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Device Physics of Solution Processable Solar Cells

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Device Physics of Solution Processable Solar Cells

by

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A dissertation submitted in partial fulfillment
Of the requirements for the degree of
Doctor of Philosophy
Department of Physics
College of Arts and Sciences
University of South Florida

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ABSTRACT

This Ph.D work reports the studies of photovoltaic devices produced by solution processable methods. Two material systems are of interest: one is based on organic semiconductors, and another on organic/inorganic hybrid composites. Specifically, organic photovoltaic (OPV) devices are made using photoactive materials consisted of a p-conjugated polymer [Poly(3-hexylthiophene), or P3HT] and fullerene derivative [phenyl-C60-butric acid methyl ester, or PCBM] in a bulk heterojunction (BHJ) structure of donor/acceptor network. On the other hand, hybrid photovoltaic (HPV) devices are made from blend of quantum dots and p-conjugated polymers. The QD material presented here are of the lead sulfide (PbS), and lead selenide (PbSe), whereas the polymers are either P3HT or Poly(3-dodecyl thienylene vinylene) (PTV) with controlled regio-regularity.

For OPV devices, two different device geometries are investigated, namely, the conventional or normal structure where indium tin oxide (ITO) is used an anode, and a metal cathode is fabricated by thermal vapor deposition (TVD). In this geometry, thin layer (about 30~35nm) of poly(3,4ethyleneedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is deposited from aqueous solution onto ITO as hole transport layer (HTL). The second geometry, called the inverted structure, uses ITO as the cathode of the device. A thin layer of cesium carbonate (Cs2CO3) (about 1~2nm) is applied over the
ITO and functions as electron transport layer (ETL), thereby decreasing the work function of ITO and allowing it to function as the cathode. In this case, PEDOT:PSS is mixed with 5vol.% of dimethylsulfoxide to increase conductivity for serving as anode.

Two solution processable methods, spin-coating and spray processes were investigated, and a detailed study of nanomorphology influence under different annealing conditions, different solvents and thickness are reported. The main contribution of this Ph.D. work was the development and implementation of a layer-by-layer (LBL) all-spray solution-processable technique to fabricate large-scale OPV arrays, with more than 30% transmission in the visible to near IR range. Comparing with traditional laboratory OPV fabrication based on spin-coating and using metal as cathode contact, which greatly limits transparency of solar cells and posts difficulty for large scale manufacturing, this LBL spray process solves these two problems simultaneously. This technology eliminates the need for high-vacuum, high temperature, low rate and high-cost manufacturing associated with current silicon and in-organic thin film photovoltaic products. Furthermore, this technology could be used on any type of substrate including cloth and plastic.

Single cell OPV with active area of $4\, mm^2$ was used as preliminary test device to obtain fabrication parameters for multi-cell OPV arrays. Three different sizes of OPV arrays were fabricated and tested under various illumination conditions. Starting from a 4” x 4” array with 50 cells in series connection 4” x 4” substrate consisting of 50 cells with total active area of $30\, cm^2$, a scaled up 1’ x 1’ array was fabricated as a proof of concept, and whose results are reported. Scaled down arrays, called micro arrays, are also presented in this work. OPV micro array has the potential application in DC power supplies for
electrostatic Microelectromechanical systems (MEMS) devices. The first generation micro array consists of 20 small (1mm$^2$) solar cells connected in series for a total device area of approximately 2.2cm$^2$. The 2$^{nd}$ generation micro array with 60 cells shares the same size substrates and single cell active area as the first generation. However, the 2$^{nd}$ generation micro array cell has a new design with reduced series resistance and improved cell occupancy by 3 fold.

Infrared quantum dots (QD) such as PbS and PbSe have potential in photovoltaic applications. These solution processable quantum dots with tunable electronic properties offer very attractive approach for expanding spectral sensitivity of p-conjugated polymers to infrared region of solar spectrum. However, these QDs often have defects originated from either incomplete surface passivation or imperfections in the quantum Dots. The electronic levels of defects often are within the bandgap of the semiconductor. These in-gap states are of great importance since they affect the final destiny of excitons. Continuous wave photoinduced absorption spectroscopy has proven to be a convenient and successful technique to study long-lived photoexcitations of in-gap states. Part of this Ph.D work was the investigation of a peculiar gap state found in films of PbS QDs. This gap state bears confinement dependence, with a lifetime about 2µs. A detailed analysis of the Stokes shift, temperature dependence of PL, absorption and photoinduced absorption reveals the unconventional GS is a new state of a trapped exciton in a QD film. This gap state is directly relevant to exciton dissociation and carrier extraction in this class of semiconductor quantum dots.
As synthesized PbSe and PbS quantum dots usually have bulky ligands such as oleic acids or TOPO (trioctylphosphine oxide). This capping layer is necessary to prevent nanocrystals from coalescence, however, the bulky ligands hinder charge extraction from and charge transport through the nanocrystals, as well as exciton dissociation at the nanocrystal/polymer interface. Common ways to manipulate ligands include ligand wash and ligand exchange in solution, and ligand removal on films. Through this Ph.D. work, a novel method using electric field to manipulate quantum dots ligands for interface of quantum dots and polymer, which possibly could facilitate charge extraction from the quantum dots and charge transfer between quantum dots and polymers, without the need of harmful chemicals. Over four orders improvement of photoconductivity at zero bias and more than six orders improvement at 5V reverse bias in a sandwich structure quantum dots photovoltaic device, and more than 5x improve in film smoothness.

After thorough fundamental study on QD optoelectronic properties, hybrid photovoltaic (HPV) device was fabricated using a blend solution of PbS QDs and P3HT. Two different solution processes are used to form the QD/polymer active layer, one is the traditional spin coating method, and another is the spray technique developed in this Ph.D. Work. Different film morphology was observed with these two methods. Although the film is slightly rougher in the case with sprayed QD/polymer active layer, the phase segregation is more distinct and with smaller domain, which is beneficial for charge transport.
CHAPTER 1: INTRODUCTION

1.1 Fundamentals of Photovoltaic

Photovoltaic was first discovered by Becquerel in 1839 [1,2], when he produced a current by exposing silver electrodes to radiation in an electrolyte. Photovoltaic effect is due to the absorption of light - photons - in a semiconductor, which can create an electric current under certain conditions.

All practical photovoltaic cells have intentionally built-in asymmetry. Without asymmetry, there would be no reason for current to flow to certain direction. A $pn$ junction would be the simplest structure for photovoltaic cell. Due to the difference in carrier density in n-side and p-side, diffusion of electrons and holes would cause a double layer of charges near the junction. This space is called depletion layer or space charge region. The resultant electric field would create an internal voltage drop at the junction. This built-in voltage can be shown to be:

$$V_d = \frac{kT}{e} \ln \frac{N_D N_A}{n_i^2} \quad (1.1)$$
Where $N_D$, $N_A$ are the dopant density for electrons and holes, respectively; $n_i$ is the carrier density for intrinsic semiconductor.

When forward bias voltage $V$ is applied to the junction, the potential barrier is lowered and electrons are injected into the p side, and holes injected into the n side. Upon detailed derivation [3, 4], we get:

$$I = I_0 e^{eV/kT} - 1) \quad (1.2)$$

$I_0$ is known as the reverse saturation current of the junction and is associated with the minority carrier injection. Later on it will be shown that $I_0$ should be minimized to reach higher solar cell efficiency.

When considering the depletion region recombination, Equation 1.2 will have to be modified by a parameter $\gamma$ as:

$$I = I_0 e^{eV/kT \gamma} - 1) \quad (1.3)$$

where $\gamma$ is between 1 and 2. Good solar cell performance demands small $I_0$ and $\gamma$. Many other types of junctions also exhibit the behavior represented by Equation 1.3, these include certain metal/semiconductor (Schottky) junction, electrolyte/semiconductor junction and junctions between two unlike semiconductors. However, the physics is the same as for pn junction.
1.2 Basics of Solar Cells

1.2.1 Light absorption and carrier generation

For a semiconductor with a bandgap $E_g$, photons with energy higher than $E_g$ would be absorbed by the semiconductor and generate a pair of electron and hole (Wannier exciton). Solar cells made of narrow bandgap materials can be expected to generate more current. Absorption of light from direct semiconductors, for example, GaAs, can be utilized when $E_f - E_i = h\nu$. The absorption in an indirect semiconductor, for example, Si, is quite different. Phonon assistance is necessary for the absorption to occur. The absorption coefficient in this case is several orders of magnitude smaller than that of the direct semiconductor absorption.

1.2.2 Carrier recombination

If “excess” charges are created in a semiconductor, i.e., if the carrier concentrations are made to exceed their equilibrium values, such as by photo-carrier generation, the excess charges die away by recombination. There are three major recombination processes: Radiative Recombination, Auger Recombination, Recombination via defect levels (traps).

(1) Radiative recombination

Radiative recombination is when electrons “fall back” from the conduction band into the valence band and thus annihilate the same number of holes. This process is the exact inverse to absorption. Similar to absorption, this process is more likely to happen in direct
semiconductors than in indirect semiconductors. Radiative recombination is also called band to band recombination. In *direct* semiconductors with moderately high doping densities, this process is the dominant recombination.

(2) **Auger recombination**

In the Auger effect one electron gives up its extra energy to a second electron in the conduction or valence band during recombination, thus moving it to a higher energy level. This excited electron then gives up this additional energy in a series of collision with the lattice, and eventually returns to its original energy state. Auger recombination dominates at very high doping level.

(3) **Recombination via defect levels (traps)**

In lightly doped semiconductors, recombination through recombination centers (also known as defect levels or traps) may dominate. Another concept closely related to recombination is diffusion length. The definition is:

\[ L = \sqrt{D\tau} \]

Where D is the diffusion constant of the carrier and \( \tau \) is its lifetime.

1.2.3 **The Current - voltage characteristic of solar cell**

The following gives a general description about the Current - voltage characteristic of solar cell.
1. Short circuit current $I_{SC}$

Upon shining of light on the diode, the balance between the tendency of diffusion and the impeding effect from the potential barrier (Equation 1.1) are tipped. If the two terminals of a diode are connected together, a current, aptly called short circuit current $I_{SC}$, would flow in the circuit from p-side to the n-side. When both light and external voltage $V$ are present, the total current is the sum of $I_{SC}$ and current in Equation 1.3:

$$I = I_0(e^{V/\lambda TV} - 1) - I_{sc} \quad (1.4)$$

Assuming the charge carriers generated inside the space charge region are swept out immediately after generation and there is no charge recombination, then only those charge carriers generated either in the space charge region or at a distance smaller than one diffusion length from the junction contribute to current.

Many factors affect $I_{SC}$. Longer lifetime of the charge carriers hinder the recombination, therefore increases $I_{SC}$. The doping profile can be managed near the junction such that electric fields are set up in a direction so as to aid the collection of photo-generated carriers. $I_{SC}$ also increases linearly with incident light intensity up to saturation, so focusing the sunlight would also help to increase $I_{SC}$. Fig. 1.1 shows the typical I-V characteristic curve for an illuminated solar cell.
Figure 1.1. I/V Curve. Current-Voltage characteristic of a solar cell

2). Open circuit voltage $V_{OC}$

The open circuit voltage $V_{OC}$ is obtained from Equation 1.4 when $V=0$:

$$V_{oc} = \frac{\gamma kT}{e} \ln \frac{I_{sc}}{I_0} \quad (1.5)$$

In order to increase $V_{OC}$, minimization of $I_0$ as well as increasing $I_{SC}$ are necessary. Also, $V_{OC}$ increases linearly with the bandgap $E_g$, though $I_{SC}$ decreases with increased $E_g$. As a result, we may expect solar cell efficiency to peak at certain $E_g$. Temperature is another important factor that affects $V_{OC}$ as $V_{OC}$ increases linearly with temperature.
3). Fill factor (FF)

Fill factor is defined as the ratio of the area of the largest rectangle that can fit under the I-V curve to the product $I_{SC}$ and $V_{OC}$. i.e.,

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}}$$  \hspace{1cm} (1.6)

with $V_m$, $I_m$ being the voltage and current at the optimal operating point. The fill factor normally lies in the range 0.75 to 0.85 for semiconductor solar cells.

4). Energy conversion efficiency

The energy conversion efficiency of a solar cell is defined as the ratio of the photo-generated electric output power to the incident photon power:

$$\eta = \frac{V_m I_m}{P_{in}} = FF \frac{V_{oc} I_{sc}}{P_{in}}$$  \hspace{1cm} (1.7)

5). External quantum efficiency (IPCE)

The external quantum efficiency (EQE) of a solar cell is sometimes called IPCE, meaning the incident-photon-to-collected-electron efficiency for a certain wavelength $\lambda$.

$$IPCE(\lambda) = \frac{1240 \times I(\lambda)}{\lambda(P_{in})}$$  \hspace{1cm} (1.8)

where the wavelength $\lambda$ has the unit $nm$. 
Figure 1.2. Equivalent circuit for a single junction solar cell [5].

1.2.4 Loss Analysis

Fig. 1.2 shows the equivalent circuit for a single junction solar cell. The photo generated current $I_{ph}$ is in the opposite direction of the forward current $I$ of the diode. The diode is described by the Shockley equation [5]:

$$I = I_0(e^{(V-IR_s)/kT} - 1) + \frac{V - IR_s}{R_{sh}} - I_{ph}$$

Two major kinds of losses are of particular importance. One is the electrical loss; another is the optical loss. Electrical loss includes recombination loss and ohmic contact loss. The contact resistance can be divided into shunt resistance ($R_{sh}$) or parallel resistance and series resistance ($R_s$). $R_{sh}$ is determined by leaking currents along the edges. Point defects in the p-n junction can also lead to a low parallel resistance, whereas $R_s$ consists of several components: contact resistance of metal-semiconductor, ohmic resistance
of the semiconductor and resistance of the metal contact. Shunt resistance $R_{SH}$ and series resistance $R_S$ are important for the fill factor. For optimal efficiency, $R_{SH}$ should be as large as possible while $R_S$ is minimized.

Optical loss can be from reflections (over 30%), and inefficient absorption of light. The key factor to minimize optical loss is to reduce reflection from the surfaces and increase the absorption of active layer.

1.3 Specifics of Organic Photovoltaic

Organic semiconductors refer to a class of carbon based materials in which the $\pi$ electrons are delocalized over several carbon atoms due to conjugation, i.e., alternative single bond ($\sigma$ bond, formed by head-on overlap of $p$ orbitals) and double bond ($\sigma +\pi$ bonds, $\pi$ bond is formed by sideway overlap of $p$ orbitals) [6]. There are usually two categories of organic semiconductors, depending on their molecular weight (Fig. 1.3). The first is called small molecular semiconductors such as Zinc phthalocyanine (ZnPc). In general phthalocyanine and its derivatives are p-type electron donors, whereas perylene and its derivatives are n-type electron acceptors.
Figure 1.3. Organic Molecular Structures. (a) organic small molecules and (b) conjugated polymers and fullerene derivatives used in organic solar cells [7].

Thin film solar cells based on organic semiconducting materials are inexpensive and hold the prospective of low cost, large-scale production. The early organic solar cells were based on a single layer of molecular organics between two asymmetric metal electrodes. The power conversion efficiency (PCE) for such cell reached 0.7% for merocyanine dyes in the late 70s [8, 9]. In 1986, C.W. Tang made the next breakthrough in a bilayer heterojunction structure (PCE >1%) [10]. Ever since, a PCE of 4.2% has been achieved in evaporated bi-layer device [11]. Recently a heterojunction solar cell with a PCE of 5% was fabricated via co-evaporation of C_{60} and CuPc [12]. Following the work of Hiramoto et al. [13], an organic p-i-n structure with PCE of 2.4% was reported [14].

Organic semiconductors are different than the conventional semiconductors such as Si or InAs. First of all, their band gaps are much larger, usually between 2- 3.5eV, secondly, absorption of photon by organic semiconductors create tightly-bound exciton (called Frenkel exciton) which has much less mobility and shorter diffusion length than Wannier excitons in conventional semiconductors [6].
Thirdly, their absorption coefficients are much larger than those of the conventional semiconductors. Difference in optoelectronic properties means that organic photovoltaics (OPV) is different than the normal PV as discussed in the previous section. This results in some modifications of the aforementioned photovoltaic effect in conventional semiconductors. There are four steps in OPV process: (1) light absorption, (2) exciton dissociation, (3) charge transport and (4) collection. Absorption of a photon creates an exciton (bounded electron-hole pair); exciton diffusion to a region (for instance, the interface of two different components), where exciton dissociation (or charge separation) happens; finally the separate charge transport to the anode (holes) and cathode (electrons). Exciton diffusion length is usually very small in organic semiconductor (~10nm). Therefore, without proper donor-acceptor interface, majority of excitons will be annihilated.

One of the breakthroughs in realizing higher efficiencies in organic solar cells was the intimate mix of donor and acceptor in components in a bulk volume such that each donor/acceptor interface is within a distance of exciton diffusion length of each absorption site. This concept of bulk heterojunction (BHJ) was first introduced in a polymeric solar cell based on conjugated polymers (poly(2-methoxy-5-(2 prime-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV)) and fullerene C_{60} in 1995 [15]. This turned out to be a major breakthrough in OPV. In the past two decade, majority of research has been conducted in nanomorphology control to optimize interface properties [16, 17]. Optimization of charge collection was also done through proper choices of electrodes and modification of semiconductor/metal interfaces [18]. The best BHJ polymeric solar cell reaches PCE~8% [19, 20].
However, this value is still not high enough to make organic solar cells commercially viable. Quest of other novel approaches to greatly improve the performance of conventional polymeric solar cells can be done first by analyzing the main factors that cause the low power-conversion efficiencies in the present polymeric solar cells: (i) less than optimal overlap between the solar power spectrum and the absorption spectra of most organic molecules and polymers. (ii) loss of photon energies exceeding the optical gap, $E_g$ of the semiconductor as heat.

