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Fabrication of Organic Bulk Heterojunction Solar Cells by Screenprinting

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ABSTRACT

An organic solar cell composed of Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene)(MEH-PPV) and (6,6)-phenyl C61-butyric acid methyl ester(PCBM) was fabricated by screenprinting. This study is part of a research to drive the cost of PV production down and enable widespread use of the sun's energy. MEH-PPV, a conjugated polymer, becomes semiconducting upon photodoping and when in contact with PCBM, a fullerene derivative, a continuous photocurrent is obtained. Screenprinting was possible because of the ability of both MEH-PPV and PCBM to be processed from a solution of Chlorobenzene. Screenprinting experiments showed that solution has very thin viscosity and requires very high print speeds, 300 to 600 mm/s or more, for best film uniformity. Screenprinting process was also successfully applied to ITO etching and on glass substrates opening the way to the possibility of a fully screenprinted organic solar cell.

1. INTRODUCTION

The harvesting of light by polymer systems by photoinduced energy and electron transfer similar to photosynthesis in plants is gaining attention from researchers of various disciplines - physics, polymer chemistry, electronics, and materials science. Particular interest is given to polymers because of new synthetic methods that make it possible to modify, functionalize, and derivatize the different active components [1]. The early organic solar cell devices were patterned after their more efficient inorganic counterparts. However new properties of the materials that comprise the diode could be explored for process simplification. The research in organic solar cells is aimed primarily to bringing the cost of production down by taking advantage of non vacuum large scale manufacturing of polymer materials.

Bulk heterojunction devices are currently deposited on conducting transparent substrates using spincoating, which produces a uniform layer of the active material over the entire surface of the substrate [2]. Patterning of the surface must be done with lithographic techniques that add several process steps into the manufacturing flow. A simple, low-cost method has to be

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developed to be able to produce solar cells that will enable the cost savings projected for this technology to be realized.

Currently, organic solar cells are fabricated by spin-coating a solution of the active polymer donor/acceptor matrix on a flat substrate [3]. In spincoating, droplets of the solution are deposited over the substrate and spread into thin films by the rotational motion of the substrate. Because of this control on the area or location of deposition is not possible without the addition of patterning or lithographic steps. To enable the cost of organic solar cells to go lower, other methods like inkjet printing, screenprinting, and stamping must be explored. Among these, screenprinting was selected due to its simplicity, adaptability, speed to set-up and process, and affordability.

Polyphenylenevinylene (PPV) and (6,6)-phenyl C61-butyric acid methyl ester (PCBM) are the two soluble components of a bulk heterojunction. Fullerenes have high electron affinity which allows fast transfer of the electron from the conjugated polymer [1]. This results in long living charge separation. Considering the combination of the electronic and chemical properties of these materials, this study aims to determine the feasibility of screenprinting as a fabrication method for organic solar cells and identify the challenges in the development of the process.

2. METHODOLOGY

The methodology was made up of two activities, screenprinting parameter were first determined prior to solar cell fabrication.

2.1. Screenprinting Characterization

In the determination of the screenprinting parameters, solutions of ADS200RE poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) or MEH-PPV was mixed with Nano-C (6,6)-phenyl C61-butyric acid methyl ester or PCBM with chlorobenzene in the concentrations given by the Table I. The solution was left on the magnetic stirrer for 24 hours.

Solution name (wt/vol % PPV)	PCBM (mg)	MEH-PPV (mg)	Cholobenzene (ml)
0.7%	5.6	1.4	2
1.0%	8	2	2
2.0%	16	4	2

Table I. Solution Compositions for the Active Area

The solutions were dispensed on the screen and the squeegee applied this solution on the substrates using the parameters listed in Table II. The uniformity of the solutions was gauged using a flatbed scanner and the Image Tool software.

For the resist to pattern the ITO, Coates XZ06 solvent soluble resist (black) was printed on ITO glass substrates with the parameters on Table II. The profile and thickness of the resist was determined using Dektak 3030 profilometer. The active area and resist were then screenprinted on the prepared substrates using the ESSEMTEC screenprinters (Figure 1).

