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ELECTRICAL AND MORPHOLOGICAL PROPERTIES OF INKJET PRINTED PEDOT/PSS FILMS

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ABSTRACT

Organic solar cells and LEDs are becoming more popular because their low cost materials, potential manufacturability, and recent gains in efficiency make them feasible for widespread commercialization in the near future. One significant manufacturing problem, especially for OLEDs, is the cost associated with creating patterned devices with spatially non-specific deposition methods such as spincoating. Inkjet printing can remove this problem. In recent years, inkjet printed polyethylene(3,4-dioxythiophene)/ polystyrene sulfonate (PEDOT/PSS) has been incorporated into many organic devices to help charge transfer, but there has not been much research regarding the effect of different printing parameters on the electrical and morphological film properties. In this work, an atomic force microscope, four point probe, and Kelvin probe were used to study the effects of printing parameters on roughness, conductivity and workfunction. Inkjet printed PEDOT films were also compared to spincoated films to determine how the polymer deposition method affects the above properties. Generally, inkjet printing created rougher but more conductive films with a smaller workfunction. Additionally, it was demonstrated that the workfunction of PEDOT films could be tuned over a range of about 0.5 V by changing the solvent mixture or substrate surface pretreatment. All additives to the as received PEDOT/PSS suspension caused the workfunction to decrease. It was discovered that workfunction decreases as printing voltage increases, but the trend reverses after annealing the films. This phenomenon suggests that when DMSO interacts with PEDOT, the workfunction changes. Finally, the results support previous publications suggesting that DMSO increases conductivity through a screening effect and also by changing the distribution of PEDOT and PSS in the film.

INTRODUCTION

In the last several years, there has been increasing interest in organic electronics due to their low cost materials, high theoretical efficiencies, and potential manufacturability [1, 2]. Examples of organic devices range from capacitors and organic photovoltaics (OPV) to organic light emitting diodes (OLEDs)[3-5]. A recent review of manufacturing costs in organic electronics concluded that

while organic devices may not become widespread in all areas of electronics, OLEDs and OPVs have enormous potential to penetrate their respective markets[2]. However, there are significant basic and manufacturing hurdles, particularly patterning issues, to overcome before organic devices can become widespread[2].

This paper reports on the use of inkjet printing as an alternative deposition technique to spincoating for OPVs and OLEDs. Even though spincoating is an inexpensive, fast and easy way to deposit

liquid precursors for organic devices, it has several major drawbacks. First, it wastes a large amount of the material. In any manufacturing process, it is preferable to waste as little as possible both for cost and disposal reasons. Perhaps a more pressing issue, is that spincoating is extremely non-specific. In other words, it is fine for coating entire surfaces, but it provides essentially no spatial resolution, which is a serious problem for electronics. Currently, lithography is used to preferentially remove the coating where it is not wanted, but this adds equipment and multiple steps to the manufacturing process, increasing cost. Also, as more complicated 3-D structured devices with more layers are required, it will become increasingly difficult to develop effective lithographic techniques. Inkjet printing has the potential to remove all of these disadvantages. It allows deposition only where desired, which minimizes wasted material and eliminates the need for extra lithographic steps. In theory, each layer of an organic device could be printed in rapid succession using different inkjet heads, which allows for effective large-scale production. Thus, inkjet printing offers a major advantage over other deposition techniques.

Contacting active polymer layers in organic optoelectronics is not a simple process and interfacial properties are critical to device performance[6]. The copolymer polyethylene(3,4-dioxythiophene)/polystyrene sulfonate (PEDOT/PSS) is currently one of the most used organic transparent conductors for making these contacts[7]. While inkjet printing has been used to deposit PEDOT/PSS for electronic devices, there has been no known study regarding the effect of inkjet printing on the electrical and morphological properties of PEDOT/PSS films[3-5, 7, 8]. This study examined the conductivity, surface roughness, and workfunction of inkjet printed PEDOT/PSS films in order to gain a better understanding of the effect of printing parameters such as solvent, temperature and voltage.