Infrared quantum dots with tunable electronic properties offer very attractive approach for expanding spectral sensitivity of polymeric solar cell to infrared region of solar spectrum. Further more, they offer a novel approach to drastically increase efficiency of organic solar cells due to efficient multiple exciton generation upon absorption of high energy photons.

1.4 Quantum dots: Basic physics

Quantum dots are essentially nanocrystals consists of tens to hundreds of atoms, due to the small size of nanocrystals (smaller than Bohr radius of the bulk semiconductor), strong quantum confinement results in discrete energy levels and bigger bandgap comparing with the bulk semiconductor (Fig.1.4), such bandgap is extremely sensitive to volume change of the QDs and can be tuned over a large energy range simply via
synthetic control over the QD-size [21]. For instance, PbSe QDs have bandgap tunable from $1.1eV$ (QD diameter ~4nm) to $0.4eV$ (QD diameter 16nm). Combination of PbSe or PbS QDs with organic semiconducting polymers is promising to expand the current absorption spectrum to near infrared region of the solar spectrum. In addition, these infrared QDs also strongly absorb solar photons of higher energy (larger absorption coefficient at higher photon energy). It is well known that absorption of most polymers begins to drop after $2.8eV$ ($\sim$450nm), adding QDs would also compensate for loss of high energy photons in polymer films.

PbSe and PbS QDs have generated strong research interest due, in part to the discovery of multiple exciton generation (MEG) that possibly could boost quantum dots solar cell efficiency [22, 23]. MEG was first suggested to occur via impact ionization (ImI) [22, 24]. The latter is an Auger-type effect, in which a high-energy exciton relaxes to the band edge via transfer of energy of at least $1E_g$ to a valence band electron,

**Figure 1.4.** Quantum dot Structures. (a) Rock salt crystal structure of a PbSe nanocrystal. (b) Quantized energy levels of a PbSe Quantum dots. The dashed line represents the in-gap state of trapped exciton in PbS Quantum dots [32]. (c) Absorption spectra of PbSe Quantum dots with different sizes. Arrows indicate the first excitonic peak ($1S_h-1S_e$) in the infrared region.
which is then excited above the energy gap to produce an additional exciton (Fig.1.5). Recently it was found that MEG is a much faster process (sub-ps) than Auger recombination (hundreds of ps), and some other mechanisms were suggested to explain the MEG process [23, 25].

![Figure 1.5](image)

**Figure 1.5.** Multiple Exciton Generation (MEG) (a) allows a conversion of electron excess energy into additional current, while normally this excess energy would be lost as heat (b). The efficiency of MEG in PbSe nanocrystals steeply grows above the 3 $E_g$ threshold (c) [25].

However, these initial observations are contrasted by more recent experiments, which indicate that MEG rates may either be negligible, or at least much smaller than reported earlier [27-30]. In this context, it is difficult to foresee whether MEG will really lead to the promised efficiency increases or not. We have developed a novel way to manipulate the quantum dot ligands, and the preliminary results have shown significant increase in photoconductivity, improved nanomorphology and possibly, more efficient exciton dissociation (see section 5.4). Hypothetically, further research on this interface engineering method, with the guide of fundamental study proposed here, could have potential to realize MEG effect.
We have recently discovered a below-gap state (BG.S) that shows a confinement-dependent absorption (IR-PA) in the near infrared range in the original PbS QD films (Fig.1.6). By measuring the frequency dependence of this IR-PA, we estimate the lifetime of this BG state to be around several microseconds. Our recent results have confirmed the nature of this IR-PA was due to the trapped excitons on the nanocrystals. We believe this BG state could be used to monitor photoinduced charge transfer (PCT) between QD and polymers, similar to the case seen in π–conjugated polymer and fullerene systems [33-37]. Our preliminary data in Fig.1.7 further illustrate why this BG.S. can be used as a spectroscopic gauge to obtain quantitative information about PCT. When PCT happens between QDs and polymer, either it is electron transfer from polymer to QDs, or hole transfer from QDs to polymers depending.
on the pump excitation energy, we expect to see the change of relative strengths between IRPA of QDs and polaron peak $P_2$ from the polymer. By also measuring the PA of each constituent, we could derive a simple formula about PCT rate:

$$\text{Define } R = \frac{I_{P_2}}{I_{IR-PA}} \quad (1)$$

$$r_{PCT} \propto \frac{R_{\text{composite}} - R_{\text{individual}}}{R_{\text{individual}}} \quad (2)$$

Figure 1.7. Photo Induced Absorption of PbS. (a) Photoinduced absorption (PA) spectra of a PbS NC (2.5nm) film (open square) and a P3HT/PbS QD (2.5nm) nanocomposite film (solid line) measured at $T = 10K$. BG state is revealed as the near IR peak (IR-PA), whereas the polaron absorption from P3HT is marked $P_2$; (b) Molecular structures of P3HT and PbS QD.
1.5 Hybrid Solar Cell

QDs mixed with conjugated polymers have been actively studied following the work of Greenham, Alivisatos, and coworkers [38-40]. Progress in this direction has been made via study of the QD-polymer composite morphology [41] by using polymers that are functionalized to attach to QD surfaces [42] and by improvement of electron transport via incorporation of branched or elongated nanoparticles [43].

Upon the development of high-quality IR-absorbing QDs [21, 44-46], near-infrared photovoltaic effects have been demonstrated in devices consisting of PbS QDs and conducting polymers [47-52]. In ref.47, Sargent and co-workers reported for the first time a small IR photoresponse of up to $1.6\mu m$ of a device made of PbS and MEH-PPV. More recently, they showed improved photovoltaic effects from bi-layer devices with PbSe QDs, after performing post-synthesis ligand exchange with the QDs (ref. 48). In ref. 49, the authors demonstrated a new way of synthesizing the composite QD/polymer \textit{in situ}, which accounted for the improved device performance in the visible region. The earlier work of Jiang \textit{et.al.}, demonstrated photovoltaic performance from nanocomposites of regio regular poly-(3-hexylthiophene) (RR-P3HT) and PbSe QDs [51], which was the first report about the photovoltaic effect under solar AM1.5 illumination ($100mW/cm^2$ in such a system). Recently, similar results were presented in Ref. 52. Their results showed improved efficiency, IR absorption from QDs contributed $> 30\%$ of the overall photovoltaic effect.
One common problem with QD/polymer mixture is the difficulty of achieving a uniform
dispersion of QDs once the film was formed, and QD aggregation was common [51].
Traditionally, the mixture film was formed by spin-coating, which results in non-uniform
distribution of QDs within the polymer matrix due to the centrifugal effect.
Hypothetically, QD/polymer film formed by spray, shows a much more improved
morphology. This Ph.D. work has done some initial exploration about this direction (see
section 5.5).

In order to make organic solar cells and hybrid solar cells a viable solution to the
society’s energy needs, lowering manufacturing cost for large scale is a must. Large area
OPVs have been demonstrated using printing [53, 54], spin-coating and laser scribing
[55-57], and roller painting [58]. ITO, a transparent conductor, is commonly used as hole
collecting electrode (anode) in OPV, and a normal geometry OPV starts from ITO anode,
with the electron accepting electrode (cathode), usually a low work function metal such
as aluminum or calcium, being added via thermal evaporation process.

There are two different approaches in inverted geometry. One approach is ITO-free wrap
through by Zimmermann et.al. [59], another approach is to add an electron transport layer
onto ITO to make it function as cathode. Inverted geometry OPVs in which the device
was first built from modified ITO as the cathode have been studied both in single cells
[60-63] and solar modules [64].
OPV single cell utilizing spray technique has been previously reported [65-67]. However, all these work involve either the use of high vacuum deposition, and/or with spin-coating process. For the inverted solar array fabricated EXCLUSIVELY by spray, the work presented in this thesis is the first of its kind. Comparing with conventional technology based on spin-coating and using metal as cathode contact, which greatly limits transparency of solar cells and posts difficulty for large scale manufacturing, the new spray technology solves these two problems simultaneously. This technology eliminates the needs for high-vacuum, high temperature, low production rate and high-cost manufacturing associated with current silicon and in-organic thin film photovoltaic products. Furthermore, this technology could be used on any type of substrate including cloth and plastic.

This Ph.D. work demonstrates the development of a complete solution processable fabrication method for potentially high efficiency solar cells using conjugated polymers and colloidal quantum dots, based on fundamental study of the material system and various device structures.
1.6 References


55. M. Niggemann, B. Zimmermann, J. Haschke, M. Glatthaar, A. Gombert, Organic solar cell modules for specific applications—From energy autonomous systems to large area photovoltaics, Thin solid films, 2008, 516, 7181.


69. X. Wei and Vardeny, Handbook of Conducting Polymers II, Chapter 22, Marcel Dekker, Inc., New York, 1997

70. C. G. Yang, E. Ehrenfreund, M. Wohlgenannt, and Z. V. Vardeny, PHYSICAL REVIEW B **75**, 246201 _2007._


CHAPTER 2: EXPERIMENTAL

2.1 Continuous Wave Photoinduced Absorption Spectroscopy

Continuous Wave Photoinduced Absorption Spectroscopy (cw-PA) is also called pump & probe or photomodulation spectroscopy (Fig.1.9). A cw-Ar⁺ laser (pump), with its energy larger than the optical gap of the investigated material, excites the sample film and generates long-lived photoexcitations; a tungsten-halogen lamp is used to probe the modulated changes \( \Delta T \) in transmission \( T \) among the interested energy range, usually the subgap regime. A lock-in amplifier is employed with an optical chopper for photomodulation. A series of solid-state photodetectors are coupled with light sources and optical components to span the detection range from UV to NIR. The advantages of cw-PA are that both neutral and charged excitations may be studied and there is no need to introduce dopants into the film [1].

In consideration of light transmission through a thin film with thickness \( d \), refractive index \( n \), absorption coefficient \( \alpha \) and reflection coefficient \( R \), the general formula of transmission \( T \) is:

\[
T = \frac{(1 - R) e^{-\alpha d}}{1 + R^2 e^{-2\alpha d} - 2R \cos 2\delta}
\]  

(2.1)
where $\delta = \frac{2\pi nd}{\lambda}$ is the optical phase shift per pass. Since the films investigated in this proposal are cast from solutions, their thickness is not perfectly uniform. Thus, the interference effects are cancelled out. Also, neglecting all effects due to reflections on the surface of the polymer film, the probe light transmission through the sample may be written as:

$$T = I_0 e^{-\alpha d} \quad (2.2)$$

where $I_0$ is the incoming light intensity. Upon laser illumination, contributions of absorption bands due to the photoexcitations will alter $\alpha$ ($\alpha$ can be increased due to induced absorption or reduced due to induced bleaching). Derivative of equation Eq. (2.2) with respect to $\alpha$ gives $\Delta T$

So we can express the normalized change of transmission as:

$$PA = \frac{\Delta T}{T} = -\Delta \alpha d = \sigma n_e d \quad (2.4)$$

with $n_e$ the density of photoexcitations, and $\sigma$ their optical cross section.
Summary about the major functions of cw PA spectroscopy:

(1) the density of photoexcitations \( n_e \) by \( PA = \frac{\Delta T}{T} = n_e \sigma d \), with \( \sigma \) their optical cross section, \( d \) the film thickness;

(2) the lifetime \( \tau \) of photoexcitation by varying modulation frequency \( f \) by

\[
PA_Q/PA_{in} = 2\pi f
\]

(3) the activation energy \( E_T \) of sub-gap state by varying sample temperature \( T \)

(4) the recombination kinetics by varying pump light intensity

The versatility of this spectroscopy is that the absorption and photoluminescence (PL) measurement are also carried out using the same setup. Combination of these non-contact optical probes is able to reveal the information about the spectral and temporal distribution of any below-gap, long lived states.
The unprecedented success has been demonstrated in numerous amorphous semiconductor systems including π–conjugated polymers [2-4]. Particularly, the probe of efficient PCT in PCPs and fullerene (or C\textsubscript{60}) derivatives was the herald of a drastic increase in polymeric solar cell efficiency [5-8].

2.2 Device Physics Characterizations

The current-voltage \((I–V)\) characterization of the solar array was performed with a Newport 1.6 KW solar simulator under AM1.5 irradiance of 100\textit{mW/cm}^2. The incident light power was measured by a calibrated Newport Oriel thermopile detector. No spectral mismatch with the standard solar spectrum was corrected in the power conversion efficiency (PCE) calculation. The incident photon converted electron (IPCE), or the external quantum efficiency, of the device was measured using 250\textit{W} tungsten halogen lamp coupled with a monochromator (Newport Oriel Cornerstone 1/4\textit{m}). The photocurrent was detected by a UV enhanced silicon detector connected with a Keithley 2000 multimeter. The transmission spectrum of active layer was performed on the same optical setup. The energy conversion efficiency \(\eta\) and external quantum efficiency \(IPCE\) were calculated according to Eq. (1.7) and (1.8); the filling factor FF was also obtained using Eq. (1.6).
2.3 Conductivity probed by FET

The conductivity of a material can be probed by a field effect transistor (FET). An FET has 3 main components, a source, a gate, and a drain. The amount of current allowed to flow from the source to the drain, depends on the voltage applied to the gate. The device uses p-type silicon, which is a silicon wafer doped with an element from group IIIA of the periodic table. The purpose of p-type doping is to create an abundance of holes, or can be viewed as the lack of electrons. A layer of silicon dioxide (SiO$_2$) is grown on the p-type doped wafer, to a thickness of about 20nm. The SiO$_2$ acts as an insulating layer of the FET, and protect the gate from coming into direct contact with the source and drain. The source and drain are metal contacts that sit on top of the SiO$_2$. Fig. 2.2 presents four FET’s on one silicon wafer, that share a common gate. The FET’s shown here vary only by the distance (channel length $L$) separating their corresponding source and drain. We use the FET’s to probe the conductivity of active layer materials used in our OPV devices by either spin coating or spraying, and specifically, in between the source and drain.

\[
R = \rho \frac{L}{A} = \rho \frac{L}{wd}
\]

\[
\rho = \frac{Rdw}{L}
\]

\[
\sigma = \frac{1}{\rho} = \frac{L}{Rdw}
\]
Where $R$ is the measured resistance between source and drain, $L$ the channel length, $w$ the channel width, and $d$ is the thickness of material. $\sigma$ is the conductivity of the material.

Fig. 2.3b shows the dimension of a FET channel.

**Figure 2.2.** 2D Field Effect Transistor. above, shows the 4 FET’s on one silicon substrate, and their respective gold contacts. The grey semicircle to the right represents the common gate shared be all 4 FET’s
Figure 2.3. FET Channels. a) FET channels of varying lengths. b) The length (L) is considered to be the distance between the channels, and varies between the 4 FET structures (2µm, 5µm, 20µm, and 50µm).

The figures below (Fig. 2.4 – 2.7) show the fabrication process of such FET device.

Figure 2.4. FET Substrate. a) FET fabrication starts with a p-type silicon wafer. b) Silicon dioxide is then grown on the wafer using a dry method, and is ~20nm thick.
Figure 2.5. FET and Photoresist. a) a thin layer of positive photoresist is spin coated on top of the substrate at a rate of 4500rpm for 45s. The substrate is then soft baked for 3min at 90°C. b) An optical mask having the desired pattern makes a hard contact with the photoresist in a Karl Suss mask aligner. The substrate/mask is then exposed to UV light for 1s at 25mW/cm².

Figure 2.6. FET developing and Gold Coating. a) Photoresist exposed to the UV light will wash away in the developer (Shipley® MF319), leaving a pattern of unexposed photoresist that was protected by the chromium pattern during exposure. b) Using TVD, a 300Å thick layer of gold is grown on top of the photoresist.
Win the photoresist, and thereby lifting off the gold on its surface. b) The common gate it created by scratching away the SiO₂ layer at its location.

2.4 Solar Cell Fabrication Techniques

In this Ph.D. work, four different OPV structures are presented. Several fabrications methods are used such as spin coating, spraying, and thermal vapor deposition. Some of the parameters for study are spin rates, solution concentrations, annealing temperatures and duration, as well as size of droplets and pressure in spraying process. OPV modules have additional steps for creating the series and parallel connections, which can be found in their respective chapters. The fabrication techniques described in this Ph.D. thesis are protected by several patents.