Parameters	Settings		
Active Area			
Gap (mm)	0	4	6 or greater
Speed (mm/s)	10	100	More than 300
Screen (Mesh)	120	-	190
Viscosity of the solution	High	Average	Low
Screenprintable Resist			
Gap (mm)	0	2	4
Speed (mm/s)	10	50	100
Screen (Mesh)	120		

Table II. Parameter Settings for the Active Area

a b

Figure 1. Screenprinting equipment a) Automatic printer was used for low speed (10 mm/s up to 100mm/s printing b) table top printer was used for high speed printing (more then 100 mm/s)

2.2. Fabrication of Solar Cells

Solar cell fabrication had four parts, substrate preparation, screenprinting, metallization, and electrical testing. In substrate preparation, the ITO coated glass (Merck Display with a thickness of 1.1 mm, size of 45 mm by 45 mm, ITO layer from 20-100nm) was cleaned first in acetone immersed in an ultrasonic bath and boiling IPA then dried with an N_2 gun. The surface was then further cleaned using oxygen plasma for 10 minutes. After cleaning the substrates followed two different patterning procedures, lithography and screenprinting.

In patterning by lithography, the sample was spincoated with a photoresist and patterned using conventional lithography techniques. In screenprinting, a resist (Coates XZ06) was deposited on a screen containing the device patterns. The motion of the squeegee forced the resist through the screen patterns to deposit on the substrates. The patterned resist was then

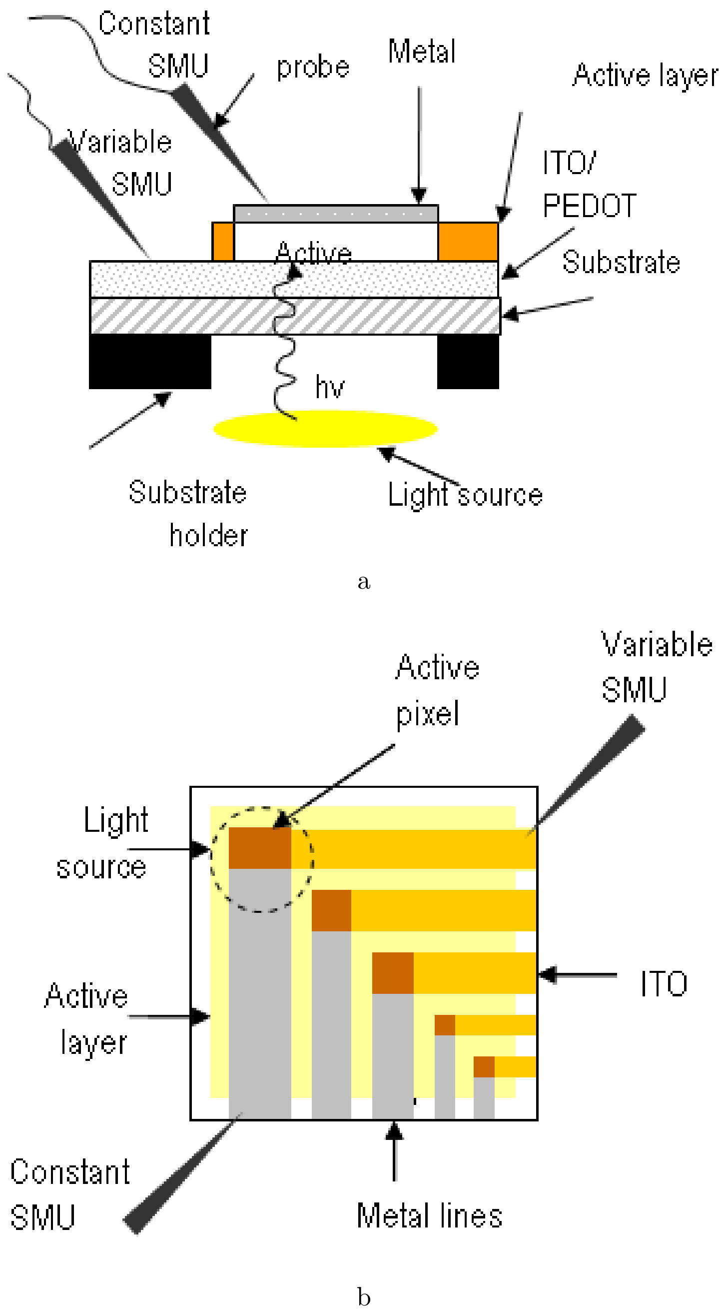

Figure 2. Schematic of solar cell performance measurement a) side view b) top view

