# **Evaluation of the Commercial Potential of Organic Photovoltaics**

by

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#### ABSTRACT

Recent years saw a steady increase in the record efficiencies achieved by organic photovoltaics. These have stimulated further interests and pursuit among the enthusiasts, in terms of both academic research and commercialization efforts. Indeed, organic photovoltaics offer a wide range of unique advantages, such as mechanical flexibility, being light-weight, and can be dyed in different colors. Above, it can be mass produced using roll-to-roll printing methods and offers ultra-low production costs.

However, organic photovoltaics face other great challenges, which need to be overcome before they can truly compete with other thin-film photovoltaic technologies. Organic photovoltaics have very low module efficiency and short lifetime, as compared to inorganic photovoltaics. This thesis provides a survey of current research efforts in addressing these problems. A survey of the current photovoltaic market, including thin-film photovoltaics, is also provided. A detailed cost model is proposed to see if the ultra-low cost of organic photovoltaics can compensate for their low efficiency and short lifetime.

Thesis Supervisor: Caroline A. Ross Title: Toyota Professor of Materials Science

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## 1 Introduction

## 1.1 Towards a Solar Energy Age

With concerns about rising oil prices, energy security, and climate change, the world has been experiencing unprecedented political and socio-economical momentum for clean renewable energies. This is not the first time the world faces an impending energy crisis. However, this is perhaps the first time the world sees the energy and the climate as entangled challenges that need to be overcome soon. The demand for oil has surged with globalization and with the rising demands in developing countries such as India and China. As industrialization permeates in these developing countries, it is estimated that the global energy demand will more than double by 2050<sup>26</sup>. Furthermore, the world is learning rapidly that the concomitant emission of greenhouse gases leads to worrying climate change. It is thus imperative to cut down CO<sub>2</sub> emission by switching to clean renewable energy resources.

Harnessing the solar energy presents a desirable solution, as the solar energy itself is clean, abundant and free. A power flow of 120,000 terawatt (TW) from the Sun showers the Earth constantly<sup>26</sup>. It is estimated that covering just 0.16% of the Earth's surface with 10%-efficient PV systems would provide 20TW of power, nearly twice the world's consumption rate of fossil fuel energy<sup>26</sup>. It has also been estimated that a 161kmx161km piece of land (or approximately 1.6% of total US land area) could generate all of US energy needs with 10% efficient solar cells<sup>56</sup>. While such estimates are not to be taken for granted, it shows the potential of solar cells in addressing the energy and environmental problem.

However, the sunlight has the disadvantages of being diffuse and intermittent, delivering only about 170 Wm<sup>-2</sup> of power, such that conversion into useful forms of energy would involve highly efficient photovoltaic system, concentration and storage. This necessarily brings up the cost and complexity of installing such systems.



Figure 1 Solar Spectrum outside the atmosphere and at sea level<sup>39</sup>

Figure 1 shows the solar spectra outside the atmosphere and at sea level. The flux at sea level is lower because of absorption of photons by the atmosphere, in particular  $O_3$ ,  $H_2O$ ,  $CO_2$  and  $O_2$ . Only ~20% of the solar power is available in the visible range, while most of the power is delivered in the infra-red range.

### 1.2 Standard Test Conditions

For effective comparison, all solar cells are tested under standard illumination conditions. The standard test condition (STC) for solar cells, regardless of design and material, is the Air Mass 1.5 spectrum (AM1.5G), an incident power density of 1000 WM<sup>-2</sup> (also known as '1 sun', as it is without concentration), and at an ambient temperature of 25°C<sup>26</sup>. This is equivalent to 844W/m<sup>2</sup>. It must be noted that the average power density on earth's surface is 170 WM<sup>-2</sup>, significantly lower than the standard test condition.



Figure 2 Solar irradiance at various altitudes and zenith<sup>41</sup>

# 1.3 Organic Photovoltaics as Second-Generation Solution

Access to affordable solar electricity is still unattainable, mainly due to the high costs of traditional solar cells and the availability of low-cost coal electricity. Currently, solar energy only provides 0.2% of global energy needs<sup>26</sup>. However, the rising oil prices and increasing concerns about climate change has spurred the growth of solar electricity generation over the past decade. Since the 1990s, the global PV production has doubled every two year. Indeed, 2006 was dubbed as the 'year of the solar IPOs', where several companies made high-profile initial public offerings (IPOs), generating a market capitalization value above \$1 billion<sup>26</sup>.

Nonetheless, even such fast-paced growth is insufficient for PVs to achieve grid parity with coal electricity. Currently, silicon solar cells cover more than 85% of the global photovoltaic production. However, silicon solar cells are still not cheap enough to allow widespread market diffusion without government incentives. In 2010, the average price of a solar module is approximately \$4 per peak Watt<sup>44</sup>. Furthermore, installation and balance of system components, add significant further costs. This include including controllers, circuit breakers, wiring and



mounting frame. Such costs, in addition to direct manufacturing costs of the modules, are estimated to be at least half of the total installation costs<sup>52</sup>.

This leads to efforts in seeking alternative routes to cheaper photovoltaics. Organic photovoltaics (OPVs) present as one of the alternatives. Professor Martin Green of University of New South Wales, Australia, suggested a PV roadmap. The roadmap categorized PV technologies into three generations of development. The traditional crystalline Si PVs are classified as first-generation PVs. They are characterized by efficiencies lower than the present single-junction limit of ~30%-40%, and relatively high costs. The second generation PVs have slightly lower efficiencies but significantly lower costs. These are the thin-film PVs (TFPVs), including organic thin-film photovoltaics. TFPVs require far less materials and utilize less expensive manufacturing processes such as vapor deposition and printing. Third generation PVs are predicted to have significantly higher efficiencies, utilizing new physical phenomena<sup>57</sup>.

Figure 3 Cost breakdown for roof-top photovoltaic installation in US, showing that installation and balance of system components present more than half of the total costs<sup>52</sup>.



Figure 4 in a developmental roadmap proposed by Professor Martin Green, organic photovoltaics are portrayed as second-generation photovoltaics with lowest manufacturing costs among other PV technologies. The dotted lines represent module costs<sup>57</sup>

Organic photovoltaics, as a member of thin-film photovoltaics, offer a set of unique advantages over traditional solar cell technologies. These include<sup>1,26</sup>:

- a) Lightweight and highly flexible: polymer substrates can be employed in OPVs, instead of glass substrates in traditional solar cells. The resulting PV modules have great mechanical flexibility that allows for integration with products of various shapes and sizes. Innovative solar PV products are also possible, such as PV panels that can be rolled up to minimise storage space.
- b) The use of non-brittle polymer substrate also means that the OPVs are tough, durable and much easier to handle.
- c) The roll-to-roll manufacturing processing of OPVs allows for products of various lengths and widths, thus enabling easy customization.
- d) The roll-to-roll processing also means extremely high throughput volume, significantly reducing the manufacturing costs of OPVs.
- e) Highly sophisticated deposition methods are required in the processing of silicon PVs and other thin-film PVs, such as high-temperature deposition and requirement for very high vacuum conditions. The processing simplicity of OPVs, including room-temperature deposition and ridding of stringent vacuum requirements, means further cost reduction.
- f) OPVs can be made translucent or dyed with different colours to give them a unique aesthetic appeal and render them as ideal building-integrated components<sup>26</sup>. Transparent and coloured photovoltaic facades have been installed on buildings, using inorganic thin-film photovoltaics<sup>26</sup>. In such circumstances, the aesthetic value of the PVs is perhaps equally significant as its 'green-ness'. It is hoped that OPVs can eventually achieve the necessary efficiency and stability to successfully compete in the building-integrated photovoltaic (BIPVs) market.