MATERIALS AND METHODS

For all experiments, the polymer Baytron P HCV2 from Bayer was employed as an aqueous suspension of PEDOT/PSS, which from now on will be referred to simply as PEDOT. It was printed both as received and diluted with various solvents. All dilutions were done by mass and for simplicity, when referring to the mass percent of PEDOT, we include the water contained in the Baytron suspension. The actual solid content in the aqueous suspension is 1.1-1.4% according to the manufacturer. Ethyl alcohol (ethanol) was 190 proof general use HPLC-UV grade from Pharmco; dimethyl sulfoxide (DMSO) was B&J brand high purity solvent from American Scientific; the surfactant used (only where specifically mentioned) was Surfynol 2502 from Air Products. Solutions were filtered with the smallest nylon filter for which the suspension remained stable, either 0.2, 0.45 or 2.7 μm , before being used for printing to avoid clogging the inkjet head. The piezoelectric inkjet head, Teflon tubing, connectors, and holder were supplied by MicroFab and controlled by a Gateway Pentium III computer using LabView. The substrates were Fisherbrand plain glass microslides and were translated using a Newport X-Y stage controlled by a Newport Universal Driver programmed in LabView. Substrates were pre-cleaned using either a water and ethanol rinse, or a 10 min sonication

in isopropanol followed by oxygen plasma cleaning for 5 minutes at about 157 watts power and approximately 0.57 torr oxygen pressure. Films were printed within a few hours of the cleaning procedure. Printing temperatures refer to the metal heating element directly below the substrate. Since glass is not a good thermal conductor, the actual substrate surface could be significantly lower than the programmed temperature. However, for all experiments substrates were placed on the heating element several minutes before printing in an attempt to produce consistent results.

Sheet resistances were measured using a Signatone four point probe connected with a Keithley programmable current source and system DMM. Film thickness was determined using a Dektak profilometer and surface roughness was determined using a Park Scientific atomic force microscope (AFM) with a 100 μm stage in contact mode. The relative workfunction of various films were compared by measuring their contact potential difference (CPD) with a McAllister Technical Services KP6500 Kelvin probe. A more negative contact potential difference translates to a larger workfunction (further from vacuum). The uncertainty in the CPD was set at 0.1 V, which was the maximum variation seen in the calibration Indium Tin Oxide (ITO) standard throughout the entire study.

RESULTS

Initial work focused on the printing of as received PEDOT to determine nominal thickness, roughness, and conductivity to use as control to compare against all other ink permutations. Compared to typical spincoated films (literature and this work), the initial inkjet printed films of PEDOT were significantly thicker and rougher but more conductive (Table 1). Since the desired thickness for the PEDOT layer in OLEDs and OPVs is between 80 and 150 nm all subsequent printing was performed with diluted solutions[9]. This also allowed us to easily see the effect of modifying the solvent and additives. As expected, film thickness scaled roughly to the PEDOT content. Diluting the PEDOT with water did not have a significant effect on the film's roughness or conductivity (Table 1).

DMSO was added to the PEDOT films to see if it would increase the conductivity. This effect has been recorded previously with spincoated films, although the mechanism is still under some debate [10, 11]. An addition of 5% DMSO increased the conductivity by approximately a factor of 10 (Table 1). Adding DMSO caused the ink droplets to bead up and made printing films difficult. This effect was thought to be from an increase in surface

Sample description	Thickness (nm)	Roughness (nm)	Conductivity (S/cm)
Inkjet Printed PEDOT	350	8-10	4.3
Spincoated PEDOT	160	3	3.1
Inkjet - 1:1 PEDOT/water	150	10-12	4.7
Spincoat - 1:1 PEDOT/water	60	3	3.7
Inkjet - 1:1 PEDOT/water +5% DMSO	300	Very rough and non-uniform	33
Inkjet - 1:1 PEDOT/water + 5% DMSO +1% Surfynol	300	31	51
Inkjet - 1:1 PEDOT/water + 1% DMSO +1% Surfynol	180	25-28	31

Table 1. Properties of various inkjet printed and spincoated films.

