

Low-cost Solar Cell Fabrication by Drop-on-Demand Ink-jet Printing

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Abstract

This paper presents an ink-jet printing process that makes the manufacturing of polymer solar cells a viable, low-cost alternative to expensive, conventional silicon-based solar cells. The process involves printing thin films of a conductive polymer and an organic bulk-heterojunction (BHJ) materials such as conjugated polymer-fullerene derivative blend onto ITO coated glass or flexible plastic substrates, and sandwiching the two polymer layers between an anode and cathode to generate electricity when exposed to sunlight. Ink jet-printing uses a very minute amount of expensive BHJ materials making it a low-cost method that can be used for printing on flexible, plastic substrates as well as rigid substrates.

Key words: Drop-on-demand ink jet printing, organic solar cells, and organic bulk heterojunction materials.

Background on drop-on-demand inkjet printing

In the 1950's, Hansell observed the production of drops by electromechanically induced pressure waves [1]. In this type of system, a voltage pulse applied to a piezoelectric material that is directly or indirectly coupled to the fluid induces a volumetric change in the fluid. This volumetric change creates pressure/velocity transients within the fluid that are directed to produce a drop from an orifice [2].

Two broad approaches are typically utilized for ink-jet printing of materials for manufacturing applications. In "Continuous, Charge and Deflect" [3] ink-jet printing technology, illustrated in **Figure**

1, fluid under pressure issues from an orifice, typically 40-60 μm in diameter, and breaks up into uniform drops by the amplification of capillary waves induced onto the jet, usually by an electromechanical device.

The drops are electrically charged and deflected by the charging and the deflection field respectively, to their desired location, either to the catcher or one of the several locations on the moving substrate. This approach is suitable for high-speed coverage of relatively large areas since drops up to 0.5mm in diameter may be generated at rates up to 1 MHz.

A more widely used and simpler approach for smaller drop (20-100 μm), lower frequency (up to

Continuous Ink-Jet Technology

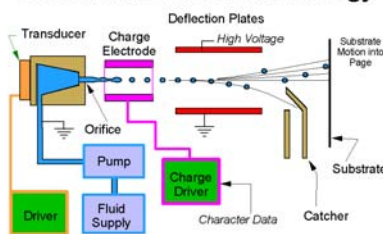


Figure 1 Continuous, Charge & Deflect ink-jet system.

Demand Ink-Jet Technology

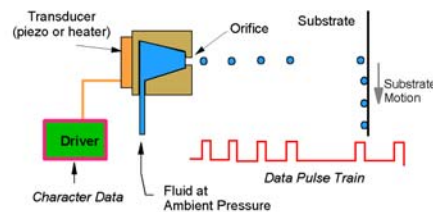


Figure 2 Drop-on-Demand ink-jet system.

20KHz) printing applications is the “Drop-on-Demand” (DOD) technology shown in **Figure 2**. In DOD, a drop is only ejected from the device orifice when a voltage pulse is applied to a transducer. Since the fluid at ambient pressure in the device is coupled to the transducer, the acoustic waves generated by application of an electrical pulse eject a drop from the device orifice. The DOD device produces drops that are approximately equal to the orifice diameter of the droplet generator [4].

Solar cell structure and its functioning mechanism

A typical solar cell structure using organic bulk heterojunction materials looks such as the one shown in **Figure 3**. Here ITO coated (160nm) glass

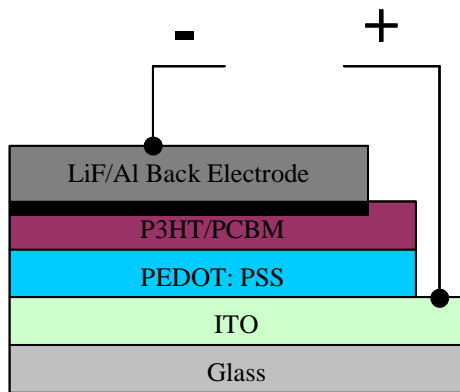


Figure 3 A Typical layered structure of organic solar cell.