baked at around 50°C to remove the remaining solvents and immersed in an ITO etchant (Transene TE-100) for an hour and rinsed in flowing DI water and N_2 dried. The resist was stripped off with chlorobenzene to expose the patterned ITO. A layer of PEDOT:PSS (Baytron P poly (3,4-ethylene dioxythiophene) : poly (styrene sulfonic acid) was spin coated on the substrate surface.

The active layer was screenprinted using the parameters from the screenprinting characterization step. After printing the active layer, the lithium fluoride was evaporated at around 600°C on the active layer for 30s. It was followed by aluminum at 1200°C for 8 minutes to complete the device metallization.

Electrical measurements were carried out in N_2 environment, room temperature with a variable-intensity fiber optic as source for the illumination of around 100W. The variable source measurement unit (SMU) probe was connected to the ITO and the constant SMU was connected to the metallization (Figure 2). Single and linear voltage from -2 to 2V was applied with a compliance of 40mA by the HP Agilent oscilloscope. The current-voltage curve was plotted and recorded. The important solar cell characteristics were determined from the IV curve by taking the following information: Voc (open circuit voltage), voltage reading where the current is zero; Isc (short circuit current), current reading where voltage is zero; Fill factor, ratio of the area of the Vp×Ip over Voc×Isc; Efficiency is Vp×Ip over the total power input to the circuit.

3. RESULTS AND DISCUSSION

3.1. Screenprinting

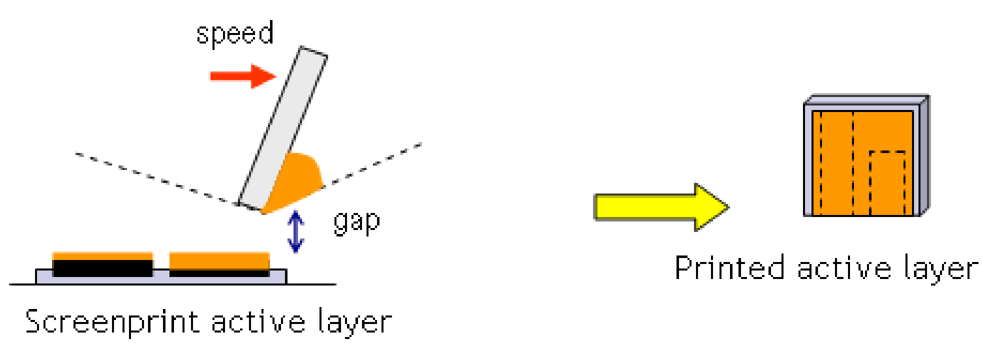

Figure 3. Schematic of the Screenprinting Process

From the characterization of the screenprinting process, the print speed, the snap-off distance, and the squeegee pressure, together with the viscosity of the printing medium are the parameters that affect the uniformity of the printed thin film. The print speed increases as the size of the features decrease. However, this is only applicable for settings of gap between 0 and around 4 mm when the primary mechanism of ink deposition is still through the concept of screenprinting wherein the ink is pushed through the mesh openings with the action of the squeegee (Figure 3). At higher gaps however, the print characteristics change which show a difference in the deposition mechanism. Here, the ink is spread through the substrate by an action similar to doctor blading [10]. In this case, however, a thickness of the material seeps through the mesh, with the aid of gravity, instead of the hydraulic pressure created by the motion of the squeegee and is spread by the motion of the squeegee. This is the reason for the lack of gasketting at the end of the print cycle and thus the ink smear at one end. The changes in the uniformity of the printed films with respect to the deposition parameters are shown in Figure 4. Inks with low viscosity particularly show this behavior. For the 0.7% solution it is easier to form a thin film with a consequence of edge smearing as a result, even at higher speeds. This was very evident in the blend where even at the highest speed setting, the flow behavior was similar. In the 1% solution, a higher speed was required to make the feature size of the blend equal to that of the pure polymer only. Also in the large gap region, a higher gap (beyond machine capability) was required before the segregation or non-uniformity in the film could be removed. The 2% solution did not show the same behavior and because this solution showed good printability, the setting of large gap for this concentration was not pursued further.