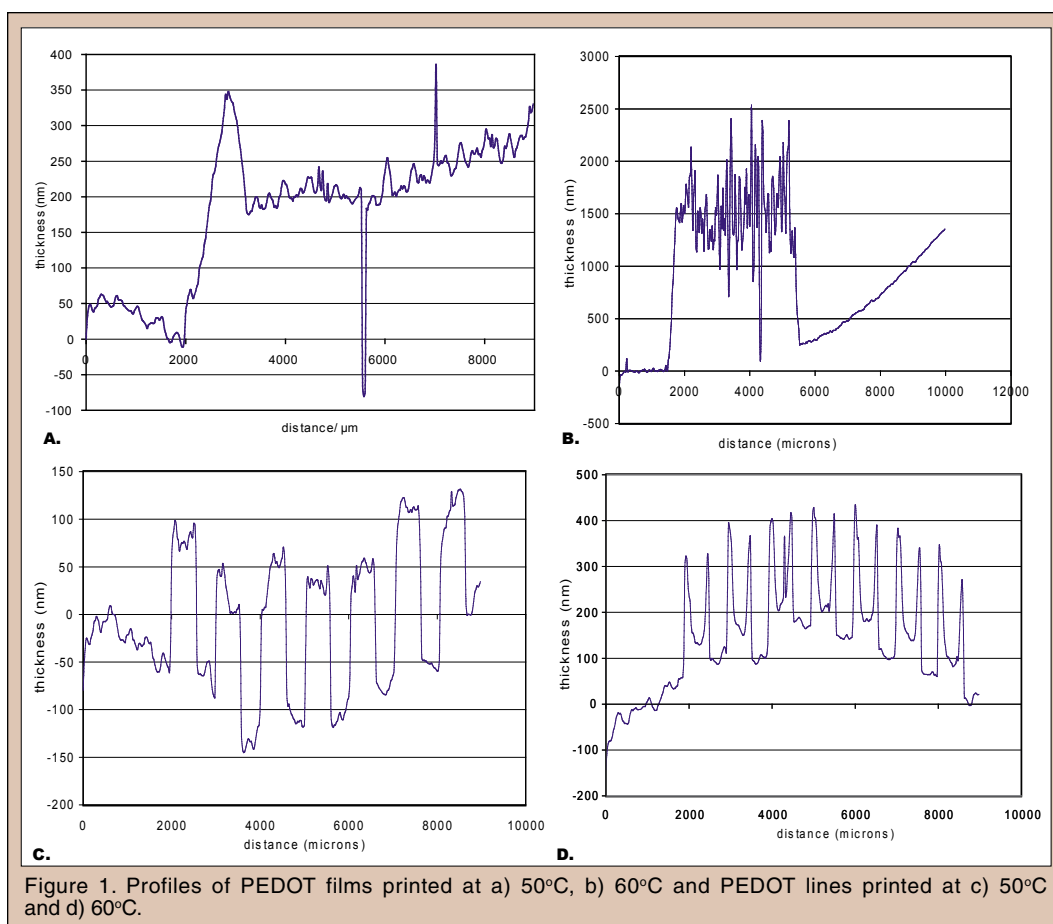


Figure 1. Profiles of PEDOT films printed at a) 50°C, b) 60°C and PEDOT lines printed at c) 50°C and d) 60°C.

tension, so the surfactant Surfynol 2502 was added to the ink to lower the surface tension and facilitate spreading. This addition not only created visibly more uniform and smoother films, but also increased conductivity by a factor of about 1.5 (Table 1). When Surfynol was used alone, it still increased conductivity, but also increased roughness (Table 1). Overall, adding DMSO also increased the roughness by about a factor of 2-3 (Table 1).

Several inkjet printing parameters were explored in an attempt to create smoother films. It was found that increasing the substrate temperature increased film roughness and thickness (Fig. 1). Increasing printing voltage also increased film roughness and thickness. The printing voltage could not be tested above 90V because of concerns about damaging the jet and below 30V most solutions would not print reliably. Printing frequency (drops per second) was held constant at 800 Hertz throughout all experiments and thus it is not known how that parameter affects film characteristics.

The workfunction of PEDOT films is an important consideration for making contact in organic electronic devices, so its sensitivity to solvent and printing parameter was explored. It was found that workfunction could be tuned over a range of about 0.5 V simply by adjusting the solvent mixture or changing the surface pretreatment (Fig. 2). There were several key results. First, pre-treating the glass surface with oxygen plasma increased the workfunction by a little over 0.1 eV. Secondly, inkjet printed PEDOT films had a smaller workfunction than spincoated films from the same solvent. Thirdly, addition of various solvents and surfactants including ethanol,

DMSO, and Surfynol all reduced the workfunction. Fourth, for PEDOT diluted only with water, the printing voltage had no effect on workfunction, but when DMSO and Surfynol were added, as the printing voltage increased, the workfunction decreased (Fig. 3). After annealing the films containing DMSO and Surfynol, this effect reversed (Fig. 4). Finally, it was found that varying the DMSO concentration between 1 and 5% or varying the Surfynol concentration between 0.33 and 1% had no appreciable effect on the workfunction.

