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Electrophoretic deposition onto an insulator for thin film preparation toward electronic device fabrication

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An electrostatic film fabrication method utilizing the dielectric layer, entitled dielectric barrier electrophoretic deposition (DBEPD) has been proposed. We demonstrated the fabrication of uniform organic semiconductor thin film onto any kind of substrate by DBEPD. Optical absorption spectra of colloidal poly(3-hexylthiophene) (P3HT) film prepared by DBEPD exhibited the clear vibrational structure attributed to highly ordered domains. It was in contrast to the relatively disordered structure as shown in the case of P3HT film prepared by conventional electrophoretic deposition (EPD). Organic field effect transistors fabricated by each method showed similar organic field effect transistor characteristics, however, the uniformity of DBEPD film was superior to EPD film. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4766126]

Thin film preparation methods utilizing the application of dc electric fields, known as electrophoretic deposition (EPD), have been widely studied as economical coating techniques.[1] Colloidal materials dispersed in a suspension rapidly migrate to the electrodes under voltage application and form a colloidal thin film. Recently, several researchers have attempted to apply EPD techniques towards the fabrication of organic electronic devices such as solar cells,[2,3] light emitting diodes,[4] and chemical sensors.[5] These attempts suggest the possibility of EPD for organic device fabrication. Moreover, the merits of EPD, such as high material usage efficiency and low energy consumption, offer its advantage towards the fabrication of organic electronic devices.[6] Furthermore, several studies regarding the use of EPD for insulating substrates have been reported in the recent past.[7]

The successful development of printable electronic devices relies on the utilization of functional and solution processable polymeric semiconductors. In this context, easy film preparation such as spin coating dip coating or doctor blading plays their pivotal role towards the application of these functional materials as active device component However, the process of film preparation often affects the electronic characteristics of the film. For instance, the influence of solvent evaporation rate on the properties of polymer films has also been discussed.[8,9] The use of colloidal materials for film preparation can avoid these effects. Moreover, the unique structure of colloidal polymer semiconductors, such as their fiber structure, has drawn attention owing to the potential for improving the performance of organic electronic devices.[10–12]

In this paper, we would like to propose an EPD method mediated by the presence of intervening dielectric layers, entitled dielectric barrier electrophoretic deposition (DBEPD). The key feature of DBEPD is its ability to apply the voltage without physical contact between the electrodes and the suspension. Figures 1(a) and 1(b) compare conventional EPD and DBEPD systems. In conventional EPD, the working electrode (deposition electrode) and counter electrode are directly submerged in a suspension. Since film preparation has often been affected by unexpected phenomena such as electrochemical reaction, therefore, EPD using non-polar solvents has been attracted the attention due to better control of the film thickness, film surface roughness compared to using polar solvents.[7,13] However, EPD system cannot avoid electrochemical reaction due to the physical contact between electrode and solvent. Additionally, the application of high voltage between closely spaced electrodes in the flammable solvent is not suitable for large scale production using EPD.

DBEPD essentially solves such problems because the electrodes and substrates are separated by intervening dielectric layers with high electric impedance. Voltage application through the dielectric layer can generate a colloidal film onto both conductive as well as insulating substrates inside the cell. The dielectric layer is expected to prevent unexpected phenomena during deposition such as electrochemical reaction, discharge, and Joule heating which often causes a problem in conventional EPD.

Regioregular (poly(3-hexylthiophene) (P3HT)) purchased from Merck (lisicon SP001) was used for DBEPD without further purification. P3HT suspensions were prepared according to the following procedure. P3HT was dissolved in toluene, and then 40 mol. % of hexane was poured into the P3HT/toluene solution to generate a 0.005 wt. % P3HT suspension for the measurement of electronic absorption spectra and thin film deposition using EPD and DBEPD. The suspensions were prepared under an Argon atmosphere. Both EPD and DBEPD were performed in a dry box (RH < 12%). A Matsusada HAR5R30 dc power supply was used for voltage application.

