CONJUGATED POLYMER PHOTOVOLTAIC SOLAR CELLS – MANUFACTURING, TROUBLESHOOTING

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Abstract

Due to their lighter weight, conjugated (semiconducting) polymer cells have a potential of displacing conventional silicon cells. The most studied conjugated polymer solar cell is the bulk heterojunction cell. Here, the active layer is made up of a mixture of the conjugated polymer donor and the C_{60} based - fullerene acceptor. The efficiency of the cell is determined, using a solar simulator and the AM1.5G standards, after determining existence of an open circuit voltage (V_{oc}) and short circuit current. Using Design of Experiments (DOE), V_{oc} has been maximized. The variables considered in the DOE were solvent type, number of layers of PEDOT:PSS and polymer/fullerene mix, as well as spin-coating times and speeds, and annealing time, temperature and applications per cell layer.

Introduction

Ever since the silicon cell was discovered, in 1946, it has been the standard. A decade later impurities were placed in silicon, creating positive-hole-donor and electron-acceptor regions, and the modern solar cell was made. Despite 50 years of development, silicon solar cell performance cannot match the cost of nonrenewable energy sources (coal, oil, etc.). In the late 1970's the government gave subsidies for renewable energies and even today, solar energy cannot compete with non-renewables without these subsidies.

Conjugated (semiconducting) polymers are an alternative solution to silicon. They are flexible and inexpensive, since the layers are in the nm scale and can be deposited on flexible substrates such as PET. Silicon cells are rigid since their thicknesses are on the 100 μ m scale and can only be deposited on glass. The average efficiency of a polymer solar cell is around 3% – 5%. However, if the efficiency is increased to 10% the technology would be viable and cost effective.

The first part of this research is to produce an optimized efficient working cell. The easiest design from which to get a working cell is a bulk heterojunction cell. The cell will start with PCBM as an acceptor and P3HT as the donor and utilize PEDOT: PSS. Once an efficient cell is obtained, the next step of the research will be to scale-up to an industrial process. With flexible substrates, cells can be made in many desired shapes through thermoforming. For scaling, different methods of material deposition will be required, as spin-coating only applies to small surfaces.

The efficiency of solar cells can be computed using eq1. [1].

 $\eta_e = (V_{oc} * I_{sc} * FF) / P_{in}$ (1) where,

FF (Fill Factor) = $(I_{mpp} * V_{mpp}) / (I_{sc} * V_{oc})$ (2) and the other parameters, as defined in Fig.1 are,

 V_{oc} - Open Circuit Voltage

I_{sc} - Short Circuit Current

 P_{in} – Incident Power

Impp – Max Power Point Current

 V_{mpp} – Max Power Point Voltage

There are many variables that have been experimented with to increase the efficiency of a conjugated polymer cell. They are the conjugated polymer (donor) type, fullerene acceptor type, solvent type, filtering, polymer/fullerene to solvent concentration, acceptor to conjugated polymer ratio, top electrode metal type (which increases work function), spin coater time and speed, adding PETDOT:PSSto eliminate shorts, and annealing[2].

Basic Cell Structure

The starting point for each cell is an ITO (Indium tin oxide) covered substrate, either PET or glass. The ITO layer serves as the transparent electrode. This is followed by depositing an active layer, such as a simple polymer, a polymer layer and fullerene layer, a mixed polymer and fullerene layer, or a layer of PEDOT: PSS and a layer of polymer/fullerene mixture. Finally, either a silver or aluminum metal electrode is deposited over the active layer. A portion of the active layer is removed so that a conductive epoxy droplet can be deposited on the ITO electrode (Fig. 2).

There are three types of conjugated polymer solar cells. They are the single layer cell, the double layer cell, and the bulk heterojunction cell.

The single layer has an active layer of a sole conjugated polymer. This type was not chosen for this research project because it is of very low efficiency, due to lack of an acceptor/fullerene [3].

The double layer cell was also eliminated from this study because of layer thickness restrictions. Due to the diffusion length of the exciton, between 5 and 20 nm, the layers must be in that same order.. If the layer is any thicker the hole and electron will either disassociate or recombine[3].