OPVs, together with other thin-film PVs, are thus envisioned as second-generation PVs that could circumvent the barrier of high costs associated with traditional silicon solar cells. However, unsolved problems of low power conversion efficiency, poor operational stability, and short lifetime pose great challenges for this vision. As compared to conventional Si solar cells (>20% efficiency) and thin-film solar cells (>10%), it is hoped that OPV can succeed in the market where their low cost, substrate flexibility, and ability to perform in dim light can provide them with competitive advantage<sup>2</sup>.

## 2 A Brief Historic View<sup>1</sup>

In a photovoltaic system, the light is captured and converted to useful work. In nature, the light is captured by highly efficient photosynthetic complexes and transferred very efficiently to reaction centres, where the energy is stored<sup>26</sup>. The two steps occur so fast that the energy loss is minimal. Direct evidence showed that such high efficiency in these organic complexes is made possible by long-lived, wavelike energy transfer within the complexes<sup>26</sup>. There is therefore great incentive to mimic nature. Such concepts give rise to organic photovoltaic systems.

Before the mid-1980s, conventional organic photovoltaic cells consisted of an organic active material, sandwiched between two dissimilar metal electrodes. In these single-layered cells, the built-in potential is derived from the difference in the work functions of the electrodes, or from a Shockley-type potential barrier at one of the metal/organic contacts<sup>47</sup>. Such cells exhibit strong dependence on the nature of the electrodes, strong field-dependence of charge generation and poor fill factor<sup>47</sup>.

In 1986, Tang et al. demonstrated a bilayer heterojunction (figure 5a) between a layer of copper phthalocyanine (CuPc) and a layer of perylene tetracarboxylic derivative (PV), where a power conversion efficiency of 0.95% was obtained using monochromatic light<sup>47</sup>. This novel bilayer design demonstrated that the interface between the organic layers was crucial in determining the cell performance. It significantly reduced the dependence on bias field<sup>47</sup>. It served as the prototypical organic photovoltaic, from which the modern organic photovoltaics stem off.

However, OPVs face a dilemma that was not solved by the bi-layer design. For effective light absorption, a minimum thickness of 100nm is required for the photoactive layer. However, due to the short exciton diffusion length (10nm), a thin photoactive layer is required. The solution was to have a diffused interface (figure 5b) between the acceptor and donor, so as to increase the donor-accepter interface area, such that more exciton diffusion could occur. This eventually evolved into the-state-of-the-art disordered bulk heterojunction (BHJ) design (figure 5c). The application of dispersed bulk heterojunction of MEHPPV and C60 and later soluble derivatives of C60, increased the power conversion efficiency to 2.5%<sup>1</sup>. These are achieved by spin-coating a polymer-fullerene blend or by co-evaporation of conjugated molecules<sup>26</sup>.



Figure 5 a) bilayer design (b) diffused bilayer heterojunction (c) disordered bulk hterojunction<sup>5</sup>

# 3 Principles of Operation



3.1 Optical Properties of Inorganic Materials Vs Organic Materials

Figure 6 Absorption coefficients versus photon energy for monocrystalline silicon (c-Si), amorphous Si (a-Si), and polycrystalline Si (uc-Si)<sup>52</sup>



Figure 7 Absorption spectra of some organic compounds in relation to wavelength of photons<sup>52</sup>

Figure 6 shows the absorption strengths of some inorganic semiconductors in relation to the photon energies, while figure 7 shows the corresponding absorption spectra for organic compounds. It can be seen that the absorption properties of organic compounds is distinct from their inorganic counterparts. The absorption coefficient of silicon semiconductors, for instance, increases steadily with the photon energy –as long as the photon energy is greater than the 'cutoff' energy - namely, the band gap energy of the semiconductor. As will be explained in Section 3.2, inorganic semiconductors exhibit band gap energies. If the photon energy is greater than the band gap energy, the photon will be absorbed and photo-excite an electron from conduction band to valence band. Thus, above the 'cutoff' energy, all photons will be absorbed and the inorganic semiconductor exhibits a continuous absorption spectrum.

Organic molecules, however, have discrete excited states, in contrast to energy bands in inorganic semiconductors<sup>52,53</sup>. In an organic compound, simple, double and triple bonds can be formed between adjacent carbon atoms. Interactions in the  $\pi$ -orbitals lead to splitting of energy levels. Further splitting leads to formation of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), as shown below. As a result, organic compounds exhibit discrete excited states, when the electrons in the HOMO are photo-excited by incident photons. Such properties allow a design of highly efficient organic tandem cells, with each cell optimally absorbing in a narrower range in the solar spectrum.



Figure 8 Molecular interactions lead to energy splitting and eventually lead to the formation of HOMO and LUMO in organic materials<sup>53</sup>

More significantly, most of the available organic semiconductors have optical band gaps close to 2eV. While silicon absorbs sunlight far into infra-red region (up to 1400nm), the organic materials absorb mainly the blue region of the sunlight, as shown below. Clearly, there is little overlap with the standard AM1.5 terrestrial solar spectrum. This severely limits the efficiency of the OPVs.



Figure 9 Absorption coefficients of some commonly used organic materials in OPVs, in relation to wavelengths of photons. The dotted line in the background is the standard AM1.5 solar spectrum<sup>62</sup>.

## 3.2 Conventional Inorganic PV<sup>26,37</sup>

A conventional photovoltaic consists of two layers of semiconductor, one doped with p-type material (acceptor) and the other with n-type material (donor), which are sandwiched together to form a p-n junction.



Figure 10 Construct of a semiconductor p-n junction<sup>37</sup>

The excess electrons from the n-type side annihilate the excess holes from the p-type as they diffuse towards each other, forming a depletion zone. In this depletion zone, the immobile dopant ions then create a positive charge on the n-type side and a negative charge on the p-type side. This induces an electric field in the depletion layer. Equilibrium is reached when two opposite currents flow across the depletion zone, one of minority carriers (electrons in p-type and holes in n-type) and the other of majority carriers (electrons in n-type and holes in p-type). The majority carriers move by diffusion. The minority carriers are carried across the depletion layer under the influence of the built-in electric field.