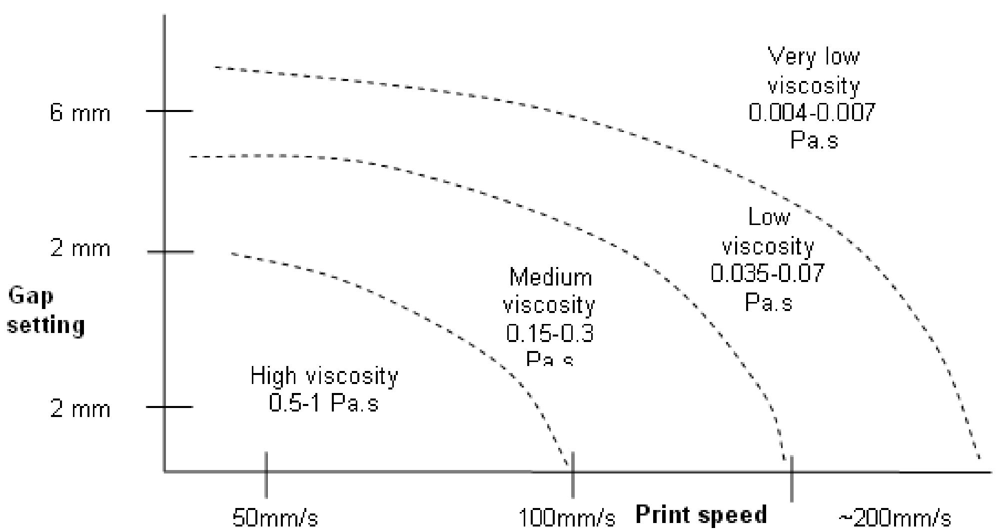

Figure 4. Chart showing the effect of various screenprinting parameters on the uniformity of the films deposited. Screen mesh was kept constant at 190 M.

At the default gap setting, an experiment was done to determine the interaction of squeegee pressure and print speed - with the assumption that the effect on the feature size of these parameters is linear. An extrapolation was made to determine the print speed where the features will be eliminated (Figure 5). Based on the graphs, very high print speeds are needed to print a uniform film. These speeds are currently higher than the maximum speed capability of the automatic printer motor. Therefore was decided that the manual printer, whose print speed is dependent on the operator, will be used to make screenprinted devices.

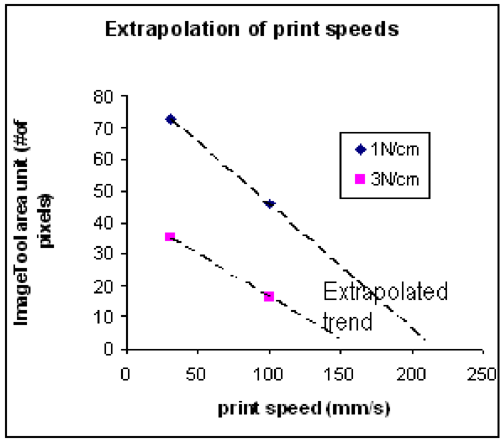

Figure 5. Extrapolation of the Feature Size and Print Speed for Squeegee Pressure