DISCUSSION AND CONCLUSION

From Table 1 it is clear that there is a difference between inkjet printed and spincoated PEDOT films. The difference in thickness

can reasonably be attributed to the fact that all of the deposited material in inkjet printing remains on the substrate to form a film. A small increase in roughness may be expected from the longer drying time, which allows the material to agglomerate and couples to possible uneven solvent evaporation. However, a four-fold increase probably cannot be explained by this phenomenon alone. From microscope images, inkjet films had visible "pot holes" while individually printed lines did not. This suggests that subsequently printed lines somehow roughen the previous lines. We suspect that this is from micro-splashing that occurs when the droplets hit the substrate surface, although it may also be caused by the burst of air accompanying each droplet. As mentioned earlier, increasing voltage also increased roughness, which would be expected from either of the two previous explanations, because a higher printing voltage essentially translates to a faster droplet ejection. If splashing is the main problem, then incorporating highly dynamic surfactants with the ink should help reduce the roughness. This will be explored in future research. It is also possible that the above mentioned effects could be explained by charged droplet interactions. However, if this were the case, we would expect to see little or no difference in roughness between individually printed lines and printed films, which does not fit with the results.

The increased conductivity of the inkjet versus spincoated films is not entirely understood, but may be due to preferential polymer alignment or orientation that occurs with the longer drying time. Attempts to look at surface ordering of the films to confirm this hypothesis were inconclusive, but the smaller workfunction for

inkjet compared to spincoated films also supports a more ordered film. It is also possible that the coordination of PEDOT to its stabilizing copolymer PSS, or the distribution of the two is different in inkjet printed versus spincoated films, which may explain both the conductivity and workfunction effects. Several groups have reported that spincoated PEDOT/PSS films are phase separated with a lower ratio of PEDOT to PSS near the surface than in the bulk film [10, 12]. In particular, Jonsson et al. found that as they increased the surface ratio of PEDOT through addition of solvents, they also increased the conductivity [10]. It is possible that inkjet printing mixes the copolymers more effectively than spincoating, which would produce a higher surface ratio of PEDOT to PSS compared to the spincoated films. Compositional analysis of the films was not performed, but would be necessary to confirm this hypothesis. It is also possible that inkjet printing creates more ordered films by promoting the formation of micro-spheres representing different droplet domains. Upon annealing, these domains might be mixed or destroyed to create a more disordered film.

Figure 1 shows that there is a dramatic difference between PEDOT films printed at 50°C and 60°C. Looking at the single lines of PEDOT printed at the two temperatures, it is clear that the increased roughness and film thickness that accompany the higher temperature are caused by a difference in drying dynamics. At higher temperature, when the solvent evaporates more rapidly, suspended material conglomerates at the edges of the line. As the film is printed line by line, these differences become even more exaggerated leading to a very rough film. This supports that to achieve the smoothest film, it is preferable to maintain a low printing temperature or to control the solvent removal kinetics, such as with surfactants.

As noted earlier, the increase in conductivity of PEDOT films with the addition of DMSO has been well documented but the

mechanism is still uncertain. However, an increase in conductivity from adding Surfynol has not to our knowledge been previously reported. This effect was initially presumed to be due to better connectivity between adjacent lines of the film, caused by the increase in spreading. However, films without Surfynol showed equal sheet resistance along the axis of the printed lines and in the direction perpendicular to the lines, which would not be expected if there were poor connectivity between lines. Since Surfynol is a surfactant, composed of a long chain ester, it is not likely to be acting as a dopant; rather, it probably acts as a dispersing agent, mixing the PEDOT and PSS more thoroughly. This explanation is corroborated by the fact that adding Surfynol to a pristine PEDOT suspension increased the conductivity by about a factor of 1.5 (Table 1).