The bulk heterojunction cell (Fig. 2) was chosen in this study due to its many advantages. The active layer is a mixture of the conjugated polymer and fullerene, leading to the creation of polymer fullerene interfaces everywhere. Hence, both polymers and electron acceptors are in contact with each electrode, generating bi-continuous pathways to each electrode, eliminating pathways that lead nowhere[3]. Cell efficiency is measured by creating a currentvoltage curve (IV) depicted in Fig. 1. This is done by the use of a solar simulator using a AM 1.5 G light source standard. This light has an intensity of 1000 W/m^2 and a spectral distribution that matches the sun on the earth's surface at an incident angle of 48.2 degrees [4]. An alternate process to see if a solar simulator will produce a measurable result is to measure the open circuit voltage. This can be done using a multi-meter. Values in the range of 200 mV to 300 mV are considered acceptable.

In the first DOE, (Table 1) we studied the layering of PEDOT: PSS. It was found that two layers of PEDOT: PSS eliminate shorts. When maximizing V_{oc} , it was best to spincoat one layer, heat treat it, and repeat the process for a second layer.

Design of Experiments

Materials (purchased from Aldrich) Table 1 : Materials List

Material	Туре		
Solvent	Chlorobenzene/		
	Dichlorobenzene		
Conjugated Polymer	P3HT		
Fullerene Acceptor	PCBM		
Additive	PEDOT:PSS		
Substrate	ITO Coated Glass/PET		
Metal Electrode	Aluminum/Silver		

PEDOT: PSS is a conjugated polymer that acts as a hole transport layer. It is also beneficial in eliminating shorts. It is spun before the polymer/fullerene layer directly on top of the substrate/ITO layer. PEDOT:PSS proved essential in getting a working cell. All cells made without PEDOT: PSS resulted in zero values of V_{oc} . There are three types of PEDOT:PSS available based on relative conductivity – high, medium, and low. Initial testing, with simple cells produced results that showed that low and high conductivity led to low V_{oc} . Medium gave values on the order of 25 - 180 mV. High conductivity PEDOT:PSS contains dimethyl sulfide which interferes with the polymer/fullerene layer[5].

Substrate

PET was used in early experiments, however, due to its inherit surface waviness unnecessary effects were introduced into the cell structure. Hence a smooth, nearly flat glass plate was used as a substrate for initial cell construction.

Conjugated Polymer and Fullerene Type

P3HT and PCBM were chosen for use in a bulk heterojunction cell as they are the most widely accepted materials. PCBM is used more then PCBB or C_{60} as it contains a chain connected to the C_{60} "buckyball" that enables better mixing of solvents. P3HT is available is conductive grades, where one of the grades is electronic, which assists in cell performance. From literature research we determined the PCBM to P3HT weight ratio is one to one [reference].

Filtering and Polymer/Fullerene to Solvent Concentration

There is a relationship between filtering and Polymer/Fullerene to Solvent Concentration. From experimental research the acceptor/fullerene solvent mixture must be filtered to 0.2 µm. Since a small amount of mixture was required, (less than 25ml) syringe filters were used. It is not possible to filter the solution to 0.2 µm immediately. Therefore, six filter sizes were utilized, each smaller then the one preceding. They are 2.7 μ m \rightarrow 1.6 μ m \rightarrow 1.0 μ m \rightarrow $0.7 \,\mu\text{m} \rightarrow 0.45 \,\mu\text{m} \rightarrow 0.20 \,\mu\text{m}$. Next, the mixture concentration was maximized while still filtering to 0.2 µm. The concentrations that worked were 0.0625%, 0.125%, and 0.25%. Solutions higher in concentration did not filter correctly. The concentration of the solution is also a contributing effect in the thickness of the P3HT/PCBM layer.

Metal Electrode Type and Shadow Mask

Two different metals were used for the top metal electrode, evaporated silver and sputtered aluminum, where silver has a better conductivity and aluminum has a larger work function. Evaporated silver cells resulted in full shorts. A shadow mask is a steel plate 1mm thick with holes in it to allow metal to be deposited through. The shadow mask used has four 5mm by 5mm square holes in it. This allows for four replicates with each cell.

Spincoater Time and Speed

Spincoater speed and time are variables that control the thickness of the deposited layer. Many speeds from 500 RPM to 2500 RPM were examined. They were examined in the second DOE (Table 2). These values were used for all layers of deposited polymer/ fullerene and PEDOT:PSS.

Annealing and Layering

Both the PEDOT: PSS layer and the polymer/ fullerene layer need to be annealed. In the first DOE (Table 1), all annealing was done at 100 C for 2 minutes. The spincoated materials were generated in two ways. Putting on one layer, then annealing followed by another layer then annealing again. The other method was to deposit two layers one after the other and then anneal them. The results showed that for the PEDOT: PSS it was best to spincoat a layer then anneal then repeat. However, for the polymer/ fullerene layer it was best to spin coat two layers one on top of the other then bake.