Patterning of the ITO/Glass Substrate

Indium Tin Oxide (ITO) coated glass is used as the substrate for all of the following devices. The ITO coated glass used was purchased from Delta Technologies, and has a sheet resistance between 4 – 15Ω/□. Photolithography is used to pattern the ITO. The substrate is cleaned with acetone, and cotton by hand, and blown off with N₂ gas. A layer
of photo-resist (Shipley® 1813), a photo-active polymer, is spin coated onto the ITO at a rate of 4300rpm for 45s. To evaporate the solvents out of the photo-resist layer, the substrate is subsequently soft baked on a hotplate at 90˚C for 3min. After cooling, the substrate is put in a Karl Suss mask aligner, where it is exposed to UV light through an optical mask. The optical mask is a glass mask that has the desired ITO pattern etched onto the glass in chrome. The mask aligner is used to align the optical mask with the substrate, where it makes a hard contact with the substrate. The photo-resist layer is then exposed to UV light through the patterned optical mask. After exposure, the substrate is then developed in the corresponding developer (Shipley® MF319). Positive photoresist was used for this process. Positive resist exposed to the UV light will be washed off during development process, whereas the photoresist protected by the chrome pattern on the optical mask stays on the substrate. The substrate is then rinsed with DI water, and hard baked on a hotplate at 140˚C for 5min. An etching solution of HCl and HNO₃ in DI water is prepared and heated to ~100˚C on a hotplate. The substrate is then placed in the bath of etching solution where any exposed ITO that is not protected by photo-resist is etched off. Etching takes ~10min, after which the substrate is rinsed with DI water.
**Figure 2.8.** ITO/Glass Substrate. a) shows an ITO coated glass. The ITO is approximately 100nm thick. b) a thin layer, ~1µm, of positive photoresist (Shipley® 1813) is spin coated on top of the ITO, and a soft bake at 90°C for 3min is performed to evaporate some of the solvents in the resist.

**Figure 2.9.** UV Exposure. a) An optical mask made from glass and having the desired pattern on it in chromium, is used to pattern the photoresist. The mask makes a hard contact with the substrate and is exposed to a dose of UV light. b) The mask functions a stencil for the UV light on the photoresist, and after exposure, the pattern can sometimes be seen in the resist.
a) Photoresist exposed to the UV light will wash away in the developer, leaving a pattern of unexposed photoresist that was protected by the chromium pattern during exposure.

b) The substrate is then hard baked at 130°C and is then etched in a solution of HCl and HNO₃ for ~6 min at 100°C. During this process, ITO not protected by photoresist will etch off the substrate, leaving the desired ITO pattern.

**Figure 2.10.** Developing and Etching of ITO. a) Photoresist exposed to the UV light will wash away in the developer, leaving a pattern of unexposed photoresist that was protected by the chromium pattern during exposure. b) The substrate is then hard baked at 130°C and is then etched in a solution of HCl and HNO₃ for ~6 min at 100°C. During this process, ITO not protected by photoresist will etch off the substrate, leaving the desired ITO pattern.

**Figure 2.11.** Patterned ITO Substrate. The substrate is then cleaned with acetone to wash the resist, followed by sonication cleaning at 50°C in trichlorobenzene, acetone and isopropanol. A final UV-ozone for cleaning for 15 min finishes the process for patterning the ITO.
ITO/Glass Substrate Cleaning

After the excess photoresist is washed off by hand with acetone, the patterned ITO substrate is cleaned by sonicating in trichloroethalene, acetone, and isopropanol for 20min each at a temperature of 50°C. The substrate is then cleaned by UV ozone for ~15min, and is stored in the glovebox.

Patterning of Shadow Mask

The earliest devices represented in this paper where performed using stainless steel shadow masks fabricated in house, using photolithography. The method to pattern the photo-resist is the same method for patterning the ITO/glass substrate found above. Etching is achieved with a solution of ferric chloride (FeCl₃). After etching, the shadow mask is rinsed with DI water, and cleaned by hand with acetone and isopropanol.

This method to fabricate shadow masks is effective and very inexpensive for pattern sizes > 1mm, but limited feature size and complexity warranted later research devices to be fabricated with shadow masks purchased from Towne Technologies.

Active Layer Solution Preparation

The final active layer solution contains 1:1 mixture of the donor material P3HT and the PCBM acceptor material. Different P3HT and PCBM materials from various suppliers are investigated, with variable molecular weight ranging from <20K (low molecular weight, LMW) to >50K (high molecular weight, HMW) for regio regular P3HT, and different fullerene derivatives such as PCBM(C₆₀), and PCBM(C₇₀). Various solvents have also been used for the active layer solution, including chloroform, chlorobenzene, and dichlorobenzene. The two solutions are then mixed together at a ratio of 1:1, and
allowed to stir at 60 °C for another 24h. Prior to use, the final active layer solution is stirred for a minimum of 1h.

Conventional OPV Structure with an Aluminum Cathode

In the conventional structure that uses an aluminum cathode, the ITO functions as the anode of the device. After the final cleaning of the substrate, the entire fabrication process is completed in the glove box. Filtered PEDOT:PSS is spin coated on top of the patterned ITO at rates between 5000 and 6000rpm. In this structure, the PEDOT:PSS serves as a hole transport layer (HTL) to better facilitate the collection of holes by ITO. A thin layer of PEDOT:PSS also helps to smoothen out the ITO, which helps create a better interface between the ITO and the active layer. Two types of PEDOT:PSS are investigated here, PH-500 and PH-750, which were purchased from Clevios. The substrate is then annealed at 120 °C for 10min. After the substrate has cooled, active layer solution are spin coated over the PEDOT:PSS layer of the substrate. Active layer spin rates investigated for this paper range from 500 to 900rpm. Spin coating time has been held constant for all spin coated active layer devices. The edges of the substrate are then wiped with solvents and cotton to gain better access to the contacts for testing.

Depending on the solvent used in the active layer solution, the time allowed for the substrate to dry varies between 3 and 12h. The final layer in the conventional OPV structure uses Thermal Vapor Deposition (TVD) to deposit a 1000Å layer of aluminum, which functions as the cathode. Patterning of the cathode utilizes a shadow mask. After the shadow mask has been correctly aligned and placed over the active layer with double-sided tape. The substrate is then transferred to the deposition chuck of the TVD
chamber. The final thickness of the aluminum is ~1000Å. The subsequent 10min annealing process with temperatures ranging from 100 - 150 ºC greatly improves device performance, and is also reported in this thesis. The final annealing concludes the fabrication process.

**Inverted OPV Structure Using Cesium Carbonate**

In this OPV structure, the function of the ITO is switched from the traditional roll of anode, to cathode, hence the term, inverted structure. This is accomplished by either spin coating or spraying a thin layer (10 – 20Å) of Cesium Carbonate (Cs$_2$CO$_3$), which lowers the work function of ITO from ~5.7eV to ~3.4eV. The Cs$_2$CO$_3$ solution is prepared by stirring 2mg/mL of Cs$_2$CO$_3$ in 2-ethoxyethanol for 1h. If the Cs$_2$CO$_3$ layer is to be spin coated, the optimal spin rate is 6000rpm for 90s. If, however, the layer is to be sprayed onto the substrate, N$_2$ is used as the carrier gas for the airbrush. The substrate is then annealed at 170 ºC for 10min. The active layer, for the inverted structure, can also be either spin coated or sprayed on with an airbrush. An extensive look at airbrushing techniques and parameters is examined for this paper. Like the Cs$_2$CO$_3$ layer, the active layer is sprayed outside of the glove box, and the carrier gas used is N$_2$. As with the conventional OPV structure, the time allowed for the active layer to dry with the inverted structure, varies between 3 and 12 hours, depending on the solvent used. The drying is done in the glove box. On completion, the substrate is taken out of the glove box. The final layer is a modified PEDOT:PSS which is used as anode in the inverted structure, and can only be achieved by spray coating. To a filtered solution of PEDOT:PSS, 5% of dimethyl sulfoxide (DMSO) is added and allowed to stir at room temperature for 1h. The solution is then sonicated for 1h at 50 ºC. Doping the PEDOT:PSS with DMSO (e.g.
mPED), increases the conductivity of the original PEDOT:PSS, allowing this final layer to function better as an anode. The mPED layer is sprayed with an airbrush with the N$_2$ carrier gas.

**Inverted OPV Structure Using Self-Assembling Monolayer (SAM)**

Like the inverted OPV structure using Cs$_2$CO$_3$, the function of the ITO is switched from anode to cathode. This structure, however, uses self-assembling Monolayer (SAM’s) to lower the work function of the ITO. In particular, propyltriethoxysilane was chosen as the SAM for these inverted OPV device. With a clean, patterned ITO/glass substrate in the glove box, a 3mM solution of the SAM is stirred for 10min in ethanol. The substrate is put in the SAM solution for 48h, to ensure the growth of the SAM’s on the ITO is continuous. The substrate is then rinsed in separate baths of ethanol, toluene, and isopropanol. OPVs using SAM’s to modify the work function of ITO do not receive a separate annealing. The final fabrication procedures for these devices are the same as the inverted Cs$_2$CO$_3$ structure above.

**Hybrid OPV Device Using Quantum Dots (QD’s) in the Active Layer**

These devices have been fabricated with both the conventional and inverted structures. The same spin coating and spraying fabrication methods have also been used to fabricate these hybrid cells. The difference with these cells is in the active layer, which is a mixture of PbS quantum dots and P3HT. The quantum dots chosen for the active layer has size of 2nm with the maximum absorptions spectrum at the 715nm wavelength. These quantum dots were purchased from Evident Technologies and have a concentration of 10mg/mL in toluene. Active layer solution is made by first increasing the
concentration of the QD’s to 20\text{mg/mL} by blowing drying half of the solvent away from a solution with N\textsubscript{2}. A separate solution of P3HT is made at 20\text{mg/mL} in toluene. This solution is stirred for 24\text{h} at 65^\circ\text{C}. The QD solution is mixed with the P3HT solution at a ratio of 4:1 and stirred on a hotplate for 24\text{h} at 65^\circ\text{C}. The rest of the fabrication processes are the same as for OPV devices.

2.5 Other Material Characterizations

Other material characterization methodologies used in this thesis are: atomic force microscopy (AFM), x-ray diffraction (XRD), fourier transform infra-red spectroscopy (FTIR), alpha step, and Dektak-150 profilometer, and other microscopy methods. AFM was used to look at the phase and surface morphology of various active layer materials. The use XRD was also used to determine various crystalline structures of P3HT/PCBM films. The profilometers were used to determine the various thicknesses of OPV layers, as well as the roughness of these layers.
2.6 References


CHAPTER 3: ORGANIC SOLAR MICRO ARRAY FOR APPLICATIONS IN MICROELECTROMECHANICAL SYSTEMS

3.1 Generation 1 Micro Array*

We have developed an innovative way to fabricate organic solar arrays for application in dc power supplies for electrostatic microelectromechanical systems devices. A solar array with 20 miniature cells interconnected in series was fabricated and characterized. Photolithography was used to isolate the individual cells and output contacts of the array, whereas the thermal-vacuum deposition is employed to make the series connections of the array. With 1 mm$^2$ for single cell and a total device area of 2.2 cm$^2$, the organic solar array based on bulk heterojunction structure of π-conjugated polymers and C$_{60}$ derivative [6,6]-phenyl C61 butyric acid methyl ester produced an open-circuit voltage of 7.8 V and a short-circuit current of 55 µA under simulated air mass (AM) 1.5 illumination with an intensity of 132 mW/cm$^2$. The procedure described here has the full potential for use in future fabrication of microarray with the size as small as 0.01 mm$^2$. 

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3.1.1 Introduction

Microelectromechanical systems (MEMS) usually have their own requirements for power supplies. It is desirable to have appropriate on-chip power source with the MEMS device, particularly in cases of autonomous operations such as wireless communication, sensor network, and microrobotic systems. Previous solutions for such power supplies include magnetic field induced current and voltage supplies, \(^1\) electrothermal microactuators based on dielectric loss heating, \(^2\) rechargable lithium microbatteries, \(^3\) integrated thermopile structures, \(^4\) vibration-electric energy conversion, \(^5\) and miniature fuel cells. \(^6\)

Solar cell can also be a good option for such power sources since it is self-contained and can be easily integrated with existing circuits of MEMS. Moreover, solar cell has the potential of achieving the maximum size to power density ratio compared with other miniature power sources. \(^7\) There have been previous studies about on-chip solar cell arrays for applications in MEMS devices, \(^7\)–\(^11\) and the majority of these works have been related to the silicon photovoltaic cells.

Organic solar cells (OSC) based on \(\pi\)-conjugated polymers [e.g., poly-3-hexylthiophene (P3HT)] and fullerene derivatives [e.g., \((6,6)\)-phenyl \(\text{C}_{61}\) butyric acid methyl ester (PCBM)] have attracted attention over the past decades because they may provide a cost-effective route to wide use of solar energy for electrical power generation. \(^12\)–\(^16\) These organic semiconductors have the advantage of being chemically flexible for material modifications, as well as mechanically flexible for the prospective of low-cost, large scale processing such as solution-cast on flexible substrates. The world’s next generation of
of microelectronics may be dominated by “plastic electronics” and organic solar cells are expected to play an important role in these future technologies.

3.1.2 Experimental

The photovoltaic process in OSC devices consists of four successive processes: light absorption, exciton dissociation, charge transport, and charge collection: (i) Absorption of a photon creates an exciton (bounded electron-hole pair); (ii) the exciton diffusion to a region (for instance, the interface of two different components), where exciton dissociation (or charge separation) occurs; (iii) finally, free charges move separately toward the anode (holes) and cathode (electrons), where (iv) they are collected. Several parameters determine the performance of a solar cell, namely, the open-circuit voltage ($V_{oc}$), short-circuit current ($I_{sc}$), and the so-called fill factor (FF). FF is calculated by

$$FF = \frac{I_{mp}V_{mp}}{I_{sc}V_{oc}}$$

where $I_{mp}$ and $V_{mp}$ are the current and voltage operating points for maximum power, respectively. The overall power conversion efficiency $\eta$ is defined as
Although the current power conversion efficiency (about 6%) of OSC is still not high enough to make it a practical solution for large-scale commercial applications as general electric power sources, it is promising to use OSC as a high-voltage power supply. The open-circuit voltage of single junction OSC \( (V_{oc} = 0.6–0.7eV) \) is close to that of the single crystal Si or thin film polycrystalline Si. For many electrostatic MEMS, it is more critical to have high-voltage output (from tens to hundreds of volts) rather than high current or energy efficiency, with an operatable current range usually falling between nanoamperes to microamperes. According to the design criteria of such on-chip solar cells, OSC based on \( \pi \)-conjugated polymers and fullerene derivatives is an excellent choice. First of all, isolation of the solar cell array from the MEMS substrate is easy to achieve, since OSC can be fabricated on any substrate including plastic. This also makes the integration with microsensors and microactuators relatively effortless. Second, these polymers are efficient light absorbers (with a typical absorption coefficient several orders higher than that of the conventional semiconductors such as Si), meaning the active layer can be as thin as 100\( nm \), which makes it simple for series interconnection to produce high voltage. Third, \( V_{oc} \) of a single cell of these OSCs can be easily tuned as high as 0.87\( V \) by chemical tailoring of both constituents. Fourth, the photoactive layer can be made through any solution processable fabrication methods (i.e., spin-coating, spraying, and inkjet printing) without the need of photolithography, which is mandatory with silicon-related fabrication process. These OSC can be manufactured on plastic substrates, making these cells lightweight, flexible, and very cost-effective.
The usual drawbacks of OSC (e.g., lower short-circuit current and power conversion efficiency) are not the major issues for using them as on-chip dc power sources, making OSC a perfect solution for MEMS inertia transducers, such as resonator, accelerometer, gyroscope, and pressure sensors. 19

To the best of our knowledge, there has been no report of organic solar arrays based on P3HT and PCBM as MEMS power sources. Although there have been previous studies on large area organic solar modules 20–23 a small \( (2.2 \text{cm}^2 \) ) photovoltaic minimodule having 20 cells in series was reported in this article. The anode is made by patterning indium tin oxide (ITO) on glass by photolithography, the cathode is made by thermal evaporation through a metal shadow mask, which simultaneously accomplishes the series connection of all cells. The active layer material used in our process is a blend of P3HT and PCBM, which forms a bulk heterojunction structure. In this report, a detailed array fabrication process and the characterization of both single cell and interconnected solar array are present. In the end, a brief discussion will be given about the factors that could affect the output voltage and overall power efficiency, as well as several tentative solutions for short-circuit problems within the array. Our research has focused on the design of a process to ensure full isolation of series connected cells, and this process has the full potential for use in future fabrication of a microarray with a size as small as \( 0.01 \text{mm}^2 \).
Figure 3.1. 1st Generation Micro Array. (a) Enlarged drawing of the anode, cathode, and sandwich structure of single cell with area of $1 \text{mm}^2$. (b) Illustration of the interdigitated organic solar cell array consisted of 20 single cells. The bottom (light purple) layer is photolithography-defined ITO anode, the middle (red) layer is spin-coated P3HT:PCBM, and the top (light blue) layer is thermal deposited cathode by shallow mask technique.
Fabrication Process

The first step was the design of the solar array. The ability to align the substrate with the shadow mask by eye in the inert environment as well as other process parameters were considered before a final geometric design was made for the array. Figure 1 shows such an array consisting of 20 single cells. The top panel of Fig. 1 presents details of each cell. The whole fabrication process consists of four steps.