Deposition substrates such as ITO glass and highly p-doped silicon wafers (0.1–1 S/cm) with a thermally deposited 100-nm-thick SiO_2 layer (SiO_2/Si substrates) were washed
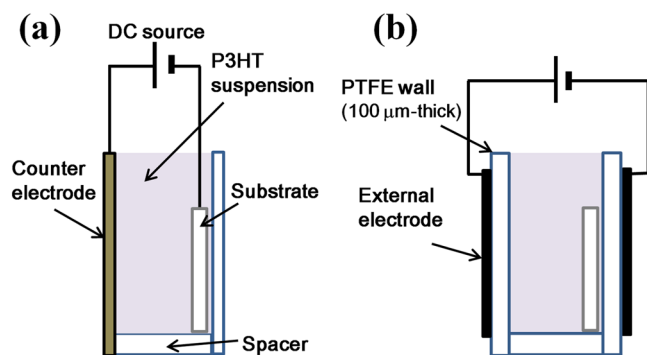
FIG. 1. Configuration of (a) EPD and (b) DBEPD systems.

FIG. 2. P3HT colloidal film deposited on ITO glass (a) and (c), and SiO₂/Si (b) and (d) using deposition methods like DBEPD (a) and (b) and EPD (c) and (d).

with methanol, chloroform, and toluene. The SiO$_2$ surface of SiO$_2$/Si was treated with an octyltrichlorosilane (OTS)/toluene solution as a standard procedure for fabrication of high performance organic field effect transistor (OFET).[14] All of the substrates were dried at 120 °C for 15 min after washing or surface treatment.

A platinum sputtered ITO glass with a 15×15 mm^2 conductive area was used as an anodic electrode. A substrate connected to the cathode of the dc source was separated by 4 mm from the anodic electrode. The space between the anodic electrode and the substrate was filled with approximately 1 ml of the suspension. The application of 300 V dc across the electrodes at room temperature deposited P3HT colloids onto the ITO and SiO$_2$/Si substrates.

The DBEPD system used in this study has 100-μm-thick PTFE walls. External electrodes with a 15×15 mm^2 area were fixed on the outer side of the PTFE walls. A 2 kV dc was applied between the external electrodes separated by 4 mm each other for deposition. In DBEPD, P3HT colloids were uniformly deposited onto the substrates when these substrates were located near the PTFE wall on the cathodic electrode side. Even without the substrates, the P3HT colloids were also deposited on the inner surface of the PTFE walls.

Figure 2 shows the P3HT colloidal film deposited on ITO-glass and SiO$_2$/Si substrates. DBEPD condition of a 2 kV/4 mm dc field for 3 min deposited P3HT film onto ITO glass (Figure 2(a)) and SiO$_2$/Si substrate (b) having a thickness of (246 nm). Meanwhile, EPD condition of a 300 V/4 mm dc field for 30 s also deposited P3HT thin films on ITO glass (c) and SiO$_2$/Si substrate (d) with the thickness of (241 nm). The P3HT included in 1 ml of the suspension was mostly deposited on SiO$_2$/Si substrate, resulting in a similar thickness using each method. This indicates that DBEPD and EPD can prepare films with higher material usage efficiency.

It is worth to mention that DBEPD deposited quite uniform film on both kinds of substrates under investigation, whereas EPD led to the deposition of relatively thicker films at the edges as compared to the center. This trend was strongly appeared to ITO glass due to an electric field concentration. Electric field generation via charging of insulator reduced the "edge effect" and contributed to fabricate the uniform film.