If Surfynol does in fact change the PEDOT film morphology by acting as a mixing agent, then it would not be surprising to see a change in the film's workfunction. Interestingly, Surfynol and DMSO seem to have an equal effect on the film's workfunction despite the fact that DMSO has a much greater effect on conductivity (Fig. 3, Table 1). Actually, as mentioned earlier, the amount of DMSO and Surfynol did not affect the workfunction – their presence at all tested levels caused a significant decrease in workfunction. However, workfunction is not simply a function of the conductivity of a film. Like DMSO and Surfynol, addition of ethanol decreased the workfunction, but unlike the other additives, the presence of ethanol decreased the conductivity. Therefore, we suggest that there are at least two different effects: the uniformity of PEDOT throughout the film, and some other phenomenon, possibly an interaction of the PEDOT with the DMSO, both of which may affect the conductivity and workfunction of the film. The similarity of effects from surfynol and DMSO may imply that DMSO acts like a surfactant for the polymer mixing but not for wetting the substrate.

There are several results that may help elucidate the unknown phenomenon mentioned above. First, increasing the printing voltage did not significantly alter the workfunction of the PEDOT film diluted in water, but it did cause a decrease in the workfunction for the films containing DMSO. Voltage did not seem to have a consistent effect on films with only Surfynol (Fig. 3). These results suggest that DMSO may have stronger interactions with PEDOT as the voltage increases, reducing the workfunction. Stronger interactions mean DMSO would be incorporated more completely into the film at higher voltages, which seems reasonable since a higher voltage causes a stronger impact of the ink with the substrate, causing more thorough mixing. A second result is that after annealing films containing DMSO at 180°C for 10 minutes, the workfunction trend reverses (Fig. 4). Since adding DMSO reduces the workfunction, the augmented workfunction upon annealing suggests that DMSO is being driven out of the film – reasonable given the boiling point of DMSO is 189°C. The post-anneal workfunction trend is also reasonable, since the films with weaker DMSO-PEDOT interactions (lower printing voltages) should not be affected much by DMSO leaving.

It is important to note that after annealing the PEDOT/DMSO/Surfynol films, the sheet resistance went up by about a factor of two. This increase was fairly consistent across the printing voltage range, which suggests that the conductivity of a film is not affected by

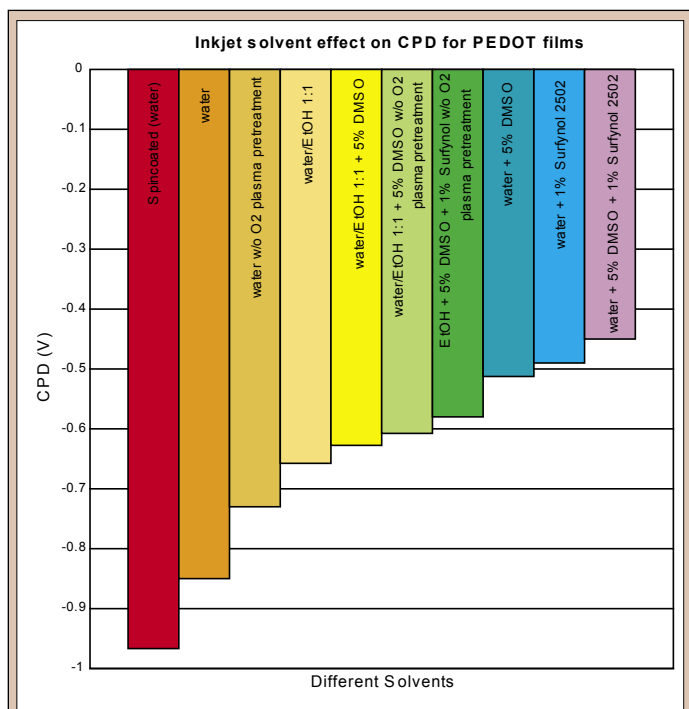


Figure 2. Contact Potential Difference (CPD) of 50% PEDOT films printed under identical conditions with various solvents and substrate pretreatments.

the strength of PEDOT-DMSO interactions. Since the conductivity of a film is moderately affected by the DMSO concentration (Table 1), it is likely that strength of PEDOT-DMSO interactions and DMSO concentration are not related. In other words, increasing the DMSO concentration will not necessarily increase the PEDOT-DMSO interactions. This agrees with previously discussed results, which showed that increasing the DMSO concentration had no effect on the workfunction, while strengthening the PEDOT-DMSO interactions by increasing the printing voltage did affect the workfunction.