Very long annealing times (10 minutes) were also compared to short annealing times (2 minutes) in the third DOE (Tables 6 & 7).

First DOE

All three DOE's were 2^3 full factorials with four replicates. The first DOE investigated the layering and annealing of PEDOT:PSS with P3HT/PCBM and changing the solvent type.

1.1							
	P3HT/PCBM	PEDOT:PSS	Solvent	Voltages (mV)			
	2L:2B	2L:2B	C	0.7	2.0	13.4	24.8
	2L:1B	2L:2B	C	21.3	17.0	29.1	27.6
	2L:2B	2L:1B	C	40.5	26.3	40.5	33.8
	2L:1B	2L:1B	C	19.8	9.1	3.3	2.5
	2L:2B	2L:2B	D	120.5	230.2	1.3	0.4
	2L:1B	2L:2B	D	313.0	210.0	14.0	108.0
	2L:2B	2L:1B	D	11.8	92.5	9.0	15.4
	2L:1B	2L:1B	D	95.3	0.0	30.4	160.1

Table 2 : First DOE Data

Where : 2L:2B - Deposit one layer then bake and repeat

2L:1B - Deposit 2 layers then bake

C - Chlorobenzene

D - Dichlorobenzene

The most significant effect was solvent type. The model predicted a maximum $V_{oc} = 169.08 \text{ mV}$

Table 3 : First DOE Results				
Significant Effect	Maximizing Effect			
	Settings	on Voc		
Solvent	Dichlorobenzene	68.77 mV		
PEDOT:PSS	2L:2B	33.94 mV		
P3HT:PCBM	2L:1B	24.83 mV		
Solvent*PEDOT:PSS	As Above	38.93 mV		
Solvent*P3HT/PCBM	As Above	31.37 mV		

A check of residual versus fits indicates that when V_{oc} is at its highest it also has its highest variability. We ran one cell with the maximizing conditions given previously and got values of 170.7, 163.6, 208.3, and 183.6 mV. These values do not support the variance.

Second DOE

The second DOE investigated spincoater speed, spincoater time, and annealing time (Table 2). The model predicted a maximum at 207.1 mV. T

Spin	Time	Bake	Voltages (mV)			
Speed		Time				
1250	20 sec	Low	90.0	10.5	211.	6.5
RPM					0	
1500	20 sec	Low	307.	206.	285.	315.
RPM			0	0	0	0
1250	30 sec	Low	147.	7.1	43.2	63.9
RPM			0			
1500	30 sec	Low	20.8	246.	106.	120.
RPM				0	5	5
1250	20 sec	High	281.	30.7	112.	177.
RPM			0		5	1
1500	20 sec	High	230.	76.8	146.	270.
RPM			2		7	3
1250	30 sec	High	101.	107.	175.	57.9
RPM			3	1	9	
1500	30 sec	High	172.	54.1	68.3	109.
RPM			6			8

able 4. Second DOE Data

Where Bake Time Low - 1 min at 100°C for all layers High - 2 min at 100°C for all layers

Table 5 : Second DOE Results

Significant Effect	Maximizing	Effect on Voc	
	Settings		
Spin Speed	1500 RPM	69.56 mV	
Spin Time	20 seconds	72.14 mV	
Speed*Annealing	Annealing Low	58.89 mV	
Speed*Time	As Above	45.16 mV	

It is to be noted that annealing is not a significant effect, but its interaction with spincoater speed is. No adverse effects were shown on the residual analysis. The model shows a maximum V_{oc} of 253.12 mV. Third DOE

This DOE examined high spincoater speeds, extra layering and high annealing times for PEDOT: PSS. An extra layer is studied as two initial layers of PEDOT: PSS gives better morphology than a single layer.

Spee d	PEDOT:P SS	Bake	Voltages (mV)			
1500	2L:1B	Low	21.7	51.3	77.6	37.6
2000	2L:1B	Low	44.7	44.7	42.8	77.6
1500	2L:1B-	Low	203.5	172.8	193.2	68.5
	1L:1B			1		
2000	2L:1B-	Low	3.6	180.0	70.2	92.3
	1L:1B					
1500	2L:1B	High	4.3	148.1	136.5	219.
						0
2000	2L:1B	High	101.9	91.3	141.2	37.8
1500	2L:1B-	High	217	248.4	223.5	139.
	1L:1B					5
2000	2L:1B-	High	50.2	179.3	55.8	175.
	1L:1B					0

Table 6 : Third DOE Data

Where Speed in RPM. With PEDOT:PSS Layering – low setting is 2L:1B which means deposit 2 Layers then anneal and – high setting is 2L:1B-1L:1B which means deposit 2 layers then anneal then deposit another layer and anneal. The Annealing (Bake) Time - Low setting is 2.0 min at 100°C and - high setting is 10.0 min at 100°C.