or flexible plastic substrate is ink jet printed with poly(3,4-ethylene dioxythiophene)-poly(styrenesulfonate) to a thickness of about 100nm to facilitate hole conduction, and also to smooth the relatively rough ITO layer, which prevents short circuits in the solar cell. Next, a bulk heterojunction polymer-fullerene blend containing poly(3-hexylthiophene) in its regioregular form as electron donor and a fullerene derivative ([6,6]-Phenyl C₆₁ – butyric acid methyl ester) as electron acceptor is ink jet deposited to a thickness of about 100nm. Next, a 10Å⁰ layer of LiF is evaporated onto the photoactive polymer-fullerene layer to reduce the interface barrier for electron injection. Finally aluminum (100 nm) is vacuum evaporated onto LiF to form the back electrode to complete the solar cell device fabrication.

The asymmetry of the work functions between the cathode and the anode creates an internal electric field such that the holes move toward the ITO layer and the electron towards the aluminum cathode.

By externally connecting the electrodes a current can be generated.

Solar cell BHJ materials

There are a number of BHJ materials researchers have tried in order to print organic solar cells. Those commonly used and reported are:

1. MDMO-PPV (poly(2-methoxy-5-(3',7' - dimethyloctyloxy)-1,4-phenylene vinylene) and [6,6]-PCBM (6,6-phenylC₆₁-butric acid methyl ester).
2. poly(3-hexylthiophene) in its regioregular form as electron donor and fullerene ([6,6]-Phenyl C₆₁ – butyric acid methyl ester) as electron acceptor.
3. Inorganic-organic hybrid dispersion of Cadmium selenide (CdSe) nanorods in poly(3-hexylthiophene) in its regioregular form.

Printing patterns and strategies

A variety of patterns can be printed using drop-on-demand (DOD) ink jet process. The most commonly used patterns for printing thin films are lines, arrays and array of arrays. There are two modes used in DOD ink jet printing. They are print-on-position (POP) and print-on-fly (POF). In POP, stage(s) move and stop at each target location, then precise number of drops is dispensed before the stage(s) move to the next target location. In POF, drops of material are dispensed as the stage(s) underneath move. Here, the stage speed and spacing between the drop locations determine the rate of dispensing. While the POP is more accurate in terms of drop placement it is much slower than POF, which can enable significantly higher throughput with very little penalty in drop placement accuracy.

All our printing experiments were performed using POF mode. In either print mode, drops can be placed in non-interlaced or interlaced schemes. In a non-interlaced printing scheme, drops are placed sequentially and usually with some degree of overlap between two adjacent drops creating one smooth line. This is repeated across the whole printing area by printing successive lines with some degree of overlap to create one solid area of a thin film. In an interlaced printing scheme, alternate drops are dispensed within a line and alternate rows of lines are printed in the first pass of printing. In the second pass, printing begins with an offset filling the area between the printed drops and printed lines, creating one continuous thin film. The difference comes in the amount of time allowed for the material to spread and

dry before the next drop or line is printed. Depending on the solvent and material being printed one scheme may produce better results than the other. A matrix of experiments was generated using print modes and print schemes for a given set of materials as discussed below.

Substrates

All glass substrates were cleaned similarly. First, each substrate was cleaned with a cleaning detergent in an ultrasonic bath for 30 minutes, rinsed with DI water, and then sonicated for 15 minutes using filtered isopropyl alcohol (IPA). Each substrate was further cleaned using O₂ plasma before printing. O₂ plasma treatment alters the contact angle of PEDOT on ITO coated slides, making it less wetting.

75mm x 25mm uncoated glass substrates were used for dispensing experiments. Each was cleaned as described above and placed in the printing station. The most important goal was to obtain uniform thin films.