Finally, it is important to note that annealing DMSO doped films creates two conflicting effects. First, it has been shown that annealing PEDOT films generally increases conductivity by increasing the PEDOT to PSS surface ratio as discussed earlier [10, 12]. It has also been suggested that the presence of DMSO itself has a significant effect on conductivity, independent of film morphology [11]. Considering the above, and the fact that annealing the films increased sheet resistance, we can conclude that the presence of DMSO affects conductivity more than the film morphology.

In conclusion, inkjet printed PEDOT films are more conductive, rougher, and have a smaller workfunction than spincoated films. It was suggested that these differences arise from a better mixing of PEDOT and PSS in inkjet printed versus spincoated films. Additionally, the increase in conductivity when DMSO is added to spincoated films also is seen in inkjet printed films. Furthermore, the surfactant Surfynol was observed to also increase the conductivity of PEDOT films to a lesser extent than DMSO, while affecting the workfunction in a similar manner. The changes in film properties after annealing various films suggest that DMSO increases conductivity both by the screening effect and by altering the film morphology. These same experiments coupled with the fact that DMSO concentration does not affect workfunction, suggest that the strength of PEDOT-DMSO interactions increases as printing voltage increases, which in turn causes the workfunction to go down. Finally, the workfunction of PEDOT films can be tuned over a range of about 0.5 V by altering the solvent mixture and substrate surface pretreatment. This is a very important result because it may allow for energy level matching with a variety of different (even yet undiscovered) light emitting or absorbing polymers for OLEDs and

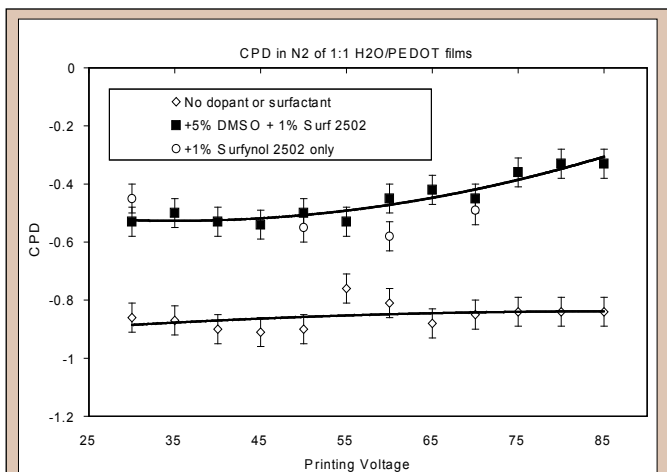


Figure 3. CPD as a function of printing voltage for PEDOT films using various solvent systems.

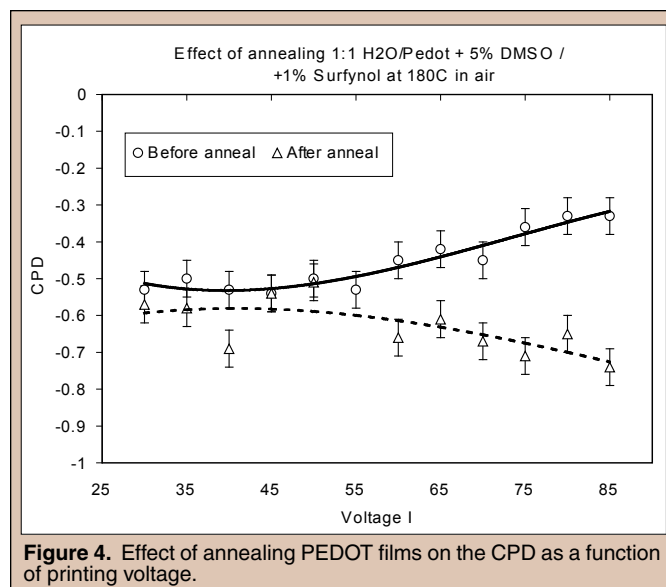


Figure 4. Effect of annealing PEDOT films on the CPD as a function of printing voltage.

OPVs. This work clearly demonstrates the viability of inkjet printing of PEDOT with the inherent advantages of patterning, efficient materials usage and 3-D structure development. Future work will focus on examination of other surfactants and additives with lower boiling points and better wetting properties.

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