When sunlight falls on the semiconductor p-n junction, photons with energy greater than the band gap energy of the semiconductors are absorbed, generating electron-hole pairs. Thus, the spectral nature of the sunlight is fundamental factor affecting the design of a solar cell. The electron-hole pairs are then separated by the electric field, which drives the electrons towards the n-type side and the holes towards the p-type side.



Figure 11 Band gap profile of a p-n junction<sup>38</sup>

The electron-hole pairs increase the minority carriers, but the majority carriers remain the same. This causes the minority carrier current to increase and shifts the current-voltage characteristic of the photovoltaic cells to shift downward, as shown below.



Figure 12 Current-Voltage characteristics of a photovoltaic cell<sup>37</sup>

The efficiency of the photovoltaics is dependent on the band gaps<sup>37</sup>. With reference to silicon semiconductors, photons in the UV and visible range of the solar spectrum have energy greater than the band gaps, and thus can be absorbed. The excess energy is dissipated as heat. Photons in the infra-red region have energy similar to the band gaps and are thus mostly absorbed without much energy loss. Photons in the near infra-red region have energies less than the band gap, and thus will not be absorbed.



Figure 13 Band gap energy in semiconductors and photon absorption: photon with energy greater than the band gap energy will be absorbed, with excess energy lost as heat. Photons with energy less than the band gap energy will not be absorbed<sup>52</sup>.

The band gap energy is thus directly related to open-circuit voltage V<sub>oc</sub> of the solar cell. As the band gap increase, the maximum V<sub>oc</sub> increases. However, the fraction of the solar spectrum absorbed decreases. Taking these into account, the theoretical optimal efficiency of a silicon PV is ~45%<sup>37</sup>. Due to electron-hole recombination, however, the optimal efficiency is reduced to ~20%<sup>37</sup>. The figure below illustrates the predicted efficiency limit in relation to the solar spectrum for various photovoltaic materials:



Figure 14 Predicted efficiency versus bad gap for photovoltaic materials, in relation to solar spectra in space (AM0) and on earth (AM1.5) at 300K, under concentrated (C=1000) and unconcentrated (C=1) conditions<sup>26</sup>.

As can be seen, the theoretical efficiency limits for inorganic single-junction photovoltaics are mostly between 20-30%. Si and GaAs, with band gaps of 1.12eV and 1.45eV, have limiting efficiencies of about 29% under unconcentrated conditions<sup>26</sup>.

### 3.3 Key Characteristics of a PV

The voltage developed when the terminals are isolated is *open circuit voltage*  $V_{oc}$ . The current flowing when the terminals are connected directly is called *short circuit current*  $I_{SC}$ . For any intermediate load, the voltage developed is between 0 and  $V_{oc}$ , as indicated by the current-voltage characteristics of the solar cell.

The current produced is roughly proportional to the illuminated area<sup>26</sup>. Thus, current density, J<sub>SC</sub>, is used for comparison. The current density is related to the incident solar spectrum through the solar cell's quantum efficiency QE(E), which is the probability that a photon of energy E = hv induces an electron transition across the band gap and to the external circuit<sup>26</sup>. The current density is given by<sup>26</sup>:

$$J_{SC} = q \int b_s(E) QE(E) dE$$

Where q is the electron charge,  $b_{sc}$  is the flux density of the incident photons. It is thus desirable to have high quantum efficiency at the energy where the photon flux density is high. The QE of the solar cell's material is itself dependent on<sup>26</sup>: (a) the absorption efficiency  $\eta_{abs}$ , which itself is a function of absorption coefficient of the material, the solar spectrum and absorbing thickness<sup>62</sup>. (b) the efficiency of exciton diffusion  $\eta_{diff}$  (c) the efficiency of exciton dissociation  $\eta_{diss}$ , and (d) the efficiency of charge collection of the device  $\eta_{cc}$ .

$$QE(E) \propto \eta_{abs} \eta_{diff} \eta_{diss} \eta_{cc}$$

The solar cell operates and delivers power within the regime of V=0 and V=V<sub>OC</sub>. The power is give by  $P^{26}$ :

$$P = JV$$

The delivered power reaches its maximum when the current density and voltage are at their maximum, namely  $J_m$  and  $V_m$ , as shown in figure 6. The fill factor FF is defined as the ratio<sup>26</sup>:

$$FF = \frac{J_m V_m}{J_{OC} V_{OC}}$$

The efficiency of the cell  $\eta$  is then defined as<sup>26</sup>:

$$\eta = \frac{J_{SC}V_{OC}FF}{P_S}$$

where  $P_s$  is the power density of the incident light. In general, solar cells with higher current density tend to have lower open-circuit voltage  $V_{OC}^{26}$ . This is a consequence of the material's semiconductor band gap.

When a load is present, a potential difference develops between the terminals of the cell. This potential generates a current which acts in the opposite direction to the photocurrent, and the net current is reduced from its short-circuit value,  $J_{sc}$ . This reverse current is called *dark current*<sup>26</sup>. Most solar cells behave like a diode in the dark, admitting a much larger current in forward bias than in reverse bias<sup>26</sup>. For an ideal diode, the dark current density varies as<sup>26</sup>:

$$J_{dark} = J_o(e^{qV/K_bT} - 1)$$

Where  $K_B$  is Boltzmann's constant, T the temperature, and  $J_o$  is a constant. Thus, the net current flowing in a circuit powered by solar cell is governed by the Shockley equation<sup>26</sup>:

$$J(V) = J_{SC} - J_{dark}$$
$$J(V) = J_{SC} - J_o \left( e^{qV/k_BT} - 1 \right)$$

In real cells, power is lost through contact resistance and through leakage currents around the side of the cell<sup>42</sup>. Electrically, these effects are equivalent to two resistances, one in series ( $R_s$ ) and another in parallel ( $R_{sh}$ ), as shown below.



Figure 15 Equivalent circuit representing a real solar cell, with parasitic series resistance Rs and parallel resistance Rsh<sup>42</sup>.

These parasitic resistances act to reduce the fill factor and hence the efficiency of the solar cell<sup>42</sup>. The series resistance arises from the cell's material resistance to current flow and from resistive contacts especially. The parallel, or shunt, resistance arises from leakage currents around the device and recombination losses, especially at defects. Thus, an efficient cell requires  $R_s$  to be as small as possible and the  $R_{sh}$  to be as large as possible<sup>42</sup>.

- 3.4 Organic Photovoltaics
- 3.4.1 Basic Construct of An OPV



Figure 16 Top<sup>63</sup>: Generic construct of an OPV. Bottom<sup>64</sup>: A schematic representation of an actual OPV device manufactured by Mitsubishi Cooperation.