A. Patterning of the anode

ITO coated glass substrates (>85% transmittance, 5–15Ω/□) were purchased from Delta Technology Inc. and cut into 1 in. x 1 in. pieces. The patterning of ITO is done via standard photolithography using a custom made photomask, as shown in Fig. 1 (light purple). The photomask was made by printing the desired pattern on one plastic transparency and taped onto a piece of 5” x 5” glass. Positive photoresist (Shipley 1813) is spun-coat onto the ITO side of the substrate at a rate of 4500rpm for 45s, creating a layer with thickness of about 1.5μm. The substrate is then soft baked on a 90°C hotplate for 90s, followed by a 3s exposure to UV light through the photomask, and the substrate is then developed in Shipley MF319 for about 1min, followed by a hard bake at 150°C for 10min. Etching of the ITO was done in a mixed solution of HCl and HNO₃. The patterned ITO substrate then undergoes sonification cleaning in trichloroethylene, acetone, and isopropanol at 50°C for 20min each, followed by drying with N₂. The glass substrate now has the desired pattern of ITO, which acts as the anode part of the solar array.
Figure 3.2. The Fabrication Process of Miniature Solar Cell Array. Start from (1) a clean ITO on glass substrate, followed by (2) spin-coating photoresist, (3) development of desired pattern by photolithography, (4) etching off the unwanted ITO, (5) washing off the photoresist, (6) spin-coating active layer (P3HT:PCBM), (7) clean off excessive material, (8) deposit cathode via shadow mask.

B. Creation of the shadow mask

A 1” × 1” piece of stainless steel was patterned following a similar photolithography procedure described above. Etching of the photoresist coated stainless steel was done using a diluted ferric chloride (FeCl₃) solution [25% in deionized (DI) water] for 2h. The patterned shadow mask (Fig. 3.1a, light blue) was rinsed by DI water and sonification in acetone and isopropanol at 50°C for 20min.
C. Formation of the photoactive layer

The original aqueous poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) (Baytron 500) obtained from H. C. Starck was diluted and filtered three times, then filtered out through a 0.45µm filter. The solution is then spun coat on top of the patterned ITO at a rate of 5000rpm for 90s after which the substrate is then heated up to 120°C for 100min. P3HT and PCBM were purchased from American Dye Source Inc. The active layer solution is made by mixing P3HT and PCBM with a weight ratio of 1:1 in chloroform, then spun-coat on top of the PEDOT:PSS coated substrate at a rate of 700–800rpm for 90s. This provides a thickness of 200nm. The excess film is then wiped off in order to allow the aluminum to make the series connections required for the device (Fig. 3.1a). The sample is then allowed to dry for a minimum of 3h in vacuum before thermal evaporation of the cathode.

Figure 3.3. Conventional Test Cell Structure. A) Top view of a substrate with 4, 2mm test cells, circled is the active area. b) Side view of a conventional OPV test cell.
**Figure 3.4.** Conventional Single Cell Performance. Current-voltage characteristics of single cell made with P3HT:PCBM mixed with weight ratio of 1:1 under simulated AM1.5G, radiation at 132.6mW/cm². The active layer was spun-coat on patterned ITO substrate at 800rpm, with a final thickness of about 200 nm. Post-device thermal annealing at 120°C for 5min was done before the I-V measurements.

**D. Deposition of the cathode**

In order for the device to function as a series array, the patterned shadow mask must be precisely aligned to the ITO substrate. With the alignment done the substrate is then fixed onto the chuck and loaded into the deposition chamber. Aluminum was chosen for the cathode due to its desirable work function (for collection of electrons) and cost-effectiveness. Deposition of aluminum was done under high vacuum (>10⁻⁷ torr), with a final thickness of 100nm. Device fabrication is completed with a final annealing on a hotplate at 110°C for 5min in the glove box, prior to the I-V measurements.
Figure 2 illustrates the fabrication process for the organic solar array. The active layer is spun-coat from a chloroform solution of P3HT:PCBM blend with a weight ratio of 1:1.

Figure 3.5. 1st Generation Micro Array. A digital picture of the organic solar array with 20 miniature cells in series.
Figure 3.6 Micro Array I/V Curve. Current-voltage curve of an organic solar array with nine functioning cells measured at simulated AM1.5G with radiation of 132.6mW/cm². The fabrication parameters are the same as single cell (in Fig. 3). The inset shows array Voc as a function of number of cells in series. An output voltage of 7.8V was achieved with 18 cells in series.

3.1.3 Results and Discussion

In order to examine the solar array fabrication procedure described above and find the operational parameters for various processes, we fabricated test OSC in a simpler geometry consisting of four single cells, each has an active area of 4mm² (Fig. 3 upper left panel). The upper right panel of Fig. 3 shows the side view of each cell in bulk heterojunction structure. Preliminary optimization was performed in terms of spin rate and thermal annealing conditions. The best performed single cell was fabricated with an active layer thickness of 200nm followed by a post-device thermal annealing at 120°C for
5 min. The current-voltage (I-V) characterization of the solar cells was performed on a solar simulator consisting of a xenon arc lamp (Oriel 66485) and an air mass (A.M.) 1.5 global filter (Oriel 81094) with irradiation of $132.6 \text{mW/cm}^2$. No spectral mismatch with the standard solar spectrum.

Table 1. 1st Generation Micro Array Data.

<table>
<thead>
<tr>
<th>Array name</th>
<th>Thickness (nm)</th>
<th>Number of cells in series</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Array 1</td>
<td>203</td>
<td>9</td>
<td>5.2</td>
<td>0.0545</td>
<td>0.605</td>
<td>0.32</td>
<td>0.76</td>
</tr>
<tr>
<td>Array 2</td>
<td>202</td>
<td>15</td>
<td>7.0</td>
<td>0.0245</td>
<td>0.163</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>Array 3</td>
<td>232</td>
<td>18</td>
<td>7.8</td>
<td>0.0135</td>
<td>0.075</td>
<td>0.13</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Summary of device parameters for three organic solar cell arrays containing different numbers of cells in series. The current voltage characteristics in dark and under simulated solar AM1.5 with an intensity of $132.6 \text{mW/cm}^2$ are present. Each cell has an active area of $1 \text{mm}^2$. The power conversion efficiency ($\eta$) was calculated using Eq. (2) in text.

AM 1.5 (with an intensity of $132 \text{mW/cm}^2$) was corrected in the I-V characterization. The best of such single devices has a short-circuit current density $J_{sc}=12.7 \text{mA/cm}^2$, open-circuit voltage $V_{oc} = 0.60 \text{V}$, FF = 0.43, and a power conversion efficiency of 2.45% (Fig. 3 lower panel). While this modest efficiency certainly has room to be improved by nanomorphology manipulations,$^{15,16}$ the main purpose herein is to find the right parameters for each fabrication process.
Using these appropriate parameters, organic solar cell array based on the same photoactive material (P3HT and PCBM blend) used above was fabricated according to the fabrication procedure described in Sec. II. The interconnected series consists of 20 cells each with active area of $1mm^2$ on a $1\text{ in.}^2$ ITO substrate. A picture of such an array is shown in Fig. 4(a). Figure 4(b) shows the I-V curve of the best performed array (array 1 in Table I). Though extra caution and efforts have been made to avoid short circuits among individual cells, the alignment of shadow mask with the ITO anodes inside the glove box turned out to be very challenging, especially when the active layer is thin (< 200nm). Not-so-perfect alignment resulted in “shadow effect,” which smeared out the contact to neighboring cells, causing unintentional lateral connection.

In this preliminary work, we also tried to increase the active layer thickness to see how it would help with short circuits of individual cells. Table I gives a summary of three solar arrays with different active layer thicknesses. It can be seen that, with thicker film, a smaller number of cells was short circuited. The inset of Fig. 3.6 plots the array $V_{oc}$ versus the number of cells in series, and a linear relation is shown; for a total of 18 mini-cells, the measured $V_{oc}$ is 7.8V.

Although the overall device performance is less impressive, and the poor FF might be due to increased lateral collection, causing the increase of series resistance ($R_s$) of the solar array. The more important point is the capability to obtain larger $V_{oc}$ in terms of the application for dc power supply. Our prefatory results demonstrate the potential to easily tune the output voltage by the number of cells in series. Further improvement of the array performance is ongoing to determine the optimization of active layer thickness.
and nanomorphology, as well as to reduce $R_s$ of the array device by means of thermal annealing and modifying the contact properties between active layer and the electrodes.

![Figure 3.7](image)

**Figure 3.7.** Improved 1st Generation Micro Array, I/V Curve. The above I/V curve is of the best performing generation 1 micro array, and was fabricated and tested after the above publication.

The results represented in Figure 3.7, are from the last of generation 1 micro-array, which was fabricated after the above publication [24]. The higher performance than previously published is contributed to a thicker active layer (~250nm), brought on by an active layer spin rate of 600rpm for 90s. An output voltage of 11.5 V and short-circuit current as large as 170µA under simulated solar AM1.5 illumination were achieved with this micro-array.
3.1.4 Summary

In conclusion, a miniature organic solar array was designed, fabricated, and characterized for application in MEMS device power supplies. The photoactive layer was formed by spin coating a thin film of \( \pi \)-conjugated polymer P3HT and fullerene derivative PCBM blend mixed in chloroform at a higher concentration. The electrodes were patterned by photolithography and thermal evaporation through a patterned shadow mask. The optimized generation 1 device shows an open circuit voltage (\( V_{oc} \)) of 11.5\( V \), short circuit current density (\( J_{sc} \)) of 1\( mA/cm^2 \), fill factor (FF) of 0.41 and a power conversion efficiency of 1.7% under simulated solar AM1.5 illumination.

3.2 Generation 2 – 60 cell Organic Microarray

For generation 2 microarray(s), two new designs are employed to carry out a series of experiments. The two designs have the same active area of 60\( mm^2 \), however, the first design has 60-1\( mm^2 \) cells in series. We refer to this array as the series microarray. While the second array has parallel connection among 6 rows, each row has 10-1\( mm^2 \) cells in series. We refer to this array as the parallel microarray (see figures 3.8).

Both microarrays are fabricated on a 1” x 1” ITO/glass substrate. The ITO patterning and cleaning procedures can be found in chapter 2, as well as the other fabrication methods. The fabrication of 6 micro arrays was carried out with 3 different OPV structures. Each of the 3 OPV structures has one series and one parallel configuration. The normal OPV structure uses an aluminum cathode, whereas the inverted structure uses either \( \text{Cs}_2\text{CO}_3 \) or SAM as electron transport layer to modify the ITO work function, and m-PEDOT as
anode. Comparing with generation 1 microarray, with the generation 2 microarrays not only has more cells on the same size substrate, it also has reduced series resistance and improved cell occupancy. Furthermore, the fabrication is more precise and easier to carry out, as opposed to the 1st generation microarray.

3.2.1 Device architecture

The figure below (Fig. 3.8) shows the layout of generation 2 micro arrays.

Figure 3.8. 2nd Generation OPV Micro Arrays. a) 60 – 4mm$^2$ cells in series b) 6 rows of 10 – 4mm$^2$ cells connected in series, connected in parallel
3.2.2 Experimental

All fabrication techniques are outlined in Chapter 2. Both the parallel and series arrays use the same shadow mask for series connection wiping. Both arrays are designed such that only one wiping pass is needed to expose the series connection areas of the ITO (figure 3.10).
All 6 arrays had their active layer sprayed on using a 10mg/ml solution of a P3HT (HMW), and PCBM (C_{60}), mixed (1:1) in DCB, which are represented in figures 3.12. The devices are then allowed to dry overnight afterwards.

Figure 3.11. 2nd Generation Substrates. a) parallel microarray, and b) series microarray

Figure 3.12. 2nd Generation Active Area. After the PEDOT:PSS, Cs2CO3, or SAM layers have been established for their respective OPV microarrays, the active layer solution was sprayed on the a) parallel microarrays, and b) series microarrays
The series connections are to be made by wiping off the excess material.

Figure 3.13. 2nd Generation Wiping Mask. The same shadow mask is used to wipe the locations on the microarrays where the series connections are to be made in both the a) parallel microarrays, and b) series microarrays.

Parallel and series shadow masks are aligned to their respective substrates. All inverted arrays are then sprayed with mPED (figures 3.14), and the conventional arrays use TVD to deposit 1000 Å of aluminum.
Figure 3.14. 2nd Generation Shadow Masks. Different shadow masks are used for the final layers, for the a) parallel microarrays, and b) series microarrays.

A final annealing for all the microarrays was done at 120°C for 10min. Testing of the microarrays includes I/V characterization, IPCE measurement, profilometer measurement, and AFM imaging. Figures 3.15 represent the final (inverted) parallel and series microarrays.

Figure 3.15. 2nd Generation Final Micro Arrays. The completed fabrication of a) parallel microarrays, and b) series microarrays. (Shown here are inverted OPV microarrays)
3.2.3 Results and Discussion

Conventional OPV

In figure 3.16 below, a comparison for the conventional OPV microarrays can be seen for the series and parallel designs. An open circuit voltage \( (V_{oc}) = 4.2\, V \), a short circuit current \( (I_{sc}) = 0.46\, mA \), and a PCE = 1.36% was calculated for the parallel microarray. The series microarray had an open circuit voltage \( (V_{oc}) = 12.4\, V \), a short circuit current \( (I_{sc}) = 0.06\, mA \), and a PCE = 0.34%.

![Figure 3.16. Conventional OPV microarray I/V Curve. (aluminum cathode deposited using TVD) Series vs. Parallel I/V curve.](image)

Inverted \((\text{Cs}_2\text{CO}_3)\) OPV

In figure 3.17, a comparison for the inverted OPV microarrays using \(\text{Cs}_2\text{CO}_3\) can be seen for the series and parallel designs. An open circuit voltage \( (V_{oc}) = 4.4\, V \), a short circuit
current ($I_{sc}$) = 0.33mA, and a PCE = 1.12% was calculated for the parallel microarray. The series microarray had an open circuit voltage ($V_{oc}$) = 22.8V, a short circuit current ($I_{sc}$) = 0.055mA, and a PCE = 1.00%.

**Figure 3.17.** Inverted Cs$_2$CO$_3$ OPV microarray I/V Curve. Inverted (Cs$_2$CO$_3$) OPV microarray - Series vs. Parallel I/V curve

**Inverted (SAM) OPV**

In figure 3.18, a comparison for the inverted OPV microarrays using SAM can be seen for the series and parallel designs. An open circuit voltage ($V_{oc}$) = 3.2V, a short circuit current ($I_{sc}$) = 0.30mA, and a PCE = 0.58% was calculated for the parallel microarray. The series microarray had an open circuit voltage ($V_{oc}$) = 9.8V, a short circuit current ($I_{sc}$) = 0.05mA, and a PCE = 0.31%.
**Figure 3.18.** Inverted SAM OPV microarray I/V Curve. Inverted (SAM) OPV microarray - Series vs. Parallel I/V curve

**Figure 3.19.** 2nd Generation Micro Array I/V Curves. I/V curve for all 6 microarrays under A.M. 1.5 simulation
In figure 3.19, the I/V curve of all 6 microarrays can be seen for A.M. 1.5 simulation. We can conclude that a combination of series and parallel connections in the microarrays (i.e. parallel microarray), yield a better PCE for all three OPV structures. This can partially be explained with regards to the series resistance of a parallel array being reduced, as opposed to the series array, which has all 60 cells in series, having the larger series resistance ($R_s$) of the two array designs. Furthermore, the SAM arrays consistently have the lowest PCE of the three OPV structures and array designs presented here. Since the active and mPED layers of the inverted structures were executed together, a decrease in conductivity with inverted SAM arrays is plausible. Pinholes in the SAM due to lift off of some molecules during the application and removal of the shadow masks might cause a decrease in the shunt resistance ($R_{sh}$) for the inverted SAM OPV devices, which has resulted in a smaller $I_{sc}$ for these arrays, as compared with the inverted arrays with Cs$_2$CO$_3$, and conventional arrays.
Table 2. 2nd Generation Micro Array Data.

<table>
<thead>
<tr>
<th>Arrays</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (µA)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>η(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM series</td>
<td>9.8</td>
<td>49</td>
<td>0.020</td>
<td>39</td>
<td>0.30</td>
</tr>
<tr>
<td>SAM parallel</td>
<td>3.2</td>
<td>287</td>
<td>0.119</td>
<td>33.8</td>
<td>0.58</td>
</tr>
<tr>
<td>Conventional series</td>
<td>12.4</td>
<td>62.7</td>
<td>0.026</td>
<td>26.3</td>
<td>0.34</td>
</tr>
<tr>
<td>Conventional parallel</td>
<td>4.2</td>
<td>463</td>
<td>0.181</td>
<td>41.9</td>
<td>1.36</td>
</tr>
<tr>
<td>Inverted series</td>
<td>22.8</td>
<td>55</td>
<td>0.023</td>
<td>48.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Inverted parallel</td>
<td>4.4</td>
<td>332</td>
<td>0.138</td>
<td>46</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Summary of device parameters for three organic solar cell structures, each having two different array architectures. The current voltage characteristics in dark and under simulated solar AM1.5 with an intensity of 100 $mW/cm^2$ are present. Each cell has an active area of $4mm^2$, and every array has a total active area of $2.4cm^2$. The power conversion efficiency ($\eta$) was calculated using Eq. (2) in text.

Figure 3.20. 2nd Generation IPCE. This Graph shows the IPCE of 4 microarrays, 2 are conventional, and 2 for inverted.
IPCE shows consistent results with those from I-V measurements, with parallel configuration being the higher of two. The much smaller QE comparing with a single test cell [24] points out the existence of mass recombination of photogenerated carriers, which might be due to the wide distribution of individual device performance, with the one having the least short-circuit current determining the overall array performance. This could be optimized by a more uniform morphology over the entire device area.