PEDOT

PEDOT (1.3% solids) acquired from Sigma-Aldrich Chemical Company was mixed in dilutions ranging from 1:0.5 to 1:1.33 of PEDOT to DI water. For initial printing tests a 1:0.75 solution was used. The optimum dilution was found to be 1:1.33 of PEDOT to DI water for printing onto ITO at 50°C with a 82- μ m spot pitch. By varying the rise and fall time, dwell time, and voltage settings an optimized waveform was discovered. A target velocity of 2m/s was sought for a given PEDOT solution.

PEDOT printing

Having discovered an optimized waveform and PEDOT to DI water ratio, PEDOT was printed on both plain glass slides and ITO coated 25mm square glass substrates. **Figure 4** shows printed PEDOT film on glass at room temperature. It does show that it is thicker where lines overlap.

PEDOT on glass

After dispensing onto cleaned glass, the samples were examined using a DekTak profilometer to acquire data regarding surface uniformity. Scans indicated that PEDOT on glass showed a distinct row pattern as indicated by a series of peaks and troughs in the scan graphic. To minimize this effect, the substrate was heated and a series of tests were conducted to find the optimum temperature to



Figure 4 PEDOT on glass at room temperature.

stabilize the PEDOT fluid boundary after it was dispensed onto the glass. Ultimately, heating the substrate to 50°C provided optimum PEDOT film quality.

PEDOT on ITO

Different pitches and dispensing patterns were explored at 50°C to find the optimum set of dispensing parameters. The optimum pitch was found to be 82- μ m in both x and y direction of printing.

After many experiments, an array of arrays print recipe was selected where a PEDOT was dispensed in interlaced scheme where alternating rows through the pattern and alternating drop locations within the pattern were printed. The second array was printed similarly, but offset by the radius of the printed drop. At temperature of 50° C, this pattern offered the most uniform PEDOT coating on ITO/glass as analyzed by AFM and shown in **Figure 5**. **Figure 6** shows the quality of a PEDOT film right after printing and annealing at 200° C for 5 minutes.

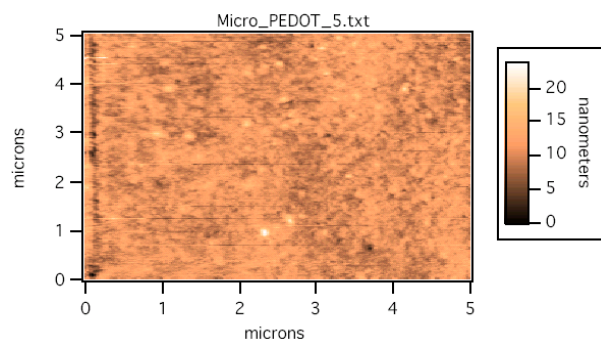


Figure 5 AFM image of PEDOT layer on ITO/glass; surface roughness (rms) is 1.7 nm.

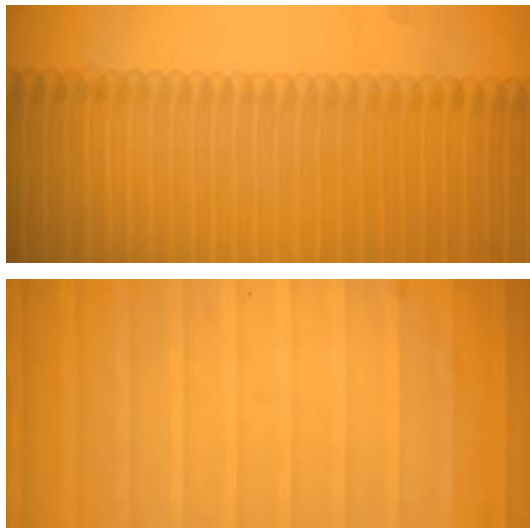


Figure 6 Printed PEDOT at 50°C. Above: note excellent edge alignment. Below (zoom): note line-to-line coverage.

P3HT on PEDOT

After a PEDOT layer was successfully printed the photoactive polymer-fullerene layer followed. The electron-donating component of the BHJ material system is P3HT. When combined with an electron acceptor such as PCBM, a photovoltaic



Figure 7 A portion of P3HT layer onto glass at 25°C.