The top diagram in Figure 16 shows the generic construct of an OPV. It consists of an organic, active layer sandwiched between two electrodes. The front electrode is transparent, usually made of indium tin oxide (ITO) sputtered onto the substrate, while the back electrode is usually a metal, e.g. Ag. The active layer comprises a donor-acceptor blend. The active blend can consist of organic molecules or polymers. The former is usually deposited via thermal evaporation, while the latter is usually deposited via wet solution processing<sup>62</sup>. The substrate used can be glass or flexible polymers.

The bottom diagram in Figure 16 shows the layout of an OPV cell in an actual OPV module, manufactured by Mitsubishi Cooperation, the National Institute of Advanced Industrial Science and Technology and Tokki Corporation in Japan<sup>64,65</sup>. This schematically shows an individual cell, in a series-connected, highly integrated module, produced by laser scribing technique<sup>64,65</sup>.



Figure 17 A highly integrated OPV module manufactured by Mitsubishi Cooperation<sup>64</sup>

The active layer compromises fullerene (C60) as acceptor and phthalocyanine (CuPc) as donor. ITO is used as the transparent electrode while Al is used as the counter-electrode. Glass is used as the substrate. An additional layer of LiF is deposited to facilitate charge transport. Lastly, as in all organic electronic devices, a barrier layer is deposited to prolong product lifetime by minimizing degradation and oxidation.

The significance of the electrode materials is illustrated in Figure 18. Figure 18(a) shows the short-circuit condition. The built-in electric field resulting from the difference in the metals' work functions is evenly distributed throughout the organic layer (dashed line). Under illumination, as in Figure 18(b), separated charge carriers can drift in this electric field to the respective electrodes: electrons to the lower work function metal and hole to the other<sup>62</sup>. The applied voltage that balances the built-in potential is called open-circuit voltage V<sub>oc</sub>. Figure 18(b) is also known as the 'flat-band condition', as there is zero net current. In transition from (a) to (b), the cell generates power, corresponding to the 4<sup>th</sup> quadrant in the I-V curve of OPVs (see section 3.4.2.). As will be seen Section 3.4.2, OPVs exhibit a current-voltage characteristic that is highly field-dependent.



Figure 18 Schematic diagrams of metal-insulator-metal model, representing the rectifying behaviour of an intrinsic organic semiconductor, the two parallel lines represent LUMO and HOMO of the organic semiconductor<sup>62</sup>

There is also evidence that injection of carriers and V<sub>oc</sub> depend on the interfaces with the electrodes<sup>62</sup>. As the contact resistance becomes smaller, the smaller the injection barriers are. As such, ultra-thin layers (<1nm) of materials are usually deposited on the electrodes to improve charge collection efficiency. LiF for instance is deposited on the metal electrode to improve contact efficiency in OPVs. PEDOT:PSS is deposited on ITO electrode to help improve cell performance.

The following sub-sections briefly describe some of the materials used in molecular and polymeric photovoltaics.

#### 3.4.1.1 Molecular OPVs

Phthalocyanine and its derivates are representatives of the p-type, hole-conducting materials that work as electron donors, used in molecular OPVs. Perylene and its derivatives are typical n-type, electron-conducting molecules used.



Figure 19 Typical materials used in molecular OPVs: zinc phthalocyanine (ZnPc) as donor, (N,N'-dimethy-perylene-3,4,9,10-dicarboximide) as acceptor and C60 as dopant for donors<sup>62</sup>

As most organic materials have an optical band gap of 2eV, the intrinsic charge carriers are low<sup>62</sup>. Furthermore, due to weak van der Waals interactions, the charge carrier mobilities are low<sup>62</sup>. As such, they can be effectively regarded as insulators. Molecular or electrochemical doping is usually done to increase the carrier concentration. Donor materials, for instance, exhibit doping effect when exposed to oxidizing agents such as iodine<sup>62</sup>. This doping is achieved by transferring electron from the organic molecule to the oxidizing agent, thus increasing the charge carrier concentrations in the hole conductor. A more controlled doping method is to co-evaporate both the donor material and C60, a strong electron acceptor. Under illumination, a photo-induced charge transfer to C60 results in large increase in photoconductivity<sup>62</sup>. As an example for n-type

doping, perylene can be doped using hydrogen, or other agents. One of its derivatives, N,N'dimethyl-perylene-3,4,9,10-dicarboximide is a good acceptor material.

As these molecules are more thermally stable but less soluble than their polymeric counterparts, they are usually thermally evaporated<sup>62</sup>. Ultra high vacuum (<10<sup>9</sup> mbar) may be required to remove contaminants such as oxygen and water. To create intermixing blend of acceptor and donor materials, co-evaporation is required.

#### 3.4.1.2 Polymeric OPVs

Three important representatives of donor-type polymers and of acceptor-type polymers are shown in the figure below<sup>62</sup>. For donor-type polymers, they are **MDMO-PPV** {poly[2-methoxy-5-(3,7dimethyloctyloxy)]-1,4-phenylenediamine}, **P3HT** {poly(3-hexylthiophene-2,5-diyl and **PFB** {poly(9,9'-diotyfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-pehnyl-1,4-phenylenediamine). For acceptor-type polymers, they are **CN-MEH-PPV** {poly-[2-methoxy-5-(2'-ethylhexyloxy)-1,4-(1-cyanovinylene)]-phenylene], **F8TB** {poly(9,9'-dioctylfluorene-co-benzothiadiazole)) and **PCBM** {1-(3-methoxycarbonyl)-propyl-1-phenyl[6,6]C61}.



Figure 20 Representatives of polymeric materials used in OPVs. Donor materials: MDMO-PPV, P3HT, and PFB. Acceptor materials: CN-MEH-PPV, F8BT and PCBM<sup>62</sup>.

For polymeric OPVs, the donor polymers can be blended with either acceptor-type molecules (e.g. fullerene) or with acceptor-type polymers. All of these materials, both acceptor and donor,

are solution-processible, due to their side-chain solubility<sup>62</sup>. As such, polymeric OPVs are usually processed from solutions.

## 3.4.2 Current-Voltage Characteristics of Organic PVs

As abovementioned, the performance of an inorganic solar cell can be approximated by the Shockley diode equation, while incorporating losses through material resistance, contact resistance and leakage currents. However, this cannot explain the current-voltage characteristics of OPVs, which is shown below:



Figure 21 Current-voltage of an organic solar cell<sup>43</sup>

The current J(V) curve for a typical organic solar cell shows a strongly field-dependent photocurrent<sup>43</sup>. As seen in the figure, the maximum photocurrent is not reached at OV, i.e. under short-circuit conditions, but only under more negative bias, corresponding to higher internal field. The reason is that the polarons (electron-hole pairs formed after exciton dissociation, but still held together by Coulombic attraction) have to be split by externally applied electric field. If the polaron pair dissociation is more difficult than usual (e.g. when the active layer is thicker), then under the same external voltage, the internal field at zero bias is lower<sup>43</sup>.