3.3 Conclusion

By examining both generations of micro-arrays, it can be concluded that generation 2 microarray has higher voltages and currents. However, device efficiencies and current densities are decreased by increase in cell number. This is the result of leak current, as well as some of the spray fabrication techniques used for the generation 2 micro-arrays. As with all of the 60 cells in series arrays, a higher $R_s$ contributes to current loss. Continuous research is needed to improve interface properties, film morphologies and conductivity. The good news is that FF is actually better with inverted devices. Although the conventional structure of OPV device still remains a leader in efficiency, the vacuum free fabrication techniques with the inverted OPV structure show the potential for the scaling up of these devices. As new photoactive materials become available, and efficiencies rise, commercialization of these types of OPV arrays becomes viable.
3.4 References

* this is from a paper:


CHAPTER 4: OVER 30% TRANSPARENCY LARGE AREA INVERTED ORGANIC SOLAR ARRAY BY SPRAY

4.1 4”x4” inverted OPV array

We report the fabrication and characterization of large scale inverted organic solar array fabricated by all-spray process. The inverted polymer solar cell geometry consists of four layers, in the order of ITO-Cs2CO3-(P3HT:PCBM)-modified PEDOT:PSS, on a glass substrate. With semitransparent PEDPT:PSS as anode, the encapsulated solar array shows more than 30% transmission in the visible to near IR range. Optimization of device is done by thermal annealing, and the optimal annealing conditions are shown to be difference in single-cell test device and the multiple-cell array. Solar illumination has been demonstrated to improve solar array efficiency up to 250%. Device efficiency of 1.80% was observed with the array under AM1.5 irradiance. The performance enhancement under illumination only happens with sprayed devices, not devices made by spin coating. This means that solar cells made with our spray-on technique performs better under sunlight, which is beneficial for solar energy application.
4.1.1 Introduction

Organic photovoltaic (OPV) devices based on π-conjugated polymers have been intensively studied following the discovery of fast charge transfer between polymer and carbon C$_{60}$.\textsuperscript{[1-9]} The photovoltaic process in OPV first starts from the absorption of light mainly by the polymer, followed by the formation of excitons. The exciton then migrates to and dissociates at the interface of donor (polymer)/acceptor (fullerene). Separated electrons and holes travel to opposite electrodes via hopping, and are collected at the electrodes, resulting in an open circuit voltage ($V_{oc}$). Upon connection of electrodes, a photocurrent (short circuit current, $I_{sc}$) is created.

These polymeric OPV holds promise for potential cost-effective photovoltaics since it is solution processable. Large area OPVs have been demonstrated using printing,\textsuperscript{[10-12]} spin-coating and laser scribing,\textsuperscript{[13, 14, 15]} and roller painting.\textsuperscript{[16]} ITO, a transparent conductor, is commonly used as hole collecting electrode (anode) in OPV, and a normal geometry OPV starts from ITO anode, with the electron accepting electrode (cathode), usually a low work function metal such as aluminum or calcium, being added via thermal evaporation process. There are two different approaches in inverted geometry. One approach is ITO-free wrap through by Zimmermann \textit{et.al.},\textsuperscript{[17]} another approach is to add an electron transport layer onto ITO to make it function as cathode. Inverted geometry OPVs in which the device was built from modified ITO as cathode first have been studied both in single cells\textsuperscript{[18-21]} and solar modules\textsuperscript{[10]}.
For the inverted solar array fabricated by spray, ours is the first of its kind. Comparing with conventional technology based on spin-coating and using metal as cathode contact, which greatly limits transparency of solar cells and posts difficulty for large scale manufacturing, the new spray technology solves these two problems simultaneously. A thin film organic solar array is fabricated employing this layer-by-layer spray technique onto desired substrates (can be rigid as well as flexible). This technology eliminates the needs for high-vacuum, high temperature, low rate and high-cost manufacturing associated with current silicon and in-organic thin film photovoltaic products. Furthermore, this technology could be used on any type of substrate including cloth and plastic.

Traditionally, solar modules made from silicon are installed on rooftops of buildings. However, it can be a hassle for the installation since these solar modules are heavy and brittle. In addition, rooftop area is limited comparing with the window area in normal building, and even less in skyscrapers. However, in order for solar cells to be compatible with windows, transparency is the first to be considered. The metal contacts used in traditional solar modules are visibility-blocking and has to be replaced. OPV modules fabricated by other large scale manufacturing techniques such as printing \cite{10, 16} and spin-coating \cite{14,15} have been demonstrated, however, all these still involve the use of metal in certain way.

Literature results have shown PCE as high as 0.42% for a solution-based all-spray device \cite{22} which was opaque. In this report, we start with a semitransparent single-cell test device which has PCE of 1.2% under AM1.5 solar irradiance, and further demonstrate the
development of an all-spray technique to fabricate large scale solar array on a 4” x 4” substrate consisting of 50 cells with total active area of 30cm$^2$. The overall transmission of the finished solar array is over 30%, and the device power conversion efficiency (PCE) of as high as 1.80% was achieved under constant AM1.5 solar irradiance. We believe this is the record of its kind.

4.1.2. Results and Discussion

In order to have a good reference point for the multi-cell array, we started with an inverted single-cell test device which consists of four identical small cells (4mm$^2$) on a 1” x 1” substrate (Fig. 1). The test device was fabricated using the same procedure described in Experimental section, with m-PEDOT 500 as anode.

Figure 4.1. Inverted Cs$_2$CO$_3$ OPV Structure. (a) Test cell top view; (b) side view.
ITO normally has a work function of \( \sim 4.9eV \). The function of ITO in traditional OPV device is as anode. There have been previous reports on tuning the work function of ITO by adding an electron transport layer such as ZnO\[^{[19]}\], TiO\(_2\)[\(^{[18]}\)], PEO\[^{[21]}\] and Cs\(_2\)CO\(_3\)\[^{[18]}\] in inverted OPV single cells. In this work, we chose to use Cs\(_2\)CO\(_3\) for its economic cost and easy handling. By spin coating a solution of 2-ethoxyethanol with 0.2% Cs\(_2\)CO\(_3\) at 5000 rpm for 60s, a very thin layer (~10Å) of Cs\(_2\)CO\(_3\) is formed over the ITO. It was reported that a dipole layer would be created between Cs\(_2\)CO\(_3\) and the ITO. The dipole moment helped to reduce the work function of ITO, allowing ITO to serve as the cathode.\[^{[18]}\]

**Figure 4.2.** Cs\(_2\)CO\(_3\) Test Cell Spin Rate Tests. I-V characteristics of three test devices without Cs\(_2\)CO\(_3\) layer (black solid line), and with Cs\(_2\)CO\(_3\) layer at difference thickness (black line with empty triangle and magenta line with filled triangle).
Fig. 4.2 shows how the Cs$_2$CO$_3$ layer affects the performance of the inverted cell. The control cell without Cs$_2$CO$_3$ (black solid line) performed almost like a resistor and had negligible $V_{oc}$ (0.03V). The difference between our result and the work in ref [21] can be explained by the use of an electron transport layer to alleviate non-ohmic contact with the cathode (PEDOT in this case) in their work. For a better controlled thickness, Cs$_2$CO$_3$ was spin coated on to the cleaned ITO substrate in these devices. As shown in Fig. 4.2, the optimal thickness of Cs$_2$CO$_3$ layer was achieved at a spin rate of 5000 rpm. At higher rate of 7000 rpm, the device was less efficient owing to the fact of a discontinuous Cs$_2$CO$_3$ layer. We found out that the optimal thickness is around 15Å.

Previous report showed Cs$_2$CO$_3$ can lower the ITO work function to as low as 3.3eV.\textsuperscript{[18]} In order to get an estimate of the effective work function of ITO/Cs$_2$CO$_3$, a control device with aluminum (100nm in thickness) as cathode was fabricated. Since aluminum is not transparent, the I-V was measured by shining light from m-PEDOT side. $V_{oc}$ of such control device was 0.24V, whereas $V_{oc}$ of the inverted cell in Fig. 2 was 0.36V measured under the same illumination condition. Since aluminum has work function of 4.2eV, this means in our case, the effective work function of ITO/Cs$_2$CO$_3$ is close to 4.1eV.
Fig. 4.3. PEDOT:PSS Transparency Measurements. a) transparency and b) resistance between ITO and the anode (modified PEDOT:PSS) at different thickness.

Fig. 4.4 shows how the thickness of m-PEDOT affects its transparency (a) and resistance (b). ITO was chose as a reference for comparison. At thickness of about 100 nm, the transparency of m-PEDOT is about 80%, comparable with ITO. As expected, the resistance decreases as thickness increases, which is consistent with the bulk model. The trade-off between transparency and resistance is another important fabrication parameter. The current array was fabricated with thickness of about 600 nm, which has moderate resistance of 70 ohm/square, and transparency about 50%. Shown in Fig. 4.4 was a comparison between transmission spectra of the active layer (P3HT:PCBM, 200nm) and
m-PEDOT anode of 600nm. The total transparency over the spectra range shown decreases from 73% to 31% after spraying on the m-PEDOT anode.

![Transmission](image)

**Figure 4.4.** Transmission Spectra of Spray On Layers, (P3HT:PCBM) of 500nm (black line with filled square), and with a m-PEDOT:PSS layer of 600nm (red line with filled circle).

Annealing has shown to be the most important factor to improve organic solar cell performance. [4,5] Table 3 shows the comparison of current-voltage (IV) and incident photon converted electron (IPCE) between three inverted test cells at different annealing conditions: 1-step annealing at 120°C (red filled circle), or 160°C (black filled square); 2-step annealing at 120°C for 10 min, followed by high vacuum for 1 h and annealing at
160°C for 10min. Figure 4.5a shows that 1-step annealing at 120°C gives the best result in test cell, with $V_{oc} = 0.48\,V$, $I_{sc}=0.23\,mA$, FF=0.44, and a PCE of 1.2% under solar illumination intensity of 100mW/cm². The second annealing step at 160°C worsens the device performance, mainly due to unfavorable change of film morphology, which was confirmed in AFM images in Figure 5.6. The PCE of 1-step annealing at 160°C was in between that of 1-step annealing at 120°C and 2-step annealing, yet the device has the worst FF. Table 1 listed the details of the IV characteristics of these three test cells.

**Table 3. Single Cell Annealing Data.**

<table>
<thead>
<tr>
<th>Test cell number</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>Annealing condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.28</td>
<td>0.48</td>
<td>0.26</td>
<td>0.86</td>
<td>160°C 10min</td>
</tr>
<tr>
<td>2</td>
<td>0.23</td>
<td>0.48</td>
<td>0.44</td>
<td>1.2</td>
<td>120°C 10min</td>
</tr>
<tr>
<td>3</td>
<td>0.16</td>
<td>0.30</td>
<td>0.35</td>
<td>0.43</td>
<td>2-step</td>
</tr>
</tbody>
</table>

Test cell I-V characteristics comparison at various annealing conditions.
Figure 4.5. Annealing Experimental Results. a) I-V of four test cells measured with AM1.5 solar illumination under various annealing conditions: 1-step annealing at 120°C (red filled circle), or 160°C (black filled square), and 2-step annealing (green filled triangle); b) IPCE of the same devices measured under tungsten lamp illumination.

In Figure 4.5b, IPCE measurement, shows 2-step annealing was worse than 1 step annealing, which was consistent with IV measurements in Figure 4.6a. There seems to be some inconsistency between PCE and IPCE for the cells annealed at 160°C and 120°C: the cell annealed at 160°C has higher IPCE yet lower PCE than that at 120°C. IPCE measurement was done under illumination from Tungsten lamp, whereas IV was done under solar simulator which has different spectrum than that of the tungsten lamp. Nevertheless, the integration of IPCE should be proportional to $I_{sc}$. The device made by 1-step annealing at 160°C, though having smaller power conversion efficiency, actually has larger $I_{sc}$ (0.28mA) than the one at 120°C (0.23mA). The ratio between integral of IPCE at 160°C vs. 120°C is about 1.3, and the ratio of $I_{sc}$ of the same devices was 1.2. The slight discrepancy might also come from the fact that the cells behave differently under strong (IV) and weak (IPCE) illuminations. Usually bi-molecular (BM)
recombination sets in under high light intensity (solar simulator), \cite{4} meaning the cell, which has more prominent BM recombination will perform poorer with high intensity illumination such as that from the solar simulator. It might be that the cell annealed at 160°C was affected by BM recombination more than the cell annealed at 120°C, due to more traps associated with rougher morphology (see Figure 4.6) serving as recombination centers. Further investigation of this discrepancy is under study.
Figure 4.6. AFM Images of Annealing Conditions. AFM images of 4 test cells under various annealing conditions as shown in Fig. 6. (a) as-made cell, (b) 1-step annealing at 120°C, (c) at 160°C, and (d) 2-step annealing. Left panel shows topography, and right panel the phase image.
Figure 4.6 shows the AFM images [topography (left panel) and phase (right panel)] of 4 test cells at different annealing conditions. 1-step annealing at 120°C (b) showed the improved film roughness and the best phase segregation of P3HT and PCBM, which explains why the device performance was the best (Figure 4.5). Device by 2-step annealing has the smoothest film, however, the phase segregation was much less distinct. This indicates that P3HT chains and PCBM molecules are penetrating through each other more after the second annealing at 160°C, and form much smaller nano-domains, which are favorable for charge transport between the domains. \[23\] However, recombination of photogenerated carriers might be enhanced due to the lack of separate pathways for electron and holes, and that was why the device after 2-step annealing performed worse than after the 1st annealing at 120°C (Figure 4.5). 1-step annealing at higher temperature of 160°C results in the roughest film (even rougher than the as-made device), and the P3HT phase and PCBM phase are hardly distinguishable. This rough film also further affects the interface between active layer and m-PEDOT, resulting in poor FF of the device (Fig.5).

### 4.1.3 Experimental

(Poly(3-hexylthiophene)) (P3HT) with regioregularity over 99% was purchased from Riekie Metals, with an average molecular weight of 42K. 6,6-phenyl C61 butyric acid methyl ester (PCBM) with 99.5% purity was purchased from Nano-C. The original aqueous poly (3,4) ethylenedioxythiophene:poly-styrenesulfonate (PEDOT:PSS) Baytron 500 and 750 were obtained from H. C. Starck. The pre-cut 4”x4” ITO glass substrates with a nominal sheet resistance of 4–10Ω/□ and Corning® low alkaline earth boron-aluminosilicate glass were obtained from Delta Technology, Inc. Cs₂CO₃ was purchased
from Aldrich. All masks for spray are custom made by Towne Technologies, Inc. The airbrush sets for spray was purchased from ACE hardware.

ITO with desired pattern was prepared by the standard photolithography method and cleaned following the procedure described elsewhere. [28] Cs$_2$CO$_3$ solution in 2-ethoxyethanol with a concentration of 2mg/mL was sprayed onto the clean ITO substrate through a custom made shadow mask with an airbrush using N$_2$ as the carrier gas. The finished substrate is annealed at 150°C for 10min inside the N$_2$ glovebox (MBraun MOD-01).

The active layer solution is made by mixing P3HT and PCBM with a weight ratio of 1:1 in dichlorobenzene at 20mg/ml and stirred on a hotplate for 48h at 60°C prior to spraying. Active layer was sprayed onto the Cs$_2$CO$_3$ coated substrate using an airbrush, resulting in a layer thickness of about 200~300nm. The device is then left to dry in the antechamber under vacuum for at least 12h. The original aqueous poly (3,4)ethyleneedioxythiophene:poly-styrenesulfonate (PEDOT:PSS) was diluted and filtered out through a 0.45µm filter. This filtered solution of PEDOT:PSS is mixed with 5vol.% of dimethylsulfoxide to increase conductivity. [22] This modified PEDOT:PSS (m-PEDOT) is then sprayed onto the substrate using a custom made spray mask. The finished device is then put into high vacuum ($10^{-6}$Torr) for 1h. This step was shown to improve the device performance with sprayed active layer. [22] The final device is then annealed at various conditions (see results section) and encapsulated using a UV-cured encapsulant (EPO-TEK OG142-12) from Epoxy Technology.
The current-voltage ($I-V$) characterization of the solar array was performed with a Newport 1.6KW solar simulator under AM1.5 irradiance of 100$mW/cm^2$. No spectral mismatch with the standard solar spectrum was corrected in the power conversion efficiency (PCE) calculation. The incident photon converted electron (IPCE), or the external quantum efficiency, of the device was measured using 250$W$ tungsten halogen lamp coupled with a monochromator (Newport Oriel Cornerstone 1/4$m$). The photocurrent was detected by a UV enhanced silicon detector connected with a Keithley 2000 multimeter. The transmission spectrum of active layer was performed on the same optical setup.

4.1.4 Results and Discussion

Figure 4.7a shows the device architecture of a finished solar array with inverted structure. The array consists of 50 individual cells each has active area of 12$mm^2$. The array was configured with 10 cells in series to increase in one row to increase voltage, and 5 rows in parallel connection to increase current. Figure 4.7b presents the cross section of a single cell and how the series connection was made with the neighboring cell. These arrays either have m-PEDOT 750 or m-PEDOT 500 as semitransparent anode.
**Figure 4.7.** Device Architecture of an Inverted 4” Array. (a) top view. (b) side view.