The deposition of the P3HT colloids onto the cathodic electrode implies that the P3HT colloids are positively charged in the suspens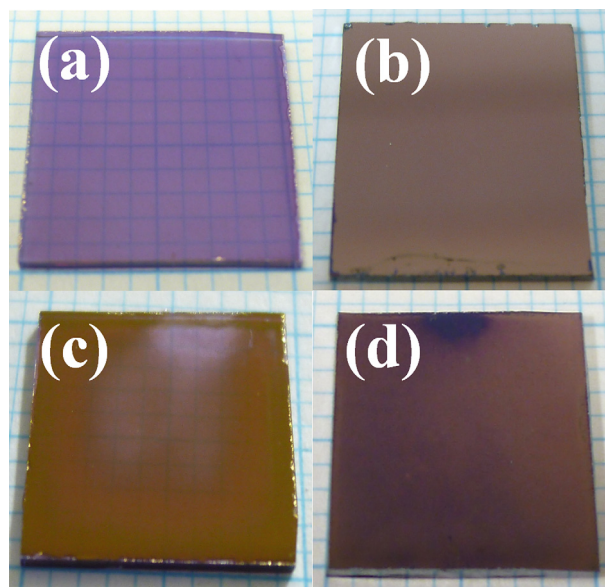ion. This result corresponds to a past study using acetonitrile (as poor solvent) for the deposition of a suspension of poly-alkylthiophene (PAT).[15] Positively charged carriers as well as holes in PAT may contribute to the charge of PAT colloids.

Figure 3(a) exhibits the UV-visible absorption spectra of 0.005 wt. % P3HT solution and suspension. The solution exhibited a broad absorption having absorption maximum near 450 nm, attributed to the π–π* electronic transition of widely distributed conjugation length of the dissolved P3HT chains. On the other hand, suspension exhibited three sharp peaks appearing at the 525, 560, and 610 nm with a small shoulder at 450 nm. Among them, absorption peak appearing at 525 nm is basically associated with the main π–π* electronic transition and this red shift as compared to solution is due to enhanced inter-molecular interactions. On the other hand, the two other peaks appearing at 610 and 560 nm can be assigned to 0-0 transition and a vibronic sideband,[16] respectively, associated with P3HT in the ordered state.[16,17] This vibronic coupling in the ordered state of P3HT is due to the inter-chain interaction involved in crystallization of P3HT by adding poor solvent. In addition, the sharp absorption peak at 610 nm which correlates well with the inter-chain interaction was proportional to the degree of crystallinity calculated from the integrated intensity of the (100) diffraction peak in wide-angle x-ray scattering profile.[18,19]

Therefore, the spectra indicate the suspension consisted of a mixture of mainly well crystallized (ordered domains) P3HT colloidal particles with a small amount of dissolved P3HT chains.

Figure 3(b) shows the absorption spectra of the films deposited on the ITO-glass by DBEPD and EPD. The DBEPD film showed well resolved vibrational structure corresponding to the suspension. Highly crystallized P3HT colloids were deposited onto the substrate keeping its degree of high crystallinity. In contrast, a blurred broad absorption structure was observed for the EPD film, which implies that unknown phenomenon caused disorder of the P3HT chain during EPD. For instance, heat possibly induces melting of the P3HT.[20]
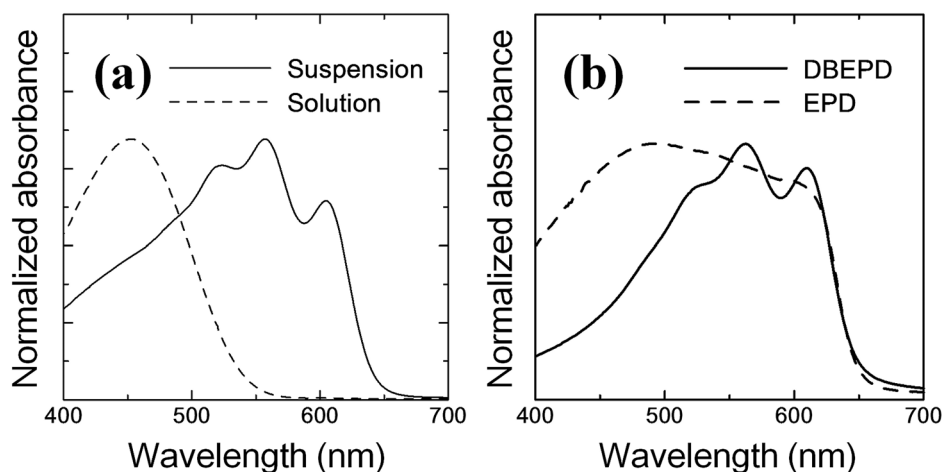
FIG. 3. UV-visible absorbance spectra of (a) in solution and (b) thin film prepared by the DBEPD (2 kV–3 min) and EPD (300 V–30 s) on ITO-glass.
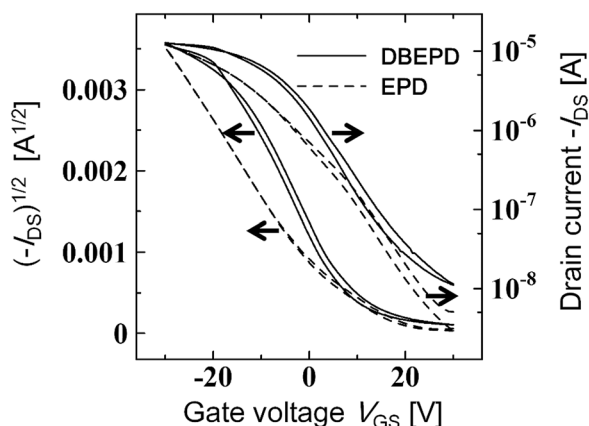