#### 3.4.3 Operating Principles of OPVs

The mechanism underlying the operation of OPV shares many similarities with that of inorganic PVs. The basic architecture of a single-junction OPV is shown in Figure 16. The core of the cell is the photoactive layer, which is generally a p-type electron-donor (D) compound and an n-type electron-acceptor (A) compound (strongly electronegative materials such as buckminsterfullerene, C60). Both the acceptor and donor are organic  $\pi$ -conjugated materials. In the solid-state OPVs, either (or both) of the compounds is a polymer.

Two electrodes are required. The work functions of the electrodes are critical in determining whether the contact with organic material is ohmic blocking, while their difference provides the built-in potential for free charge carriers to drift towards the electrodes. The cathode is usually

made with low work function metal such as Al, while a high work function material is used for the anode. One of the electrodes needs to be transparent so as to allow light to reach the photoactive layer. Indium tin oxide (ITO) is commonly used. Buffer layers between the instance, poly-For added. may be and organic materials electrodes (ethylenedioxythiophene):polystyrenesulphonic acid (PEDOT:PSS) is added above the ITO layer. This improves the HOMO $_{D}$  energy level, smoothes the ITO surface and acts as electron-blocking layer<sup>1</sup>.

The overall photoinduced charge transfer can be summarized in five main steps<sup>5</sup>:

1. Photoexcitation of the semiconducting organic material causes the promotion of electrons from the ground state (the highest occupied molecular orbital, or HOMO), to the excited state (the lowest unoccupied molecular orbital, LUMO). Excitons, charge-neutral hole and electron pairs, are generated. Light is usually absorbed mainly in the p-type material (D).



Figure 23 Schematic representation of the operating mechanism of organic solar cells<sup>49</sup>

- 2. Exciton within the diffusion length from the D/A interface will have a chance to reach the interface before decay. The diffusion length is the distance excitons travel before recombination, and is typically on the order of 10-50nm<sup>56</sup>.
- 3. If the difference in energy levels of the donor and acceptor materials is larger than the exciton binding energy, the excitons will dissociate at the interface. Excitons generated in the donor materials will dissociate by transferring electron to the LUMO level of the acceptor, while retaining positive charge. Excitons generated in the acceptors will dissociate by transferring holes to the HOMO level of the donor while retaining negative charge. These processes are energetically favourable, and thus very fast and very efficient.

The charges, however, are still held together by Coulombic attraction, and are called polarons<sup>43</sup>. The recombination rate for these polaron pairs (micro- to milli-seconds) is, however, significantly lower than that of the singlet excitons (nanoseconds)<sup>26,43</sup>. The polarons are separated if the applied field is large enough. This leads to the formation of free charge carriers. The dissociation of the polaron pairs requires electric field to overcome the Coulombic attraction. Such a field is influenced by the built-in potential due to the work function difference between the electrodes<sup>26</sup>. This explains the field-dependence of the photocurrents in OPVs.

A huge advantage of this D/A interface design, over the conventional single layer design, is that the holes are now transported in donor material and electrons in acceptor materials. Thus, electrons and holes are effectively separate from each other, and their recombination rate is greatly reduced<sup>62</sup>.

- 4. The free charge carriers diffuse to the electrodes through the donor/acceptor materials.
- 5. The charges reach the electrodes and are collected.

It should be noted that excitons in organic semiconductors are tightly bound, with binding energy of 0.3-0.5eV. This is distinct from inorganic semiconductors where immediate dissociation of excitons is observed. In addition, the charge carrier mobility in the organic materials is very low. This is because of the amorphous nature of the organic material. However, the OPVs have a strong advantage: its absorption coefficient is much larger, usually  $>10^5$  cm<sup>-162</sup>. Very thin (100nm) organic films can absorb all the light shone on them (within their absorption range), whereas a comparable 300µm crystalline silicon PV is required<sup>26</sup>.

Each of the steps describes above decreases the efficiency of the entire process. It is thus important to optimize every step through design optimization and materials optimization.

#### 3.4.4 Bulk Heterojunction (BHJ) Organic Solar PVs

As stated previously, the state-of-the-art OPVs are bulk heterojunction OPVs. This concept features a distributed junction between the donor (D) and the acceptor (A) materials: both components inter-penetrate each other, so that the interface is spatially distributed and lies within the diffusion length of each exciton generation site<sup>62</sup>. It is implemented by spin-coating a polymer-fullerene blend, or by co-evaporating conjugated molecules<sup>26</sup>.



Figure 24 Schematic representation of a bulk heterojunction solar cell, showing the phase separation of donor (blue) and acceptor (red) materials<sup>48</sup>.

Bulk heterojunctions have the advantage of being able to dissociate excitons very efficiently over the whole extent of the active layer and thus can generate polaron pairs throughout the active layer. Excitons are photogenerated, diffuse to the D/A interface, and dissociate to form polaron pairs or recombine radiatively. If polaron pairs are generated, then they can be separated with the help of an external electric field; the free charges can then move to the electrodes to generate a photocurrent, or recombine with other mobile charges<sup>26</sup>.

However, BHJ solar cells have the disadvantage of having greater difficulty of separating the polaron pairs, due to increased disorder<sup>26</sup>. Also, it is more likely that the freed polarons (or charges) will recombine with other mobile or trapped charge carriers.

In general, the BHJ design optimizes interfacial area and the donor-acceptor contact. This is usually done by fast evaporation techniques that prevent equilibrium conditions that favour phase segregation<sup>26</sup>. Conjugated polymers soluble in common solvents are particularly attractive for the production of large area PV cells because the wet printing techniques can be applied to the production of thin films of such polymers<sup>26</sup>. Some examples of such polymers include poly(p-phenylene vinylene) (PPV), poly(akyl-thiophenes) (PATs), poly(3-hexylthiophene) (P3HT), and poly[2-methoxy-5-(2'-ethyhexoxy)-1,4-phenylenevinylene] (MEH-PPV)<sup>26</sup>.

## 4 Manufacturing<sup>1</sup>

As described above, organic solar cells typically comprise a multilayer structure where each layer in the stack may be formed by an individual film-forming technique. There are many film-forming techniques available that are suited for high volume processing of paper, plastic ad textile materials where the substrate is in the form of a continuous roll of material. This is often called roll-to-roll coating<sup>1</sup>. The processing equipment usually comprises: unwinding, coating and rewinding of the material. Many more processes maybe involved such as cleaning, pre/post treatments of the fabric, heating, drying, etc. Such high-speed printing methods have been developed with the aim of achieving a very low process cost.

One of the main challenges involves choosing the right technique for organic solar cells<sup>1</sup>. Some techniques are only suitable for 0-, 1-, or 2-dimensional controls. Some techniques allow multilayer printing within the same step. Choosing the right combination of these to optimize the processing is a great challenge. Secondly, with each of these coating techniques, there is a window of operation in terms of processing speed and achievable thickness. Thus factors such as viscosity, surface tension, surface energy, additives etc become critical to processing optimization.