**Figure 4.8.** I-V of 4 Inverted sprayed-on array, measured with AM1.5 solar illumination under various annealing conditions: 1-step annealing at 120° C (dashed line), or 160° C (red thin line), and 2-step annealing (black filled square). These 3 arrays use m-PEDOT 500 as anode. The 4th array (thick blue line) uses m-PEDOT 500 as anode and was annealed at 160° C.
Figure 4.8 shows the IV of 4 arrays under different annealing conditions measured with AM1.5 solar illumination. It is clear that 1-step annealing at low temperature (120°C) gives the worst result, 2-step annealing showed improved IV characteristics (V_{oc}, J_{sc}, FF and PCE) after the second high temperature annealing at 160°C. 1-step annealing at high temperature (160°C) gives the best V_{oc}, and 2-step annealing yields the highest J_{sc}. In terms of anode, m-PEDOT 500 seems to give higher V_{oc} than PEDOT 750 (see table 2 for more array results). However, there is not much difference of PCE between 2-step annealing and 1-step annealing at 160°C, which is in contrast with the result of test device (Figure 4.5). We think the annealing duration is probably too short for the array, since it has much larger area and contains much more materials. Further investigation of annealing temperature and duration is on going to find the optimal device fabrication conditions.

**Table 4. Array Annealing Data.**

<table>
<thead>
<tr>
<th>Array number</th>
<th>I_{sc} (mA)</th>
<th>V_{oc} (V)</th>
<th>FF</th>
<th>η (%)</th>
<th>Annealing condition</th>
<th>m-PEDOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.0</td>
<td>3.9</td>
<td>0.30</td>
<td>0.68</td>
<td>2 step</td>
<td>750</td>
</tr>
<tr>
<td>2</td>
<td>11.5</td>
<td>4.0</td>
<td>0.39</td>
<td>0.62</td>
<td>2 step</td>
<td>750</td>
</tr>
<tr>
<td>3</td>
<td>6.30</td>
<td>2.8</td>
<td>0.37</td>
<td>0.22</td>
<td>2 step</td>
<td>750</td>
</tr>
<tr>
<td>4</td>
<td>13.0</td>
<td>4.0</td>
<td>0.33</td>
<td>0.56</td>
<td>160°C 10min</td>
<td>750</td>
</tr>
<tr>
<td>5</td>
<td>15.0</td>
<td>5.2</td>
<td>0.33</td>
<td>0.86</td>
<td>160°C 10min</td>
<td>500</td>
</tr>
<tr>
<td>6</td>
<td>12.0</td>
<td>5.8</td>
<td>0.30</td>
<td>0.70</td>
<td>160°C 10min</td>
<td>500</td>
</tr>
<tr>
<td>7</td>
<td>11.1</td>
<td>5.2</td>
<td>0.35</td>
<td>0.67</td>
<td>160°C 10min</td>
<td>500</td>
</tr>
</tbody>
</table>

Array I-V characteristics comparison at various annealing conditions.
We have observed a very interesting phenomenon which we call it ‘photo annealing’ (Fig. 9). Under constant illumination from the solar simulator, a sudden change of IV occurs after certain amount of time which is device dependent, ranging from 10 minutes to several hours. The device shown in Fig. 9 takes about 15\textit{min}, and reaches maximum PCE after 2.5\textit{h} under illumination. The drastic change is mostly $I_{sc}$, which more than doubles from 17\textit{mA} to 35\textit{mA} after 2.5 hours. The change of $V_{oc}$ was marginal from 4.0\textit{V} to 4.2\textit{V}. The maximum PCE of the array was 1.80\%. Table 3 listed the changes of other I/V characteristics.

**Figure 4.9.** Improvement of I-V of an Inverted Array. I/V curve under continuous AM1.5 solar illumination. The first measurement (dashed line) was done right after the array was fabricated and encapsulated.
Table 5. Change of Array I/V Characteristics, under solar illumination.

<table>
<thead>
<tr>
<th>Time</th>
<th>$I_{sc} (mA)$</th>
<th>$V_{oc} (V)$</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st day – 0min</td>
<td>17</td>
<td>4.0</td>
<td>0.30</td>
<td>0.68</td>
</tr>
<tr>
<td>–12 min</td>
<td>28</td>
<td>4.2</td>
<td>0.35</td>
<td>1.40</td>
</tr>
<tr>
<td>–150min</td>
<td>35</td>
<td>4.2</td>
<td>0.37</td>
<td>1.80</td>
</tr>
<tr>
<td>2nd day – 0 min</td>
<td>18</td>
<td>4.2</td>
<td>0.35</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Furthermore, this sudden increase of $I_{sc}$ is also accompanied by a characteristic ‘wiggles’ on the IV curve. This cannot be due to encapsulation related change of light distribution inside the active layer, since we have also observed these ‘wiggles’ with the IV of test devices which are not encapsulated. ‘Wiggles’ only appear with sprayed device (both array and test device), not with spin-coated device. It might be due to the fact that the porosity of sprayed film is much larger than the spin-coated film, and polymer chains have much more loose arrangement in sprayed device, with the heat from solar illumination, the polymer chains relax more and the film nanomorphology was improved, with possibly PCBM penetrating into the voids between polymer chains and causing better phase segregation. This effect is similar to thermal annealing performed on hot plate. As temperature drops down, the polymer chains go back to its original configuration, and IV curve is back to its original one, manifesting certain kind of
hysteresis. It also might be due to thermal activation of the previous deeply trapped carriers (i.e., polarons), which results in increased photocurrent at higher temperature.\cite{25,26} The wiggles indicate the nonuniformity of film morphology, and the overall boost of device performance is the result of ‘photo annealing’. This observation is against the conventional picture of organic solar cell, which normally shows degradation under solar illumination.\cite{26,27} We also found out that the performance enhancement under illumination only happened with sprayed devices, not the device made by spin coating. This means that solar cells made with our spray-on technique performs better under sunlight, which is beneficial for solar energy application. Further study of photo annealing dynamics and solar array lifetime is ongoing to unveil the optimal condition for solar array in field operations.

4.1.5 Summary

We have demonstrated large area organic array fabricated by all spray technique. Cs$_2$CO$_3$ was chosen to reduce ITO work function close to 4.0eV to be utilized as cathode. The fully encapsulated 4” x 4” array has over 30% transparency and can produce as high as 1.80% of power conversion efficiency (PCE) under constant illumination of simulated sunlight. Thermal annealing has proven to be essential to improve device PCE, and the optimal annealing conditions are not the same with small single cell and large solar array consisting of 50 cells. Systematic study of optical, electronic and morphologic properties of the device reveals the influence of nanomorphology over device power conversion efficiency. Moreover, our discovery of photo annealing, i.e., more than 2-fold increase of solar cell PCE under solar irradiance and with hysteresis pattern, is in contrary to the normal understanding of organic solar cell degradation under sunlight. The fact that
photo annealing was only observed with sprayed solar cell or arrays places our technique an advantageous solution for large scale, low-cost solution based solar energy applications.

4.2 Fabrication of 1’ x 1’ Large Area Inverted Array

Presented here is a 1’ x 1’ inverted OPV array that was fabricated using the all spray process (figure 4.11). The design is just a scaled up version of the 4” x 4” array with 5 rows of 10 OPV cells connected in series, connected in parallel. This array, however, has a total active area of nearly ~300 cm². The fabrication is similar to the 4” array.

Figure 4.10. A working 1ft² Inverted OPV Array. In this photograph, the transparency can be seen of this type of OPV on a large scale.
A special TVD chuck was designed and made to accommodate the larger array size in the TVD chamber. Second, our UV light source to cure the encapsulation epoxy was too small for this array. The solution was to allow the epoxy to cure slowly on its own in the glove box for 48 hours. Since the solar simulator contains part of the UV spectrum, the final curing of the epoxy was done during simulated (A.M1.5) I/V curve testing. The array was allowed to be exposed to the simulator for over 2 hours, to ensure complete curing of the epoxy. The power used during I/V testing was 100 mW/cm². During this time, I/V curve testing was done to collect time dependant data and measure the performance of the epoxy. All other fabrication processes for this OPV array are the same as with the inverted, all sprayed 4” x 4” array.

4.2.1 Results and Discussion

Figure 4.11. 1 ft² Array I-V Curve. Above, shows the I/V curve results under A.M1.5 simulation. It is easy to see the degradation of this array over a time ~2h.
Fig. 4.11 shows the I-V characteristics of a 1ft$^2$ large OPV array. For the first trial under unfavorable fabrication conditions, this result was not too bad. The first 1” x 1” array shows an open circuit voltage ($V_{oc}$) of 4.2$V$, short circuit current ($I_{sc}$) of 52$mA$, fill factor (FF) of 0.27 and a power conversion efficiency of 0.16% under simulated solar AM1.5 illumination. As seen in 4” x 4” array, we observed similar photo annealing effect, which has boosted the device PCE for over 160%.

Although this device was a successful ‘proof of concept’ fabrication of an all sprayed OPV array, the low efficiency shows the limitation of fabrication outside of the glove box. Like the 4” array, the spraying of the 4 layers, was done outside of the glove box. Due to the size of this array, device fabrication techniques took a longer time than with the 4” arrays. This could account for the low FF = ~27%, and low PCE = 0.16%.

Furthermore, an increase in series resistance could also hinder device performance. What also cannot be dismissed is the human error factor. As the substrate size increases in a device such as this, layer uniformity is also diminished. This can be shown in variable shunt resistances of the individual cells, and their series resistances, as well.
4.2.2 Summary

The results represented in Figure 4.11, clearly show that this epoxy is not suited for encapsulation of OPV devices. Inaccuracy of the human hand, and over exposure to O₂, is mostly responsible for the low PCE. This experiment shows that future work involving the scaling up of these devices needs to be done in an inert environment, and just as important, automation of the fabrication processes to ensure uniform spraying of device layers in an inert environment.
4.3 References


CHAPTER 5: HYBRID SOLAR CELLS WITH QUANTUM DOTS

5.1 Unconventional Gap State of Trapped Exciton in Lead-Sulfide Quantum Dots

Abstract

Exciton states in lead selenide (PbSe) and lead sulfide (PbS) quantum dots have been studied extensively. However, relatively less attention has been paid to the states within the quantum dot bandgap. Our experimental results have revealed a single in-gap state which bears confinement dependence yet cannot be explained by dark exciton theory, nor is it a trap state related to quantum dot surface defects as previously observed. A detailed analysis of the temperature dependence of photoluminescence, Stokes shift, absorption and photoinduced absorption indicates the unconventional GS is a new state of a trapped exciton in a QD film. With appropriate design engineering, these trapped excitons might be harvested in solar cells and other optoelectronic devices.

5.1.1 Introduction

IV–VI colloidal quantum dots such as PbSe and PbS have many unique properties to make them promising materials for optoelectronic devices. Their bandgaps, ranging from 0.5 to 1.1 eV, can be easily tuned via size control during synthesis, and their
photoresponse in the near-infrared region promises broad applications in bio-imaging\textsuperscript{1}, telecommunications\textsuperscript{2}, LEDs\textsuperscript{3}, lasers\textsuperscript{4}, photodetectors\textsuperscript{5} and photovoltaic devices\textsuperscript{6-8}. Strong quantum confinement due to a large exciton Bohr radius, and nearly symmetric and small electron and hole effective masses make these quantum dots excellent candidates for fundamental studies\textsuperscript{9-13}. Unlike in their bulk semiconductors, enhanced Coulomb interaction in quantum dots results in much more tightly bonded excitons, and the fate of excitons in these quantum dots is of great relevance to their device applications.

Although the properties of excitonic states have been thoroughly studied in the past decade, mostly employing transient spectroscopies\textsuperscript{14-18}, relatively less attention has been paid to the states within the quantum dot bandgap. Conventionally, there are two types of in-gap states: one is the dark exciton state, which is due to the exchange splitting from confinement-enhanced exchange interaction\textsuperscript{19-20}, while the other type is trap state(s) associated with surface defects\textsuperscript{21-23}.

These in-gap states are of great importance since they affect the final destiny of excitons. Figure 1 illustrates the possible fates of excitons followed by intraband relaxation (or cooling). The electron at the lowest conduction level can either be re-excited to a higher energy level (intraband transition, route (1), dashed-dotted arrow, black) via re-absorption of photons\textsuperscript{24} or impact ionization\textsuperscript{25}, or it could relax to the long-lived in-gap state (solid line, red) via route (2) (curved arrow, black). A previous report on defect states within the gap has shown that this relaxation process can be highly effective and fast ($<100\, \text{ps}$)\textsuperscript{26}. Finally, the electron could recombine radiatively within a timescale up to microseconds\textsuperscript{27-29} through route (3) (dashed arrow, black). Since route (2) is much
faster than route (3), a large amount of electrons will end up in gap states which are usually long lived, with a lifetime as long as seconds $^{30}$. We have previously reported a peculiar in-gap state that bears confinement dependence, with a lifetime about $2\mu s$ $^{31}$. This single gap state does not seem to fall into either one of the above conventional gap state categories. In this paper, we provide further and more detailed investigation into the characteristics of this unconventional gap state, employing mainly cw photoinduced absorption spectroscopy, coupled with a temperature dependence study of photoluminescence and excitonic absorption.

**Figure 5.1.** Quantum Dot Energy Level. Schematic drawing of PbS QD energy levels. Red line represents the gap state (GS). Route (1) shows intraband transition (dashed–dotted arrow, black), route (2) the relaxation of electron into the gap state (curved arrow, black) and route (3) the radiative recombination of electron and hole (dashed arrow, black).
5.1.2 Experimental

PbS QDs capped by oleic acid and stored in toluene solution were purchased from Evident Technologies, Inc. Quantum dots with diameters of 2.2, 2.5, 4.2 and 5.3 nm were studied. Exchange of the QD solvent was done by blowing dry the original solution using N$_2$ gas, and adding the same amount of chloroform to keep the concentration (10 mg/mL) unchanged. The QD film was drop-cast onto a sapphire substrate from chloroform solution. The average film thickness was around 500 nm (measured by a Tencor Alphastep 200 Profilometer). The as-cast film was left in a glovebox overnight, then kept in dynamic vacuum for 2 h before measurements. Temperature variation of the films was achieved in a Janis closed-cycle refrigerator cryostat.

We apply the cw photoinduced absorption (PA) technique to investigate the long-lived photoexcitations in the PbS QD films. The pump beam is provided by the 488 nm line ($2.54 eV$) from a cw-Ar$^+$ laser, with an optical chopper for photomodulation. A tungsten–halogen lamp is used to probe the modulated changes, $T$, in transmission, $T$. The PA signal is expressed by $-(T/T) = \alpha d$, where $\alpha$ is the absorption coefficient and $d$ is the film thickness. A lock-in amplifier is employed to amplify the signal from photodetectors. A Newport Oriel Cornerstone 1/4 m monochromator is used together with various diffraction gratings and optical filters to span the spectrum from 0.2 to 3.0 eV. Absorption and photoluminescence (PL) measurements are carried out on the same set-up. In this paper, a total pump power of 250 mW (i.e. power density of 150 mW/cm$^2$ on the sample) and a modulation frequency of 400 Hz are used unless otherwise mentioned.
5.1.3 Results and Discussion

Figure 5.3a shows the low temperature ($T = 10K$) PL and absorption spectra of four different sizes (2.2–5.3nm) of PbS QD films on sapphire. Both absorption and PL show size-dependent features reflecting the quantum confinement effects. The PL peak has a Gaussian shape with a full width at half-maximum (FWHM) comparable to the first excitonic absorption peak, indicating that the emission comes from a well-defined single quantum state. Figure 5.2a shows the energy of PL ($E_{PL}$) versus the first excitonic transition ($E_1$). A large Stokes shift (denoted by $s$) was observed in both film and diluted solution (0.7mg ml$^{-1}$) for all four size QDs. In the smallest size QDs (2.2nm) measured, the Stokes shift in solution (320 meV) was even larger than the Stokes shift in the film (284meV). A previous report has stated the size distribution contributed to the large Stokes shift\(^{49}\). However, all QDs studied here have a narrow size distribution between 3 and 6%\(^{32}\). The biggest size distribution is for the smallest size (2.2 nm). That might explain the bigger Stokes shift in the solution for this size QD.

A linear fitting of solution Stokes shifts yields a slope of 0.64, which is smaller than the fitting slope of 0.75 for the film. A zero Stokes shift should have a slope of 1.0 (broken line, black, in figure 5.2b). A smaller slope indicates a larger deviation of PL from the absorption. First of all, although Förster transfer is a common mechanism of significant redshift of the PL emission spectra in close-packed quantum dot films, this effect tends to diminish in widely dispersed, isolated quantum dots in solution. The observation that a larger deviation of PL from the absorption in solution than that in the film eliminates the possibility of a dominant role of Förster energy transfer in the observed large Stokes shift\(^{33}\). Secondly, a linear relation of Stokes shift with size also excludes the significance
of the Franck–Condon effect, which is sensitive to QD size and has a predominant effect on very small QDs (<1nm) \(^{33}\). In particular, in similar IV–VI QDs (PbSe), it was found that the Franck–Condon effect is negligible for QDs with diameters larger than 2nm \(^{48}\).
Figure 5.2. PL and Energy Levels of PbS Quantum Dots. a) PL (left) and absorption (right) spectra for four different sizes (2.2–5.3nm in diameter) of PbS QD films on sapphire measured at $T = 10K$. Excitation is from the 488nm (2.54eV) line of a cw-Ar$^+$ laser with intensity of 150$mW/cm^2$. The baseline of the spectrum for each size was shifted vertically for clarity. b) Plot of photoluminescence (PL) versus first excitonic absorption ($E_1$) of PbS QDs with four different sizes. Solid black squares are for solutions, whereas open blue circles are for films. The black line was the linear fitting of solution data, and blue line that of the film data. The inset shows transitions of PL and $E_1$. c) The size dependences of confinement energy (solid square, black), Stokes shift (solid circle, red) and transition IR-PA (solid triangle, green) of these four size PbS QDs as a function of QD diameters. Data taken from [19] were shown as open star, black, and the red line is a fitting of confinement energy using equation (1) in text.
All dots in this study are larger than 2 nm, therefore the Franck–Condon effect could be excluded. Furthermore, both slopes than the confinement energy ($E_{\text{conf}}$), which means that there is are greater than 0.5, meaning the emission state is not fixed with respect to the bottom of the bulk conduction band, as causing S and IR-PA. The similar size dependence of S previously reported in 35.