FIG. 4. Transfer characteristics of colloidal P3HT film deposited by DBEPD and EPD.

P3HT colloids would be easier to decrease the crystallinity than the solid film due to its huge surface area contacting with the solvent molecules. The high-impedance PTFE walls in DBEPD probably reduce the leakage current during high voltage application with blocking the conduction of Joule heat from the electrodes. This feature of DBEPD has a great advantage in fabrication of the film, which combines the best properties of high crystallinity and uniformity with improving safety of EPD. Relationships between crystallinity and uniformity of the EPD film are shown in supplemental material.[25]

Top-contact OFETs were fabricated by each method. Accordingly, 40-nm-thick gold source–drain electrodes were deposited onto P3HT films by thermal evaporation at 4.5 $\times 10^{-6}$ Pa. The channel length and width were 20 μm and 2 mm, respectively. OFET measurements such as the drain current-gate voltage (I_{DS}-V_{GS}) characteristics were performed under vacuum ($<10^{-6}$ Pa) using a Keithley 2612 A source meter.[21]

Figure 4 shows plots of I_{DS} vs $-V_{GS}$. Field effect mobility, on/off ratio, and threshold voltage V_{th} calculated by the plots[22] were typically 8×10^{-3}, 3200, and 10 V using DBEPD, which were relatively better as compared to those using EPD (5×10^{-3}, 4100, and 12.7 V, respectively) Indicating that the characteristics of EPD film on SiO_2/Si is similar to the DBEPD film. SiO_2 insulator would reduce the Joule heat just like the

PTFE sheet of DBEPD. In spite of having enhanced crystalline domains, the increase in the mobility of P3HT colloidal films was relatively small as compared to that spin coated films which has been reported thus far. A large number of grain boundaries around particles may strongly resist the carrier transport.[23,24]

In summary, an electrophoretic deposition method mediated by the presence of intervening dielectric layers (DBEPD) has been developed. DBEPD performed thin film deposition even on insulating substrates with high material usage efficiency. Photographs of deposited films exhibit that DBEPD was able to fabricate uniform film, whereas EPD led to the fabrication of non-uniform film due to the edge effect. A comparison of UV-vis absorption spectra of P3HT suspension and deposited colloidal films indicates that the film prepared by DBEPD kept the resolved vibrational structure of suspension. We suspect that the Joule heating from leakage current during EPD decreased the crystallinity of P3HT colloids. Finally, DBEPD is essentially safe process compared with conventional EPD. Continuing investigations into DBEPD should further expand EPD applications for advanced industrial processes.

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[25]See supplementary material at http://dx.doi.org/10.1063/1.4766126 for confirming the trade off relationships between crystallinity and uniformity of the EPD film.