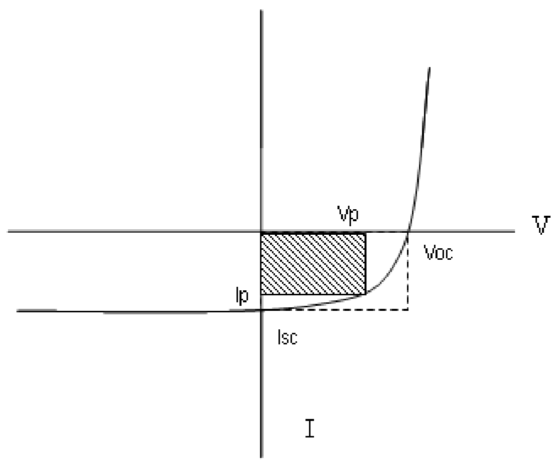

Figure 6. IV Curve of an Ideal Solar Cell upon Illumination

3.2. Functional Testing

The ideal IV curve of a solar cell is shown in Figure 6. The maximum power is the maximum product of current and voltage that can be found amongst data points in the 4th quadrant (Vp×Ip). The rectangle defined by Voc and Isc is the maximum area which could be attained and the ratio between the area Vp×Ip and area Voc×Isc is called the fill factor (FF) [3].

$$FF = \frac{(IV)_{max}}{(I_{sc} \times V_{oc})}$$

and

$$P_{max} = (IV)_{max} = V_{oc} \times I_{sc} \times FF$$

To determine the efficiency, η, the output power P_{max} must be related to the power input or incident light, P_{light}. This is given by the equation:

$$\eta(\lambda) = \frac{\{I_{sc}(\lambda) \times V_{oc}(\lambda) \times FF(\lambda)\}}{P_{light}}$$

Electrical measurements showed presence of stable V_{oc} and J_{sc} for screenprinted devices (Figure 7). The fill factor is also stable at 25 to 37 and efficiency varied from 0.3 to 0.75%. Some devices showed good efficiencies due to good J_{sc} values indicating less shunt. The cause of the low efficiencies is the presence of a slope change in the IV curve at the vicinity of V=0 that is also present in spincoated devices processed. Thus, it is seen as a possible LiF or