Significant Effect	Maximizing Settings	Effect on Voc
Spin Speed	1500 RPM	48.38 mV
PEDOT:PSS	2L:1B-1L:1B	62.17 mV
Layering		
PEDOT:PSS	High Bake	49.17 mV
Annealing		

The model shows a maximum Voc of 207.1 mV.

Conclusions

Table 8 : Variables that Maximize Open Circuit Voltage

Variable	Туре
Conjugated Polymer	РЗНТ
Fullerene	РСВМ
Solvent	Dichlorobenzene
Solvent – P3HT/PCBM	0.25% Weight
Mixture	
Filter	0.2 μm
Acceptor-Polymer Ratio	1:1
Top Electrode Metal Type	Aluminum
Spincoater Speed	1500 RPM
Spincoater Time	20 seconds
PEDOT:PSS Filter	0.7 μm
Conductivity	Medium Grade
Layering PEDOT:PSS	2 layers then anneal : 1 layer then anneal
Annealing PEDOT:PSS	100°C for 10 minutes
Layering - P3HT/PCBM	2 Layers then Anneal
Mix Annealing – P3HT/PCBM Mix	100°C for 1 minute
IT ALZA	

Future Work

The variables found to maximize Voc will be used in the future to produce cells that will be examined with a Solar simulator. Figure 3, shows one cell tested with a solar simulator. The lower curves are a reference taken in the dark and the upper curves are taken with a light source.

In future work glass will be replaced by PET as a substrate.

There is much work to do with nanotubes. Nanotubes are traditionally organic, made of carbon. While nanorods are inorganic, made of CdSe or another metal. Other variables which can be introduced include the aspect ratio of nanorods and nanotubes. Furthermore, these rods and tubes can either be wrapped or coated, aligned, and in the form of rod or tetrapod

A change in the deposition of the metal layer is necessary. During the sputtering process the material struck the outside layer with a relatively large force. This creates holes in the P3HT/PCBM layer and caused shorts. Evaporation will likely take its place. It is hard to evaporate aluminum, but easy to evaporate silver

The thickness of layers for working cells will need to be found, using the White Light Interferometer. These thicknesses will then be transferred to the industrial scale

As up-scaling is begun, different methods of deposition will be required. Spin-coating is only effective for small cells and is very wasteful. Several methods of industrial deposition exist, doctor blading (also called knife over edge coating), slot-die coating, screen printing, ink jet printing, and roll coating.

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Figure 1. Voltage Current Graph of a Solar Cell [3]



Figure 2. Diagram of Bulk Heterojunction Cell



Figure 3. Solar Simulator Current-Voltage Curve for Alternate Cell Structure-Light and Dark

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الخلايا الشمسية الفولتائية للبوليمرات المتعاقية - التصنيع ، حل المشاكل

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الملخص :

نظرا للوزن الخفيف للخلايا الشمسية للبوليمرات المتعاقبة فان هناك جهود كبيرة لاحلالها محل الخلايا الشمسية المصنوعه من السليكون. ان اكثر خلايا البوليمرات المتعاقبة الشمسية المدروسة هي خلية المفرق الهجيني. ان الطبقة الفعالة في الخلية مكونه من مزيج من البوليمر المتعاقب المانح ومادة كاربون 60 المستقبلة. ان كفاءة الخلية الشمسية تحدد باستخدام بواسطة الجهاز المحاكي الشمسي باستخدام معايير AM 1.5 G

بعد تحديد فولتية الدائرة V_{OC} وتيار الدائرة القصير . باستخدام النموذجDOE في تصميم التجارب، تيار الدائرة المفتوح تم تصعيدة. ان المتغيرات المعتبرة في التجارب هي نوع المذيب عدد طبقات PEDOT:PSS وخليط البوليمر / الفولرين بالاضافة الى زمن وسرعة الطلاء البرمي وزمن التلدين ودرجة الحرارة والتطبيقات لكل طبقة خلية. ان متغيرات اخرى مثل ادخال LiF، المجالات الكهربائية او المغناطيسية القضبان والاتابيب النانوية سيتم دراستها في المستقبل .