Figure 8 A portion of P3HT layer at 25°C onto PEDOT layer.

layer is created. **Figure 7** shows a portion of printed P3HT layer on glass at 25°C. After finding the optimum waveform, P3HT was printed onto prepared PEDOT layers on ITO/glass as shown in **Figure 8**. P3HT behaves similarly as PEDOT in that it aggregates at the edges of drops and printed lines. Favorably, however, P3HT also stabilizes when dispensed onto a heated substrate.

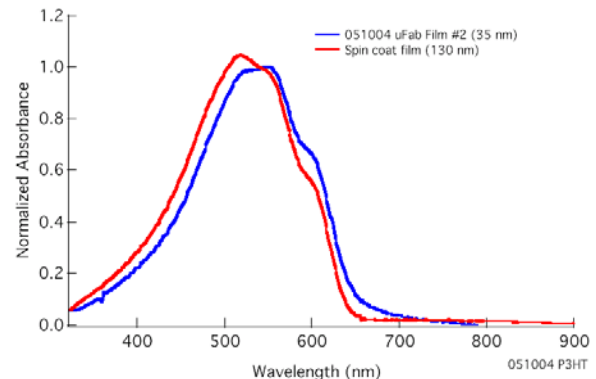


Figure 9 Comparison of absorption spectra of thin films of P3HT made by ink jet printing and spin coating.

After testing a range of temperatures and printing patterns, 60°C was chosen with an alternating dispensing pattern. **Figure 9** shows the normalized absorption spectra of P3HT films produced by ink jet printing and spin coating. They are clearly comparable.

Solar cell device printing

The complete organic photovoltaic devices were fabricated on 25mm square ITO/glass substrates. The patterning of the device area was performed by depositing SiO insulating layers onto the ITO to define a center strip 3 mm wide. **Figure 10** shows a cross-sectional drawing of the patterned



Figure 10 Cross-section of layered (partial) PV structure.

device. A 5x20mm patch of PEDOT was printed over the exposed 3mm wide central strip of ITO/glass. Over the PEDOT, polymer-fullerene (P3HT:C₆₀) blend was printed. Top aluminum cathodes were then deposited at NREL to define a device area of 0.45 cm². Devices were characterized for their J-V properties under AM1.5 simulated solar illumination.

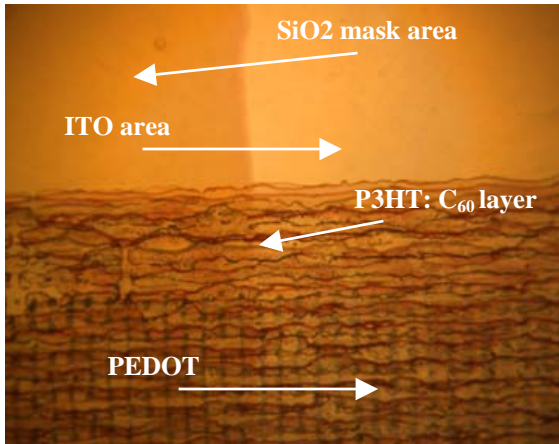


Figure 11 A section of printed device.

Figure 11 shows a top view of different overlapping



Figure 12 A completed photovoltaic device on ITO/glass.

layers of the device after printing, but without the Al cathode. Figure 12 shows a completed solar cell device with the cathode as back electrode.

Results

A small but measurable photo-voltage (360 mV) and photocurrent (0.005 mA/cm²) were

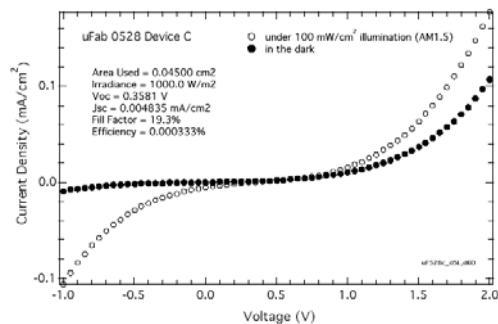


Figure 13 The current-voltage curves in light (open circles) and in the dark (closed circles) for polymer/C₆₀ photocell. Efficiency is 0.0003%.