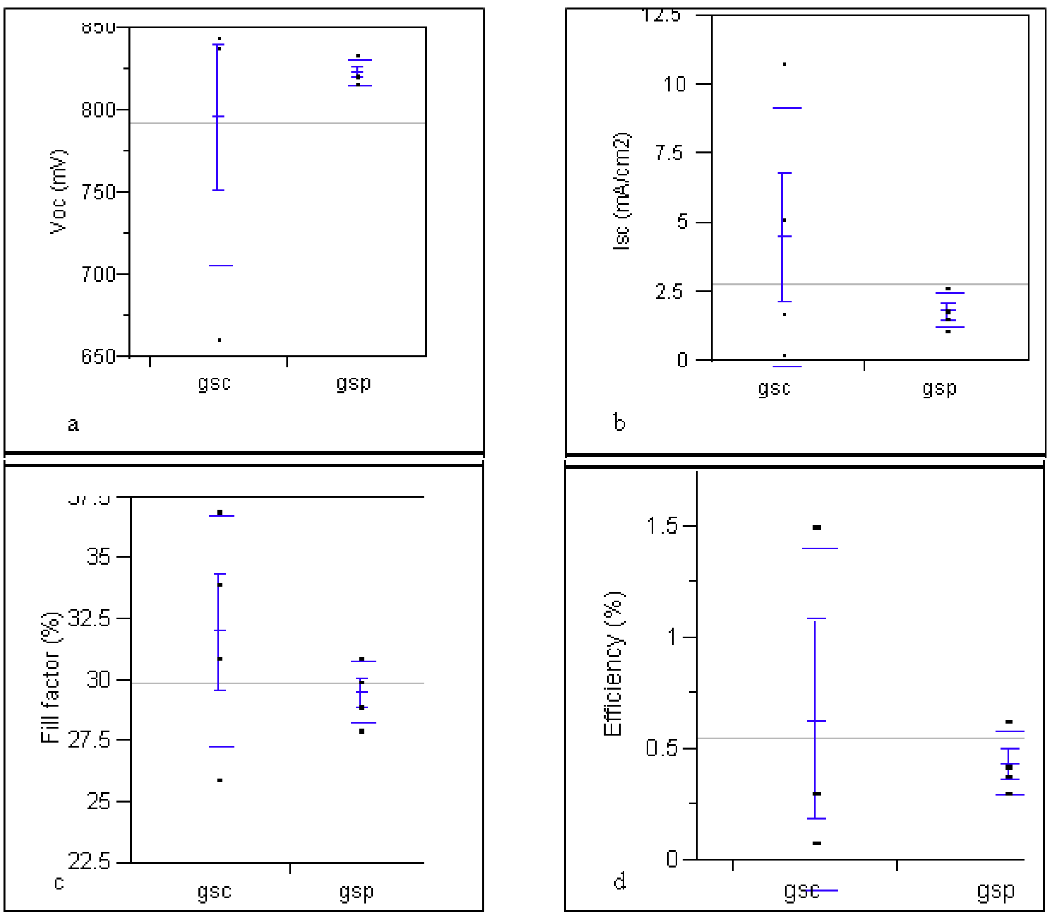

Figure 7. Comparison of electrical properties of different devices a) Open circuit voltage, Voc b) Short circuit current, Isc c) Fill factor d) Efficiency. Outermost short horizontal lines (dashes) correspond to the standard deviation while the 3 dashes connected by a vertical line indicate the mean (middle) and the standard error.

aluminum deposition anomaly.

The device performance (V_{oc} and J_{sc}) of the solar cells fabricated in this study were comparable to spincoated devices [3] except for fill factor and efficiency indicating an increase in shunt, possibly caused by non uniformity in screen printing or problems in metal deposition. This is indicated by the increase in the shunt for solar cell pixel devices that are large. Compared to small pixels, large pixels have lower efficiencies. However, devices were successfully created using as many screenprinting steps as possible in the process.

4. CONCLUSION

A bulk heterojunction organic solar cell device (Figure 8) was fabricated using screenprinting both as a patterning step and a deposition step. In this study, screenprinting parameters were established for various solutions with different viscosities. ITO lines were etched using a screenprintable resist and an active layer was deposited by screenprinting the PPV/PCBM/Chlorobenzene solutions. Electrical performance of screenprinted devices show around 0.6 to 0.7% overall efficiency and areas for further improvements are identified in the following section.

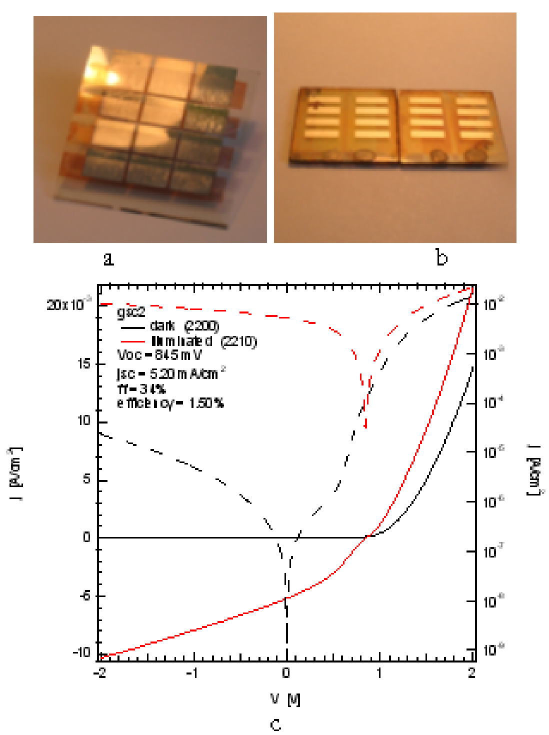

Figure 8. Solar cell devices a) module on 45 x 45 mm flex substrates b) small devices, 15 x 15 mm, consisting of eight active areas c) IV curve of the best performing solar cell within the batch of devices produced in this study.

5. RECOMMENDATIONS

The research movement that aims to produce cheap and reliable solar cells is wide and far-reaching. This research focused on screenprinting. However, in this research there are still more that needs to be done or discovered. For future research, the following activities are recommended: to determine the behavior of the solution using "'impact"' printing (screen printing that uses very high print speeds 500 to 1000 mm/s); material characterization of PCBM and other possible solvent replacement of chlorobenzene which would yield higher viscosity but have greater dissolution strength; screenprinting of P3HT and other high efficiency organic solar cell materials; screenprinting of the electrodes - a transparent one that will replace the ITO and a printable metal like silver - which will work also on flex substrates, meaning not prone to cracking; screenprintable, hermetic, and flexible protective coating.

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