To further illustrate this point, we plot in figure 5.2a the relation of confinement energy $E_{\text{conf}} = E_1 - E_{g, \text{bulk}}$ (solid square, black), Stokes shift (solid circle, red) and the transition IR-PA (solid triangle, green) with respect to the QD diameter. e–ph scattering 36, could also contribute to the Stokes The solid line represents a curve fitting using the formula

$$E_{\text{conf}} = \frac{a}{D^b}$$

(1)

where $a$ and $b$ are fitting parameters 48. The best fitting larger range than the calculated values. We believe fine yields $b = 0.95 \approx 1.0$; this is consistent with the recent result in 50, where $E_{\text{conf}}$ scales with $D^{-1}$. The Stokes shift ($\Delta S$) and IR-PA, on the other hand, clearly show different size effects than the confinement energy ($E_{\text{conf}}$), which means that there is an additional factor, rather than band edge shifting in $E_{\text{conf}}$, causing $\Delta S$ and IR-PA. The similar size dependence of $\Delta S$ and IR-PA indicates these two quantities have similar origins, which is related to the gap state (GS in figure 1).

Other mechanisms, such as band edge splitting due to e–h exchange and intervalley interactions 19, and e–ph scattering [36], could also contribute to the Stokes shift. In figure 2(c), we plotted the Stokes shift from our measurements and the data taken from a theoretical calculation in [19] (open star, black). Even with the combined exchange and
intervalley interaction splittings, our data span a much larger range than the calculated values. We believe fine structure alone cannot explain the observed large Stokes shift as well.

In summary, we consider the very large Stokes shift important evidence that the emission state is not the dark exciton level\textsuperscript{20} or shallow trap states\textsuperscript{21}, or from a hybrid state which consists of a trapped electron and a hole in the conduction level\textsuperscript{35,37}. Rather, the emission comes from a gap state that moves together with the QD excitonic levels, with about 100 meV below the lowest excitonic level (for electrons: holes have similar values) for the largest dot (5.3 nm) and 290 meV for the smallest dot (2.2 nm). The inset in figure 5.3a shows a schematic energy level diagram.

Figure 5.3b shows the temperature dependences of PL (solid square, black) and the first excitonic absorption (open triangle, red) ($E_g$ of QD) of a 4.2 nm QD film. Above $T = 50K$, a linear increase of 0.05 meV/K was obtained from fitting of the absorption experimental data. This is consistent with the previously reported $dE_g/dT$ of PbS QDs\textsuperscript{38}. The much smaller temperature dependence of the QD bandgap compared with that of the bulk (0.5 meV/K)\textsuperscript{39} was expected from weakened lattice dilation and electron–phonon coupling due to strong quantum confinement\textsuperscript{38}.

On the other hand, figure 5.3a also shows PL energy dependence on temperature. A temperature coefficient of 0.3 meV/K was derived from the data. This is similar to a previous report\textsuperscript{40}, $dE/dT|_{PL} > dE_g/dT$ indicates that emission is not originated from a band edge splitting state such as a dark exciton state\textsuperscript{19}, unlike the case of CdSe QDs\textsuperscript{36}. 

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PL intensity variation with temperature was shown in the inset in figure 3(a). We did not observe thermal activation of PL at low temperature, in contrast to such behavior reported in 20,40. This is more evidence that the emission is not from dark exciton recombination. In addition, the absence of thermal activation behavior shows negligible non-radiative recombination of carriers, indicating the good quality of the film. Furthermore, this excludes the possibility of PL coming from a trap state, as reported in 21. Figure 5.3a presents the temperature dependence of the PL linewidth taken at full width at half-maximum (FWHM). Two fitting methods were used based on the classical independent boson model (IBM) 41 of the temperature effect on line broadening. Fitting method 1 (black solid line in figure 5.3a was done by using the following equation 42:

\[
W = W_0 + \alpha T + \beta e^{-\frac{E_{LO}}{kT}}
\]

where \( W_0 \) represents the linewidth at \( T = 0 \)K or inhomogeneous broadening, \( \alpha \) is the acoustic phonon broadening coefficient, \( \beta \) is the longitudinal optical (LO) phonon broadening coefficient and \( E_{LO} \) is the LO phonon energy. The best fitting yields \( W_0 = 72.04 \pm 0.22 \) (meV), \( \alpha = 70.5 \pm 10 \) (meV/K), \( \beta = 69.23 \pm 4.70 \) (meV) and \( E_{LO} = 14.73 \pm 0.40 \) (meV). Fitting method 2 (blue solid line) was done similarly except omitting the linear term about the exciton–acoustic phonon interaction. It was clearly seen that method 1 is a much better fitting than method 2, especially at the low temperature end \( (T < 100K) \). The role of acoustic phonon scattering is quite obvious in our case. This could explain the discrepancy between our data and an earlier report 40, which were extracted using fitting method 2 shown here. In their case, the QD has a much larger size, and acoustic phonon coupling is more predominant in small QDs 38,43.
Figure 5.3. Temperature Dependences of PL. a) Temperature dependences of PL (solid square, black) and the first excitonic absorption $E_1$ (open triangle, red) of a 4.2nm QD film. Black line is a linear fit of PL data and red line is a fit for $E_1$ at $T > 50K$. The inset is a plot of temperature dependence of PL intensity (solid diamond, black). b) Temperature dependences of PL (solid circle, black) and absorption (open circle, red) linewidth taken at full width at half-maximum (FWHM). Two fitting methods based on the classical independent boson model (IBM) were used to fit PL-FWHM data (see text for details). Black line is fitted by method 1 and blue line by method 2.
A recent publication has also shown greatly enhanced acoustic phonon coupling in strongly confined PbS QDs\(^4\). similar to\(^4\), we have observed strong coupling to longitudinal optical (LO) phonons. As previously reported\(^4\), the presence of a local electric field from trapped charges would greatly enhance the coupling to polar

Diameter of FWHM at FWHM at QD (nm) 10\(K\) (\(meV\)) 295\(K\) (\(meV\)) LO phonons.

In our earlier work\(^3\), we have observed the Stark effect due to such trapped charges in our PbS QD films. We therefore attribute the strong coupling with LO phonons to the local electric field from trapped charge in QDs.

Another interesting fact is the small LO phonon energy (\(E_{LO} = 15\, meV\)) from fitting method 1, much smaller than LO phonons of the bulk (26\(meV\))\(^3\)\(^9\). There was a report that the LO phonon frequencies in PbS quantum dots can be very different than in the bulk, ranging from 227\(cm^{-1}\) for a 1s phonon to 114\(cm^{-1}\) for a 2d phonon\(^4\). Although the dominant ones in exciton–phonon coupling are the 1p and 2p phonons, fitting of our data coincides with the 2d phonon, which might be due to the fact that the excitons involved were not free excitons, but the ones ‘trapped’ in the gap state.

To further illustrate this peculiar gap state, we plot in figure 5.4a the temperature dependence of PL (solid square, black) and first excitonic absorption (open square, black) energies normalized by their respective energies at \(T = 295K\). \(E = E(T) - E(295K)\) for both PL and \(E1\). The normalized PL energy shows a monotonic decrease with increased temperature, and the lack of a ‘hook’ indicates that PL does not come from the dark exciton level\(^3\). Figures 5.4b and 5.4c show the PL of two different size QDs (2.5nm, 5.4b) and (4.2 nm, 5.4c) at \(T = 296K\) and 10\(K\), respectively. The PL lineshape deviates
from a Gaussian by a negligible amount at both temperatures for the larger QD (figure 5.4c), whereas a slightly increased side band contribution for a smaller QD at room temperature was observed (figure 5.4b). Table 1 lists the FWHM of PL for these two sizes of QDs.

According to IBM theory, the homogeneous broadening due to the exciton–acoustic phonon interaction is supposed to increase linearly with temperature and scaled as $1/R^2$ \(^{36,46}\). Our data does not seem to fall into this prediction completely. The ratio of $(R1/R2)^2$ is 0.35 for the two sizes of QDs, yet $(FWHM)_2/(FWHM)_1$ is 0.64 at 10K and 0.91 at 295K. This means that the PL linewidth broadening has other contributions. Spectral diffusion due to the variation of local electric field might be one; however, we observed a decreasing Stark effect with temperature \(^{32}\), meaning some of the trapped charges were released at higher temperature and quenched via recombination, thus reducing the average local electric field, although it was suggested that the local electric field increases with temperature \(^{36}\). We have measured the pump intensity dependence of PL-FWHM at 10 K for the 4.2nm QD. For an order-of-magnitude increase in pump intensity, the Stark effect (and consequently the local electric field) increases by more than five times, yet the FWHM of PL remains nearly the same. This indicates the limited influence from spectral diffusion, inconsistent with the previous report \(^{36}\). We also discard the inhomogeneous broadening effect, due to the narrow size distribution (3–5%) of our PbS QD samples, as indicated also in the good fitting of a single Gaussian function.
Figure 5.4. Temperature dependences of PbS. a) Temperature dependences of PL (solid square, black) and first excitonic absorption $E_1$ (open square, black) normalized by their respective energies at $T = 295K$. $E = E(T) - E(295K)$ for both PL and $E_1$. b) PL of PbS QD with 2.5nm diameter at $T = 10K$ (solid triangle, black) and 296K (open triangle, red). c) PL of PbS QD with 4.2nm diameter at $T = 10K$ (solid square, black) and 296K (open square, red). In both (b) and (c), the black line is for Gaussian fitting at $T = 296K$ (RT) and red line for Gaussian fitting at $T = 10K$, respectively.
We tentatively attribute the above discrepancies of the PL characteristics to the fact that the emission does not come from the usual dark exciton state, it is more likely from a trapped exciton state in the gap with activation energy about 15 meV. Therefore the standard IBM theory cannot explain its properties completely.

Figure 5.5a describes the temperature dependence of IR-PA, the transition from a gap state (GS in figure 5.5a inset) to the second excited state (1Pe) for a 4.2 nm QD film \(^{31}\). The inset in figure 5.5a also includes relevant transitions. The nature of this gap state (GS) is rather interesting, it has confinement dependence, yet we do not think it is the normal dark exciton state, based on the arguments given before. It is also unlikely from the trap state due to surface defects or imperfection of the QD, since the peak position of this transition does not depend on surface conditions \(^2\). We tried to fit the temperature dependence of the IR-PA (peak at 0.32 eV) using a well-known model describing the thermal activation process for traps in polymers \(^{47}\). According to the decay equation of long-lived photogenerated states (i.e. trap states): the rate equation can be written as,

\[
\frac{dn}{dt} = aG - bn^\mu
\]

with the steady-state (dynamic equilibrium) solution expressed by, \(n_{ss} = \left(\frac{aG}{b}\right)^{\frac{1}{\mu}}\), where \(G\) is the pump light intensity and ‘\(a\)’ is the generation rate, usually a constant with constant \(G\). ‘\(b\)’ is the recombination (decay) rate and is dependent on temperature and light intensity. \(\mu\) is between 1 (monomolecular recombination) and 2 (bimolecular recombination). Under constant illumination of pump light, \(b = b(T)\) mainly varies with
temperature $T$. Since the lifetime $\tau$ of GS is about several microseconds\textsuperscript{31} and the modulation frequency is $400\text{Hz} (1/f \gg \tau)$, the measured PA signal is proportional to $n_{ss}:PA(T) \propto b(T)^{-1/\mu}$, where $b(T)$ is usually described by thermal activation behavior, with the activation energy $ET$ of the trap state extracted from a fitting using $PA(T) = A(e^{-ET/k_BT} + B)^{-1/\mu}$, where $A$ is a scaling factor and $B$ is the $T$-independent part of the decay rate. In our case, $1/\mu$ was determined to be about 0.68 by the intensity dependence of PA\textsuperscript{47}. The best fitting yields $ET = 20.0804 \pm 5.4065$ (meV), with a $T$-independent contribution of $0.06284 \pm 0.01303$ (meV). The thermal activation energy is at least one order of magnitude smaller than the trap state in polymers\textsuperscript{47}. In addition, the fitting in figure 5.5a using the thermal activation model is poor. This indicates the GS observed in this work cannot be exclusively viewed as a trap state.

Figure 5.5b shows the $T$ dependence of various transitions shown in the inset in figure 5.5a. It is clear that IR-PA (open circle, pink) and the QD band edge ($E_1$, solid circle, red) has distinctively different $T$ dependence, one more evidence that the GS is not related to band edge splitting (i.e. dark exciton state).

In figure 5.5b, we also present the temperature dependence of the Stokes shift, $s$ (open square, black). For this size\textsuperscript{2} Unpublished work by the authors. We have done ligand exchange of the QD from its original oleic acids to butylamine, and the PA measurement showed an almost identical IR-PA peak.
Figure 5.5. Temperature Dependency of IR-PA. a) Temperature dependence of the intensity of IR-PA (solid square, black), the intraband transition from a gap state (GS in inset) to the second excited state (1Pe) for a 4.2nm QD film. The red line is a fitting of IR-PA based on the theory of thermally activated trap states (see text for details). The inset shows relevant transitions. b) Temperature dependence of various transitions shown in the inset of (a) IR-PA (open circle, pink); $\delta_1$ (cross, blue) is half the difference between second excitonic transition $E_2$ and the first excitonic transition $E_1$, i.e. $\delta_1 = 1/2(E_2 - E_1)$; is Stokes shift (open square, black) and the summation of $s$ and $\delta_1$ (open star, green). Also shown was the temperature dependence of $E_1$ (solid circle, red).
(4.2 nm) QD, the Stokes shift remains unchanged up to 100 K, then shows a weak decrease (about 30%) when the temperature reaches 300 K. This trend is consistent with that previously reported in CdSe QDs\textsuperscript{36}. On the other hand, the energy level difference between the first and second excitonic levels (cross, blue), $\delta_1 = 1/2(E_2 - E_1)$, has much weaker temperature dependence (it decreases 15% over the temperature range). Figure 5.5b shows an excellent fit between the IR-PA (open circle, pink) temperature dependence and that of the summation of the Stokes shift $s$ and $\delta_1$ (open star, green), which further confirmed the previous assignment of IRPA as a transition from GS to 1Pe\textsuperscript{31}.

5.1.4 Summary

In conclusion, we have investigated the characteristics of a peculiar gap state found in films of PbS QDs with different sizes. The large Stokes shift was attributed to the difference from first excitonic absorption and emission from a gap state (GS) which bears quantum confinement dependence. A detailed analysis of the temperature dependence of PL, absorption and photoinduced absorption reveals the unconventional GS is a new state of a trapped exciton in a QD film. The possibility of this GS being from trions (i.e. exciton plus residual charge, either electron or hole) is not possible due to two reasons: one, trions and biexcitons are usually generated from very high photon fluxes with a density higher than several KW cm\textsuperscript{-2}\textsuperscript{51}. In our experiments, the pump intensity was about 150 mW cm\textsuperscript{-2}, too low to create trions; and, two, the lifetime of trions is too short (\textless ns)\textsuperscript{52} for our experimental set-up to measure (\textgreater \mu s).
We believe this is the first report of a trapped exciton state in PbS QDs. This gap state is directly relevant to exciton dissociation and carrier extraction in this class of semiconductor quantum dots. Further investigation of this state can be useful in terms of broad applications in optoelectronic devices for this class of semiconductor QDs.

### 5.2 Ligands Manipulation in QDs

During the colloidal synthesis of PbS nano-crystals, organic ligomers (oligomers) are used as surfactants or ligands to passivate the surface of the QDs. Oleic acid is used as surfactant for the QDs we purchased. These surfactants are both hindrance and beneficial for use in OPV devices. Firstly, these surfactants are necessary to keep the QDs separated from each other in solution, preventing coalescence. When QD’s are stuck and bond to each other, they will become larger than the exciton Bohr radius, and these bonded QDs will behave like bulk PbS. Keeping the QD’s separate from each other is crucial for maintaining the quantization of energy levels desired for OPV devices. Unfortunately, these oligomers are highly resistive, and prevent charge extraction and hinder transport. Therefore ligand manipulation is a necessity to electronically couple QDs. Common ways to manipulate ligands include ligand wash and ligand exchange in solution, and ligand removal on films. However, these methods are proven to be difficult to manage, and often involve use of harmful chemicals [53, 55]. We have started first to follow the literature procedure for conventional ligands manipulation.
5.2.1 QD Ligand Wash and exchange: literature procedures

**QD Ligand Wash**

Following the literature procedure [54], we have tried to manipulate the original ligands of PbS QD’s was by simply washing them off. This is accomplished by blowing dry a 1mL solution of QD’s in toluene with N₂, and adding 1mL of hexane. At this stage, we are just exchanging the solvent from toluene o hexane. 2-3mL of methanol is then added to the solution. This causes the QD’s to precipitate out, and washes the ligands off. Not all of the ligands wash off, though. That would cause aggregation of the QD’s. The solution is then put into a centrifuge for 2min at 3500rpm.

