because of high spray quantity using air pressure and electrical force. Fig. 6 shows a fabricated electrode on the PET film and glass. We apply a apply volt-age of 10~15KV. Its condition had effected on the more shortly manufacturing time of 30min. And then, surface resistance is a 66Ω/□ in the transparent of 73% at wave length of 550nm.

3. Experiment of Organic Solar Cell

Organic solar cell is consists of various organic materials. Therefore, we experimented in the possibility for organic solar cell fabrication method. Fig. 7 shows a structure of organic solar cell. Generally, PEDOT:PSS and P3HT:PCBM forming method was spin coating method, while we used an ESD method for thin film forming instead of spin coating method. Firstly experiment of ESD coating method was applied to PEDOT:PSS and P3HT:PCBM layers with the exception of cathode electrode include electron-transport layer. The result of experiment, PEDOT:PSS layer was occurs a thickness of about 300nm and P3HT:PCBM layer was about 200 to 260nm. And this cell had efficiency of 1.42% with fill factor of 0.39 as shows as Table 3.

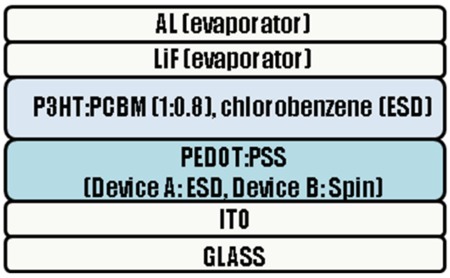


(a) Coated on the glass (b) Coated on the PET film

Fig. 6 Fabricated transparent electrode

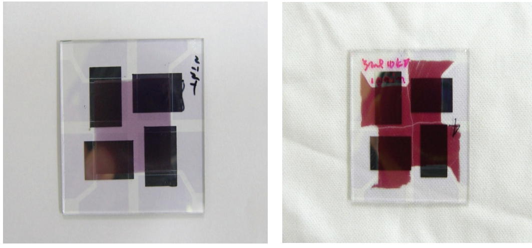
Table 2 Performance and condition of large area transparent electrode

Printing System	ESD system with dual nozzle dia. of 100um and 250um
Spray Material	Conductive Polymer(PH750)
Additive Material	DMSO(5%)
Substrate	3M PET film, glass
Apply Voltage	10~15KV



Apply Air pressure	4bar
Spray Time	30min
Curing Time	30min at 120℃
Layer Thickness	180~360nm
Transparent	73%
Surface Resistance	66Ω/□

Fig. 7 Structure of experiment solar cell



(a) Device A sample (b) Device B sample

Fig. 8 Fabricated organic solar cell using ESD spray coating method

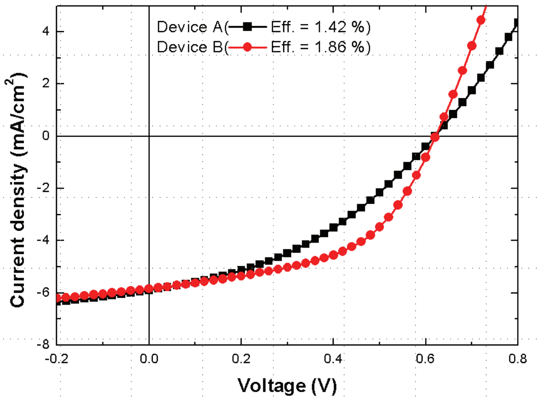


Fig. 9 I-V curve of fabricated organic solar cell

Table 3 Performance of organic solar cell using ESD method

Structure	Voc (V)	Jsc(mA/cm^2)	FF	Eff(%)
Device A	0.62	5.84	0.39	1.42
Device B	0.62	5.84	0.51	1.86

The other experiment, we experiment a hybrid concept as the applied a spin coating in the PEDOT:PSS. And P3HT:PCBM layer was more optimized ESD coating method for more high efficiency. Thus, hybrid fabrication method organic solar cell was a better efficiency than only ESD method. PEDOT:PSS layer had a thickness of below 40nm because of applied a spin coating method and P3HT:PCBM layer was occurs a thickness of about 160nm. Generally, Optimized organic solar cell has PEDOT:PSS layer of about 40nm and P3HT:PCBM layer of about 100nm. Therefore, the hybrid type organic solar cell was higher efficiency than applied only ESD method for organic solar cell. Efficiency was occurs a 1.86% with fill factor of 0.51. Figs. 8 and 9 shows a fabricated organic solar cell with current density, respectively. In this experiment, we know that ESD spray coating method is available for organic solar cell fabrication method as continuous process.

4. Conclusion

In this study, we applied a transparent electrode to conductive polymer coating process and organic solar cell fabrication. Coating process was used by ESD method and the main advantage of the ESD method is that no vacuum process is required to apply the coating. Result of experiment, we had a transparent electrode which was coated by conductive polymer on the PET film and the glass. Ours transparent electrode had a surface resistance of about 66Ω/□ and transparent of 73% at the wavelength of 550nm. And in the experiment of organic solar cell fabrication, we fabricated organic solar cell using ESD coating method. Efficiency of organic solar cell using only ESD method was occurs 1.42% and organic solar cell with ESD method in only P3HT:PCBM layer was occurs 1.86%. Therefore, ESD coating method will be applied to continuous process such as R2R process, and moreover, it will be bring to down a manufacturing cost of organic electronic device. And furthermore, we will apply to a PLED fabrication using ESD method in further research.

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