#### 4.1 Screen Printing

Figure 25 Schematic representation of screen printing process<sup>1</sup>

Screen printing is a very versatile technique that allows for full 2-dimensional patterning of the printed layer. The main distinction from other techniques is its large wet film thickness and a requirement for relatively high viscosity of the coating solution. The process is illustrated in the figure above. A screen is pulled over the substrate. The pattern is obtained by filling the screen with an emulsion that is impermeable to the screen. A squeegee is forced across the screen, and thus printing the ink into the open area in the screen.

Large scale industrial production of polymer solar cells using screen printing has been demonstrated<sup>3</sup>. The demonstration showed the production of small serially connected modules

with a module area of 132 cm<sup>2</sup> on flexible substrates. Screen printing was also shown to be highly R2R compatible, where the materials could be passed through the machine at constant speed. The screen and the support follow the web at constant speed while printing is in progress. After each print, the screen and support reverses back and the printing cycle is repeated. A rotary screen method is also possible, as demonstrated below, where the squeegee is placed inside the rotating screen and the web is rolled on the outside of the screen.



Figure 26 Alternative configuration for screen printing<sup>1</sup>

#### 4.2 Ink Jet Printing

Ink jet printing takes advantage of low cost and relatively high resolutions. The dry thickness of the ink jet printed film is given by the number of droplets delivered per area and the individual droplet volume. The printing process, however, is relatively complex. The droplets may be formed by piezoelectric-controlled compression. They are subsequently electrostatically charged and accelerated towards the substrate by electric field. There are, therefore, more stringent requirements on the compositions of the ink, which may pose a challenge in the context of polymer photovoltaics, which upon drying will become the functional layer.



Figure 27 Inkjet printing<sup>1</sup>

### 4.3 Roll-to-Roll Techniques (R2R)

In R2R processing, the substrate material is referred to as the eb and comes in the form of very long sheet wound on a roll. During printing and coating, the web is unwound from theroll, passed through printing machine and rewound into a roll. There are great incentives to integrate all the printing processes in an integrated manner, as shown below.



Figure 28 Integrated roll-to-roll processing<sup>1</sup>

This is to minimise handling damages and to increase throughput. However, in practice, this is often difficult to achieve, as it requires constant speed for all coating processes. The following section gives a brief overview of the various R2R techniques applicable to OPV processing<sup>1</sup>.



Figure 29 Techniques compatible with roll-to-roll processing<sup>1</sup>

#### 4.3.1 Knife-over-edge Coating

In this techniue, a knife is placed over the roll, and the web is pulled through, as shown on the left. This coating method is 0-dimensional technique, to allow application of an even layer over the substrate. This means that patterning is not possible. This technique produces ery smooth films if the ink has high levelling properties. However, it does not work well for inks with low viscosity, as the ink may start running over the roll.
#### 4.3.2 Slot-die Coating

This is an 1-dimensional technique which allows for coating of stripes of materials, and thus is well suited for manufacturing multilayer solar cell with stripes of different materials layered on top of each other. While the method itself is simple, the slot-die coating head can be complex, as shown below. The most important part is the mask, which controls the thickness of the stripes produced.



Figure 30 Parts of a slot-die coating head<sup>1</sup>

This method allows for electrical connection between the layers, thus enabling serially connecting devices, as shown below. Given the fact that Konarka's Power Plastic consists of serially connected photovoltaic cells, it is likely that they are manufactured in a slot-coating process.



Figure 31 Slot-die printing to produce series-connected devices<sup>1</sup>

### 4.3.3 Gravure Coating

2-dimensional printing is achievable with gravure coating. In its simplest form, it consists of two rollers, where the coating roller has an engraved pattern. The coating roller is partially

immersed in ink bath such that it is continuously refilled. The coating rollwer is then forced into contact with the support roller. Upon cntact, the ink in the gravure roller is transferred to the substrate. This method can work well with low-viscosity ink and high throughput (1-10m/s) can be achieved. However, change of pattern requires change of the roller, which can be expensive.

### 4.4 Application to OPV Manufacturing

For all the printing methods, there are currently very few commercially available printing inks for OPV manufacturing<sup>1</sup>. This in a way signifies the status of the technology and OPV product today. Of the few that are available, such as those for PEDOT:PSS and silver pastes are developed for flexible electronics.

Once the film is formed, other processes may be required before the film is rewound into a roll. Often, this involves drying and heating, which serve to dry the wet film and to thermally anneal the OPV to induce the desired morphology<sup>4</sup>.

As compared to the production methods used for other PV types, roll-to-roll printing yields significant advantages. These include lower capital costs since no high vacuum is required, exceedingly high material utilization, cheap flexible plastic substrate, continuous process, high throughput, and short energy payback. These are summarized in the table below.

Technology	Si Wafer Cells	Vacuum-based thin film on glass	Roll-printed thin film (OPVs)
Process	Silicon wafer processing	Sputtering, evaporation in vacuum	Printing in air
Process control	Fragile wafers	Expensive metrology	Built-in bottom-up reproducibility
Materials utilization	30%	30-50%	Over 95%
Substrate	Wafer	Glass	Flexible substrate
Energy Payback	3 years	1.7 years	< 1 month
Complexity	High	Low-medium	low

Table 1 Relative advantages of roll-to-roll printing of OPVs as compared to other PV types<sup>27</sup>

### 4.5 Konarka: A Casestudy

In March 2008, Konarka Technologies successfully conducted the first ever demonstration of OPV manufacturing by highly efficient inkjet printing<sup>4</sup>. The continuous roll-to-roll printing technology is significantly less expensive and capital intensive than the multi-step assembly of traditional silicon solar cells. Such printing technique also allows flexible patterning and artificial colouring of the final product. It has been extensively used in the manufacturing organic LEDs and thin-film transistors.

4.5.1 Detailed Device Construct

The basic structure of Konarka's OPV module is shown below.



Figure 32 Basic Structure of Konarka's OPVs, with its sequence of deposition shown in the top diagram and relative thickness shown in the bottom diagram.<sup>18</sup>



Figure 33 Left: detailed layout of 3 series connected OPV cell in Konarka's Power Plastic module. Right: photograph of the actual Power Plastic Product<sup>20</sup>

The basic layers comprise plastic barrier substrate, ITO electrode, PEDOT as hole conductor, an organic semiconductor layer, a metal counter-electrode, and lastly a protective cover. The active layer in this case consists of either regioregular poly(3-hexylthiophene) (**P3HT**) or poly[2,6-(4,4-

bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), blended with fullerene [6,6]-phenyl C61 butyric acid methyl ester(PCBM)<sup>50</sup>.

All of the layers are very thin. The ITO electrode layer is about 100nm thick<sup>50</sup>. The active layers are only tens of nanometers deep<sup>50</sup>. Such shallow layers allow quick drying and promote the use of fast web speeds in roll-to-roll production.