![Figure 5.6. Structures of Organic Ligands. a) Oleic acid b) butylamine](image)

**QD Ligand Exchange**

Ligand exchange in QDs has proven to improve infrared response of PbS QD photovoltaic devices and photoconductors cm 53,54. Following the procedure in [54], a ligand exchange was performed to essentially exchange the oleic acid surfactant of the QD’s with a shorter organic oligomer. In figure 5.6 above, we can see that oleic acid is a
chain of 17 carbon atoms. In contrast, butylamine has a chain of only 4 carbon atoms, and is much smaller than oleic acid. A ligand exchange starts by doing a ligand wash, as mentioned above. After the solution comes out of the centrifuge, all of the solvent is poured out, and the QD’s are dried with N₂. The QD’s are then transferred into the glove box, and butylamine is added to the QD’s for the desired concentration. Confirmation of ligand exchange was accomplished using Fourier transform infrared spectroscopy (FTIR). As can be seen in figure 5.7 below, the vibrational frequency at 3257 cm⁻¹ and between 1000-1500 cm⁻¹ are from the N-H stretching modes.

![FTIR Spectroscopy of Ligand Exchange](image)

**Figure 5.7.** FTIR Spectroscopy of Ligand Exchange. FTIR measurements on two QD films with original oleic acid (black line) and exchanged butylamine ligands (red line).

### 5.2.2 Electric Field Tuning of PbS Quantum Dots: our way

Through this Ph.D. work, *a novel method using electric field to manipulate quantum dots ligands for interface* of quantum dots and polymer, which possibly could facilitate charge extraction from the quantum dots and charge transfer between quantum dots and polymers, without the need of harmful chemicals.
By placing an electric field between the QD’s during drop cast deposition, the oligomers would align with the electric field, thereby allowing for the subsequent layers of QD’s to be in closer proximity to each other. The direction of increased conductivity would be perpendicular to the plane, and therefore favorable for OPV device fabrication.

**Figure 5.8.** PbS Quantum Dots  a) A lead sulfide quantum dot without surface passivating oligomers.  b) A PbS nano crystal with oleic acid surfactant.

**Figure 5.9.** Quantum Dot Layer. Shows a cross section of multiple layers of QD’s and how they sit in this normal configuration. Notice how far away the nanocrystals are separated from each other, especially in the plain normal to the substrate.
**Figure 5.10.** QD Layer with Electric Field Tuning. After an electric field is applied, the oleic acid oligomers want to align with the electric field, thereby decreasing the distance between QD’s perpendicular to the efield.

**Figure 5.11.** Electric Field Tuning Substrate. The ITO pattern is the same as used in chapter 2, and the aluminum was deposited using TVD and a tinfoil mask.
5.2.3 Experimental

A source/measure unit (Kiethley 238) was used to apply a voltage of up to $100V$ between the aluminum contacts, while PbS (PL=1900 nm) was drop cast onto the surface of the substrate (figure 5.11), and the potential is held constant while the QD layer dries (~10 min). Special care was given to ensure the QD solution makes a continuous contact between the aluminum contacts. The starting voltage was low (0.5 V), as voltage increases, current is also increased until a threshold voltage was reached. Depending on the concentration of solution, this threshold can vary between 20 V and 100 V. After that, the voltage was held constant for about 10 minutes. During the process, a noticeable change of film morphology is observed, and a much smoother film was achieved (Fig. 5.12b), comparing with the one from drop casting, or spin coating.

5.2.4 Results and Discussion

Photoconductivity was measured by applying reverse voltage to the PV device thus made. For comparison, a control PV device using the same QD by drop casting only was made. Comparing with the control device, over four orders improvement of photocurrent at zero bias and more than six orders improvement at 5 V reverse bias in the electric field tuning device was observed (Fig. 5.11). Furthermore, Fig. 5.12 shows AFM images of two PbS QD films before and after electric field tuning. More than 5x improve in film smoothness has been demonstrated. Our electrical tuning method not only significantly improves photoconductivity across the device, but also helps with QD film morphology which will further enhance charge mobility of these QDs. (*We have filed a US & International patent (#61/236,271).)
**Figure 5.12.** Photocurrent of QD PV Devices, measured under AM1.5 solar illumination. The empty circle is for the original QD drop casted onto the ITO substrate, whereas filled circle is for the QD tuned by electric field during drying process.

![Photocurrent Graph](image)

**Figure 5.13.** AFM Images of Electric Field Tuning of QD’s. The 6.5µm x 6.5µm AFM images (tapping mode, amplitude) of PbS nanocrystal film on ITO : (a) pristine with average roughness (A.R.) of the film about 1.5nm, and (b) electric field tuned with A.R. about 0.3nm [72].

![AFM Images](image)
5.3 Hybrid Solar Cell

Commercialization of OPV devices has not yet been accepted due to the low PCE’s associated with OPV. It is theoretically possible to achieve higher efficiency by the incorporation of QD’s within the active layer. There are two ways to incorporate QD’s with polymers. A BHJ active layer structure by mixing QD’s with P3HT is one way to form an active layer with QD’s and polymer. The other way is by applying separate layers of P3HT/PCBM and QD’s. This structure is called a tandem structure. By mixing QD’s with P3HT, the active layer of these hybrid cells have the potential to absorb more of the solar spectrum, generating more charge carriers than an active layers comprised of P3HT/PCBM alone.

Figure 5.14. Hybrid Solar Cells. a) a hybrid cell structure using QD’s and P3HT in a BHJ structure. b) A tandem OPV cell with separate layers of QD’s and P3HT/PCBM active layers. These illustrations are the conventional structure, which uses a metal cathode. The order from bottom to top is glass, ITO, PEDOT:PSS, active layer(s), and aluminum cathode.
Normal hybrid solar cell using QDs are fabricated by spin coating the active layer consisted of QD/polymer. However, one drawback of this method is the non-uniform distribution of QDs within the polymer matrix due to the centrifugal effect. Hypothetically, a QD/polymer film formed by spray coating, shows much more improved morphology. This Ph.D. work has done some initial exploration about this direction.

Two hybrid PV devices were fabricated, one is the normal structure with spin-coated active layer, another is the inverted structure using spray technique as used in the OPV devices. For both devices, a solution of QD’s (size 2nm) in toluene at 20mg/mL was mixed with a solution of 20mg/mL of P3HT, also in toluene at a ratio of 4:1. The active layer solution was allowed to stir on a hot plate for 24h at 60°C. For the normal structure device, the active layer was spin coated at 500rpm, and the device was then put under high vacuum for 1h, after which 1000Å of aluminum was deposited using TVD. For the inverted device, the cleaned substrate for the hybrid cell was sprayed with a 2mg/mL solution of Cs₂CO₃ in 2-ethoxyethanol. The active layer was sprayed on. The substrate was then annealed at 170°C for 10min. Both devices were then annealed at 120°C for 10min after completion.

Fig. 5.14 presents the I-V characteristics of the normal structure hybrid solar cell. The poor performance was mainly due to the bulky oleic acids ligands hindering charge transport between QDs and polymers, as well as the poor morphology in the active layer film.
Figure 5.15. Hybrid Test Cell. This I/V curve is the results of a test cell having a PbS (QD)/P3HT spin coated active layer in a BHJ structure.

The inverted device, unfortunately did not work at all and behaved like a resister. This can be attributed to poor layer to layer interfaces. It was observed during fabrication, that the active layer went on very course, and dried too quickly. On of the test substrates shrunk the active layer as the mPED was sprayed on and dried. This could also be due to issues with the nano-morphology, and surface tension of the active layer. In order to further characterize the morphology effect in these two solution methods, AFM was employed to reveal more the AFM images of two films, one by spin coating (fig. 5.16a) and another by spraying (fig 5.16b). As can be seen clearly from both topography and phase image, the one with spraying has course morphology, and the film is rougher (average roughness 59nm vs. 52nm in the case of spin coated film). However, the phase segregation is more distinct and with smaller domain, which is beneficial for charge transport. Further work is needed to significantly improve the poor device performance.
Figure 5.16. AFM Image of Hybrid Active Layers. AFM images [topography (left panel) and phase (right panel)] of two PbS QD films prepared with a) spin coating; b) spraying.
5.4 References


8. Luther J M et al 2008 Nano Lett. 8 3488


17. Ellingson R J et al 2005 *Nano Lett.* **5** 865


22. Konstantatos G et al 2008 *Nano Lett.* **8** 1446


27. Du H et al 2002 *Nano Lett.* **2** 1321


133


35. Fern´ee M J, Thomsen E, Jensen P and Rubinszteine-Dunlop H 2006 Nanotechnology 17 956


41. Mahan G D 2000 Many-Particle Physics (Dordrecht/New York: Kluwer Academic/Plenum)


47. Leitsmann R and Bechstedt F 2009 ACS Nano 3 3505–12


49. Moreels I et al 2009 ACS Nano 3 3023–30 (and references therein)


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CHAPTER 6: CONCLUSION

In conclusion, this Ph.D. work presents the device engineering and characterization of solution processable solar cells based on organic semiconductors (π-conjugated polymers and fullerene derivatives), and inorganic semiconductor quantum dots (PbS and PbSe). Multiple solution-based fabrication techniques were explored, with the main contribution being the development of a novel layer-by-layer (LBL) spray process to make organic photovoltaic (OPV) arrays with up to 60 single cells. By eliminating the need for high-vacuum, high temperature, and the usage of metal as electrode, this technique has potential to revolute current silicon-based photovoltaic technology.

Initial device characterization and study were carried on using simple test cells having an active area of 4mm². Based on the fabrication parameters extracted from test cells, five types of OPV arrays, sizing from 1 square inch to 1 square ft, were designed and fabricated to perform additional experimentations, with the objective of determining fabrication obstacles for future large scale OPV manufacturing. Two different device geometries are investigated, namely, the conventional or normal structure where indium tin oxide (ITO) is used an anode, and a metal cathode is fabricated by thermal vapor deposition (TVD). A normal structure OPV device has four layers in the order of ITO-PEDOT:PSS-(P3HT:PCBM)-metal. The second geometry, called the inverted structure, uses ITO as the cathode of the device. The collection of electrons by ITO was achieved
by inserting a thin layer of electron transport layer (ETL) using either cesium carbonate (Cs$_2$CO$_3$) or sale assembled monolayer (SAM). The inverted structure consists of four layers, in the order of ITO-ETL-(P3HT:PCBM)-modified PEDOT:PSS, on a glass substrate.

Two generations of miniature organic solar arrays called microarrays were designed, fabricated, and characterized for application in MEMS device power supplies. The generation 1 microarray with normal structure consists of 20 small (1mm$^2$) solar cells connected in series for a total device area of approximately 2.2 cm$^2$. The device utilizes an active layer of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PC$_{61}$BM), both of which are mixed together (1:1 mass ratio) in appropriate solvent. The electrodes were patterned by photolithography and TVD, through a patterned shadow mask. Manipulation of active layer nanomorphology has been done by choice of solvents and annealing conditions. The optimized generation 1 device shows an open circuit voltage ($V_{oc}$) of 11.5$V$, short circuit current density ($J_{sc}$) of 1mA/cm$^2$, fill factor (FF) of 0.41 and a power conversion efficiency of 1.7% under simulated solar AM1.5 illumination.

The generation 2 microarray has a new design with reduced series resistance and improved cell occupancy. This microarray consists of 60 small (1 mm$^2$) solar cells connected either in series or in a combination of series (10 cells in a row) and parallel (6 rows). Two device geometry structures were used in these microarrays. Under simulated solar AM1.5 illumination, for normal structure generation 2 microarray, $V_{oc}$=12.4$V$, $J_{sc}$=0.11mA/cm$^2$, FF = 0.26 and a power conversion efficiency of 0.34% were achieved in
series connection, and $V_{oc}=4.2\,V$, $J_{sc}=0.77\,mA/cm^2$, FF = 0.42 and a power conversion efficiency of 1.36% for parallel connection; for inverted structure generation 2 microarray using $Cs_2CO_3$ as ETL, $V_{oc}=22.8\,V$, $J_{sc}=0.09\,mA/cm^2$, FF = 0.48 and a power conversion efficiency of 1.00% were achieved in series connection, and $V_{oc}=4.4\,V$, $J_{sc}=0.55\,mA/cm^2$, FF = 0.46 and a power conversion efficiency of 1.12% for parallel connection. On the other hand, for inverted structure generation 2 microarray using $SAM$ as ETL, $V_{oc}=9.8\,V$, $J_{sc}=0.08\,mA/cm^2$, FF = 0.39 and a power conversion efficiency of 0.31% were achieved in series connection, and $V_{oc}=3.2\,V$, $J_{sc}=0.48\,mA/cm^2$, FF = 0.39 and a power conversion efficiency of 0.58% for parallel connection. The overall SAM device performance was worse than that of the $Cs_2CO_3$ microarray, and it might be due to the imperfection of SAM layer causing leakage and shorts of some of the cells. Further improvement is ongoing to obtain optimal conditions for inverted SAM microarray.

A large area OPV array (4”x4”) was fabricated using the same spray-on techniques as the micro-arrays with the inverted structure, as well as the normal structure with metal cathodes deposited by TVD. This 4” x 4” array consist of 50 cells configured as 5 rows connected in parallel, with 10 cells connected in series of each row. The total active area is 30cm$^2$. For normal structure with aluminum as cathode, the best array has $V_{oc}=4.8\,V$, $J_{sc}=0.20\,mA/cm^2$, FF = 0.61 and a power conversion efficiency of 0.60%. For inverted structure with m-PEDOT as anode and $Cs_2CO_3$ as ETL, the encapsulated solar array shows more than 30% transmission in the visible to near IR range. Optimization of device is done by thermal annealing, and the optimal annealing conditions are shown to be difference in single-cell test device and the multiple-cell array. Solar illumination has been demonstrated to improve solar array efficiency up to 250%. Under AM1.5
illumination for over an hour, $V_{oc}=4.2\,V$, $J_{sc}=1.2\,mA/cm^2$, $FF = 0.37$ and a power conversion efficiency of 1.80% was observed. The performance enhancement under illumination only happens with sprayed devices, not devices made by spin coating. This means that solar cells made with our spray-on technique performs better under sunlight, which is beneficial for solar energy application.

A scale-up of the 4” x 4” array to a 1’ x 1’ array using the same fabrication techniques was fabricated as a proof of concept. The 1ft array has an active area of $270\,cm^2$, and $V_{oc}=?\,V$, $J_{sc}=?\,mA/cm^2$, $FF = ?$ and a power conversion efficiency of % was achieved under solar AM 1.5 irradiance. Although the device performance is not very impressive, this is an important milestone to demonstrate the capability of large scale fabrication using all-spray process.

Hybrid photovoltaic (HPV) made from blend of infrared quantum dots such as PbS and conjugated polymers have been considered a promising approach to improve photovoltaic performance of OPV. However, these solar cells have shown much smaller PCE comparing with their OPV counterpart. One of the main reasons is due to mass recombination of photogenerated carriers in these photovoltaic devices. In order to find out effective ways to improve device efficiency of, we have studied the gap states of PbS quantum dot (QD) films with four different sizes over a spectral range of 0.25-0.5 eV using continuous-wave (cw) photoinduced absorption (PA). The PA spectrum shows a strong asymmetric IR absorption peak (IR-PA). Both the peak position and shape of this IR-PA indicate distinct confinement dependence. Combining with results of interband transitions and Stokes shift, we assign this IR-PA to a transition from a well-
defined below-gap state to the second excitonic level (1P). This transition could potentially be used to monitor photogenerated charge transfer in such QD systems.

By measuring the frequency dependence of this IR-PA, we estimate the lifetime of this below-gap state to be around several microseconds. This single in-gap state cannot be explained by dark exciton theory, nor is it a trap state related to quantum dot surface defects as previously observed. A detailed analysis of the temperature dependence of photoluminescence, Stokes shift, absorption and photoinduced absorption indicates the unconventional GS is a new state of a trapped exciton in a QD film. With appropriate design engineering, these trapped excitons might be harvested in solar cells and other optoelectronic devices.

As synthesized PbSe and PbS QDs usually have bulky ligands such as oleic acids or TOPO (trioctylphosphine oxide), and therefore such QDs behave more like insulators. Ligand manipulation is necessary to electronically couple these QDs. We have developed a electric field assisted ligand manipulation method. Initial results have shown 4x orders improvement of photoconductivity at zero bias and more than 6x orders improvement at 5V reverse bias in a sandwich structure QD photovoltaic device. Furthermore, AFM images of two PbS QD films before and after electric field tuning has revealed more than 5x improve in film smoothness.

Hybrid photovoltaic (HPV) device was fabricated using a blend solution of PbS QDs and P3HT. Two different solution processes are used to form the QD/polymer active layer, one is the traditional spin coating method, and another is the spray technique developed
in this Ph.D. Work. Different film morphology was observed with these two methods. Although the film is slightly rougher in the case with sprayed QD/polymer active layer, the phase segregation is more distinct and with smaller domain, which is beneficial for charge transport. Further work is needed to significantly improve the poor device performance.