measured in the devices. Reasons for the low values are primarily due to the use of fullerene C₆₀, which tends to crystallize readily in films. It is expected that significant increases in device performance will be obtained when the fullerene PCBM (a derivative of fullerene) is used in place of C₆₀, and when the film quality of printed materials is improved further. This improvement can be expected by optimizing parameters such as the solvent used, the substrate temperature, and possibly the incorporation of surfactants in the solution to enhance the wetting properties of the micro-drops when they impact the substrate surface. Figure 13 shows the result of J-V characterization under AM1.5 simulated solar illumination.

Conclusion

An ink-jet printed organic solar cell is feasible though fullerene C₆₀ is not the preferred component of BHJ material system for manufacture of organic solar cells. Fullerene derivative PCBM the material of choice was not available at the time of final print experiments. C₆₀ was difficult to initially disperse in the P3HT solution and keep dispersed during printing. Further, use of C₆₀ caused some undesirable aggregation along the print row edges as shown in Figures 14 and 15. This was slightly remedied by overprinting the material in order to fill

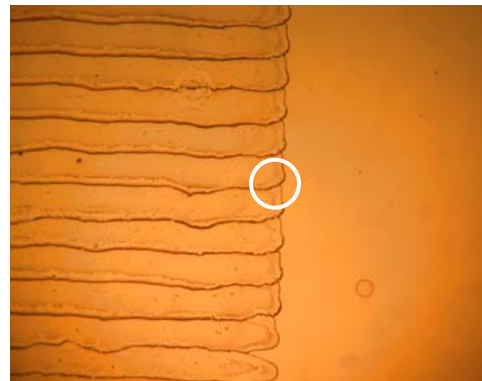


Figure 14 P3HT: C₆₀ blend printed onto ITO at 60.

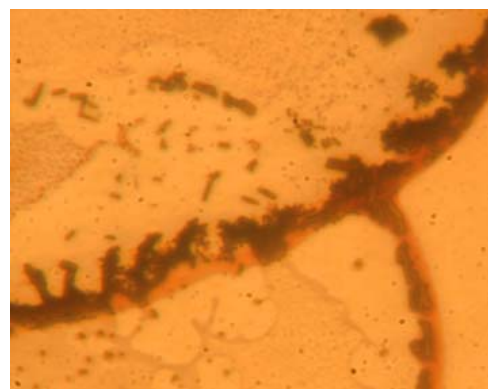


Figure 15 Zoom from Figure 14, note aggregation at edges.

the gaps caused by edge aggregation. Also, the final step of evaporating electrode onto the polymer-fullerene blend did not take place right after printing it. Collaborators at NREL agree that had PCBM been available at printing, a higher efficiency solar cell would have been possible.

We strongly believe further research using PCBM will yield much better results. The improvements in efficiency can be several orders of magnitude with use of PCBM (a derivative of fullerene) as the electron acceptor in place of fullerene C₆₀, and with better polymer-fullerene printed film quality. The printed film quality would be improved by printing polymer:PCBM blend in a glove box where oxygen and water levels are controlled to 5 ppm or less, and by evaporating Al cathode right after printing polymer:PCBM blend onto PEDOT printed onto ITO coated glass or plastic.

Our future efforts to improve the organic solar cell efficiency will thus involve:

- a) Using fullerene derivative ([6,6]-Phenyl C₆₁-butyric acid methyl ester) as electron acceptor and optimizing the polymer:PCBM BHJ ink chemistry.
- b) O₂ and H₂O controlled environment (glove box) during printing operations to prevent degradation of polymer:PCBM blend.
- c) Evaporating cathode right after printing polymer:PCBM blend, again, to minimize degradation of the blend in presence of O₂ and H₂O in air.

All these measures should result in improved charge carrier mobility, and improved morphology of the polymer:PCBM film. Hence much improved solar cell efficiency.

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