In a module, the cells are connected in a manner called Z-connection, i.e. a series connection in which the top electrode of the first cell is connected to the bottom electrode of the second cell<sup>27</sup>.



Figure 34 RR-P3HT and PCBM are used for the organic active layer in one of Konarka's products<sup>50</sup>

### 4.5.2 Solvent Formulation



Figure 35 Schematic representation of inkjet printing<sup>50</sup>

The optimization of morphology is crucial to high cell performance. This means that a suitable solvent formulation is crucial<sup>50</sup>. This is because the spreading and wetting of the liquid on the substrate and the drying behavior of the printed film are controlled by the solvent formulation and the temperature of the inkjet printing table<sup>50</sup>. In this case, a mixture of solvents with high and low boiling points [68% ortho-dichlorobenzene (o-DCB) and 32% 1,3,5-trimethylbenzene

(mesitylene)] allows production of inkjet printed OPVs with power conversion efficiency of  $\sim 3\%^{50}$ . During drying and subsequent annealing processes, the suggested solvent mixture leads to an optimal phase separation network of polymer donor and fullerene acceptor, and therefore strongly enhances the performance. o-DCB, with higher boiling point of  $180^{\circ}$ C, acts to prevent nozzle clogging and provides reliable jetting of the printhead<sup>50</sup>. Mesitylene, with lower boiling point of  $165^{\circ}$ C, acts to increase the drying rate of the solvent mixture, which is critical for optimal morphology control. The mean roughness of the active layer achieved is only 2.6nm<sup>50</sup>.

#### 4.5.3 Detailed Processing Flow

The basic process flow<sup>27</sup> to deposit these layers in an integrated roll-to-roll printing method, is shown as follows. With reference to Figure 36, the steps are numbered from 2.1 to 2.6. Specific printing methods for each step are unknown, however, although they must be compatible with the roll-to-roll processing.



Figure 36 Representation of the intermediate product, as the roll-to-roll processing is carried out from step 2.1 to step 2.6<sup>27</sup>

2.1 The plastic substrate is rolled out. It is possible that the plastic substrate is first deposited with a barrier layer (inorganic ceramics). The ITO electrode is then printed over a large area on the plastic substrate, possibly by slot-die printing.

2.2 Patterning: the electrode layer is then patterned using laser.

A photoresist or 'sacrificial layer' (labeled '33' in Figure 37) such as oil or wax, is then inkjetprinted onto the substrate to separate the individual cells. This is done so that these individual cells can then be connected in series. Another sacrificial layer '34' is printed onto the electrode layer. The second layer is chosen such that its removal does not damage the first sacrificial layer '33'.



Figure 37 Intermediate product layout. 32: plastic substrate. 31: semitransparent ITO electrode. 33 & 34: sacrificial layers. 35. Organic active layer of P3HT and PCBM<sup>27</sup>

2.3 This is followed by deposition of photoactive layer over large area by possibly slot-die printing.

2.4 Patterning: the second sacrificial layer '34' is removed by thermal evaporation, such that first sacrificial layer '33' still remains.

2.5 Metal electrode made of Al is deposited over large area, by vapor-deposition. The first sacrificial layer is now removed by UV exposure. The resulting structure is shown below.



Figure 38 Intermediate product layout after deposition of the metallic electrode layer and removal of all sacrificial layers<sup>27</sup>

2.6 The device is sealed with a barrier layer, and then rolled up in strip form. The thermal annealing process is possibly carried out before this where the device is heated at  $110^{\circ}$ C for a few seconds<sup>50</sup>.

An inkjet printing temperature of 40°C results in a uniform film and reliable printing process with respect to the spreading and formation of the film<sup>50</sup>. The steps are also controlled to prevent formation of pinholes in the layers, which will introduce shorts between the layers and degrade performance<sup>50</sup>.

# 5 Key Challenges for OPVs

One of the key motivations for OPVs is the potential to mass produce them using the roll-to-roll manufacturing techniques discussed above. It is hoped that the manufacturing costs will be rendered low enough to compensate the short-comings of OPVs and thus enable OPVs to compete with other TFPVs. Up to date, two key challenges confront the future promises of OPVs, namely, their low efficiency and short product lifetime. If remained unsolved, the promise of super low-cost OPVs permeating the market remains dubious.

# 5.1 Efficiency

Recent years have seen a lot of research efforts in pushing the record cell efficiency of OPVs. These track records have been tabulated as follows.

ACTIVE AREA/ CM <sup>2</sup>	EFFICIENCY	DEVELOPER AND CELL DETAILS	
Single junction cell:			
	6.77	Solarmer	
0.8	6.4 percent	Konarka Technologies - polymer: PCBM BHJ with one-year lifetime. Barrier layer with WVTR of 0.05 g/m²/day	
100?	6.31 percent	Solarmer – glass substrate, utilizing a novel semiconducting PTB1 material with 3 years lifetime	
	6.2 percent	UCSB and GIST	
	6.1 percent	UCSB, GIST and University of Laval researchers – PCDTBT/PC70BM cell with internal quantum efficiency of almost 100 percent.	
0.043	5.98 percent	Plextronics polymer P3HT:PCBM lab cell with lifetime of 3.3 years	
Tandem cell:			
	6.5 percent	UCSB and KIST derivatives of fullerene-P3HT in bulk heterojunction cell, with transparent titanium oxide TCO.	
	6.07 percent	Heliatek small molecule based cell	
	5.7 percent	University of Florida small molecule based cell - CuPc/C60:CuPc/PTCDI	
Module:			
	3.9 percent	Solarmer	
108	3.4 percent	Plextronics polymer P3HT:PCBM based submodule with lifetime of 3 years	

TABLE I-3: OPV TECHNOLOGY CHAMPIONS

Source: GTM Research

Figure 39 Highest efficiencies achieved, as of 2009<sup>2</sup>

However, when translated to industrial scale, the module efficiency of OPVs drops drastically to only 2-3%. The following chart illustrates the efficiency range of the OPV modules produced by Konarka using roll-to-roll processing.



Figure 40 Efficiency range of OPV modules produced by Konarka, as compared to other printing methods<sup>18</sup>

Achieving high efficiency is essential to widespread commercialization of OPVs, not only because of the need to meet power requirements of most applications, but also to reduce the levelized cost of production for OPVs, as compared to traditional Si PVs and other thin-film PVs.

The limits to the efficiency of organic solar cells are multi-fold. Firstly, there is an intrinsic tradeoff between absorption and exciton dissociation. Figure 41 illustrates the four main steps charge generation in an organic solar cell<sup>53</sup>. Step 1 involves the absorption of photons and the subsequent excitation of electrons from HOMO to LUMO, leading to formation of excitons. Step 2 involves the diffusion of excitons the acceptor/donor interface. Step 3 involves the dissociation of excitons at the interface, leading to formation of polarons (charges held by Coulombic attraction). Step 4 involves charge separation by external electric field and diffusion of charges towards the contacts.



Figure 41 Simplified steps of charge generation in organic solar cell: 1. photoexcitation 2.exciton diffusion 3. polaron pair formation and separation 4. charge diffusion towards the contacts<sup>53</sup>

The diffusion length of excitons is very short, approximately 10nm. However, the organic solar cells require at least 100nm for effective absorption of the photons<sup>53</sup>. This intrinsic competition requires a compromise. Indeed, the combined efficiencies of photon absorption (step 1) and exciton diffusion (step 2) are only ~10%, while polaron formation (step 3) and charge diffusion (step 4) occurs at nearly 100% efficiency in a planar heterojunction solar cell<sup>53</sup>. Hence, this compromise is a significant limit to OPV's efficiency.

Secondly, the organic compounds are bonded weakly together by van der Waals forces. Charge transport through the material is only possible at contacts where  $\pi$ -orbitals overlap<sup>53</sup>. In contrast to a crystalline material, the disordered nature of the organic compounds means that the overlap of electronic wavefunctions (van der Waals interactions) is limited<sup>62</sup> and hence the charge mobilities are very low, at 10<sup>-6</sup>-10<sup>-8</sup> cm<sup>2</sup>/Vs at room temperature<sup>54,58</sup>. This is in stark contrast to electron mobility of 1400 cm<sup>2</sup>/Vs and hole mobility of 450 cm<sup>2</sup>/Vs in silicon at room temperature<sup>55</sup>. In bulk heterojunction OPVs, this problem is particularly significant. Intermixing of acceptor and donor materials further reduces charge mobilities. This increases the probability of recombination of separated charges.

Thirdly, recombination of charges immediately following exciton dissociation is a major loss mechanism in heterojunction OPVs<sup>56</sup>. Excitons dissociate upon reaching the donor/acceptor interface, forming polarons. The polarons are localized electrons on acceptor molecules and localized holes on donor molecules, held together by Coulombic attraction at the interface. The polarons may annihilate via bimolecular recombination<sup>58</sup>.

Fourthly, most of the organic semiconductors are hole conductors and have an optical band gap around 2eV<sup>62</sup>. This limits the absorption range of the solar spectrum to a great extent. For instance, P3HT, one of the most studied semiconducting polymers, only absorbs photons with

energy less than 650nm<sup>66</sup>. This means that thermally excited, intrinsic charge carrier concentrations are rather low. It is thus hoped that low-band gap substitutes could be found. It proved rather difficult to develop suitable organic low-band gap materials. Several approaches have been tried: light-trapping design, substituting for lower-band gap acceptor material and using inorganic crystals to help absorption. However, these methods achieve limited success<sup>62</sup>.

Lastly, while laboratories produced record cell efficiencies of 6-8%, the actual module efficiency is significantly lower at 3-5%. This is as a result of much larger series resistance due to many cells series-connected together, and due to resistance of metallic contacts. Mass production necessarily introduces defects that are intentionally and easily avoided in laboratory conditions.

# 5.1.1 Theoretical Efficiency Limit for OPVs

For easy reference, a schematic diagram of the donor and acceptor energy levels is shown below.



Figure 42 schematic drawing of the donor and acceptor energy levels<sup>67</sup>

The maximum short-circuit current is determined by the smaller optical band gap of the smaller materials, and V<sub>oc</sub> is proportional to the difference between the HOMO level of the donor material and the LUMO level of the acceptor material<sup>67</sup>. This is because, for an efficient charge generation, energy offsets ( $\Delta E_{HOMO}$ ,  $\Delta E_{LUMO}$ ) greater than exciton binding energy are needed. This offset determines the ultimate device efficiency of BHJ OPVs. The maximum efficiency is not dependent on absolute HOMO and LUMO levels, but is solely a function of the smaller band gap and the energy offsets. The minimum offset is estimated to be 0.3eV. Assuming a semiconductor with optical bandgap of 1.4eV, at an external quantum efficiency of 65% and a fill factor of 65%, efficiencies of >10% are calculated to be possible. This is illustrated in Figure 40. This material design rule suggests the most promising strategy for high-efficiency OPVs is to optimize the LUMO-level difference.



Figure 43 Calculated efficiency under AM1.5 illumination for single-junction cells based on donor with a variable band gap and LUMO level, and an acceptor with a variable LUMO level<sup>67</sup>

Current attempts to improve the efficiency of OPVs are discussed in Section 6, which outlines the state-of-the-art approaches to overcome efficiency limitations.

### 5.2 Lifetime

Prolonging the lifetime of OPVs remains one of the key challenges today. The organic photoactive layer, when exposed to air or moisture, oxidizes rapidly. This results in degradation of photoactive and hence cell performance. Today, a typical OPV lifetime is around 1 to 3 years. This is dismal as compared to the usual 20-25 years lifetime warranty by Si and other thin-film technologies (except DSSCs). This significantly restricts the potential application of OPVs. The device thus needs to be encapsulated to increase lifetime. To ensure an effective isolation from air and moisture, high-barrier packaging films must be used. This will increase the cost of production.

Padinger et al. studied the degradation of a standard BHJ OPV cell in inert gas atmosphere, under the influence of increasing temperature<sup>69</sup>. Degradation of the cell is significant even at 31°C and in the dark, with current density dropping to 65% in just 60h. At elevated temperature of 57°C and in the dark, the current density dropped to merely 20% in 60h. Infra-red studies revealed defects and higher current density through these defects, indicating shunts in the active layer.

Kroon et al. also studied the stability of BHJ OPV cell under standard conditions<sup>70</sup>. The cell architecture comprises ITO/PEDOT/(MDMO-PPV/PCBM)/LiF/AI. The cell was encapsulated with SuryIn<sup>®</sup>/AI/PET foil. A second layer of epoxy glue was applied for further protection. As such, possible roles of water and oxygen from the atmosphere were eliminated. Three such cells were aged at open circuit: (a) in the dark at room temperature, (b) in the dark at 40°C, and (c) by continuous illumination at 50°C. Condition (a) produced no significant degradation after 460h of

ageing. (b) resulted in 30-50% decrease in efficiency after 460h. (c) resulted in almost complete degradation in 460h. Further investigations revealed that after light soaking at 50°C, photochemical degradation of the MDMO-PPV polymer occurred. Possible mechanisms of degradation were two-fold: (1) during operation, complex photo-chemical and oxidative process can occur in donor/acceptor blends and at electrode/organic material interface. (2) As discussed in Section 6.2, optimal nanomorphological control and stability are critical to long-term cell performance. Thermal agitation could result in coarsening or phase separation of the donor/acceptor phases, drastically degrading the cell performance. This is because charge transport from the active layer to the contacts has been compromised.

Neugebauer et al. studied the stability of BHJ OPV cell under the influence of  $xygen^{71}$ . When MDMO-PPV:PCBM cell, unencapsulated, was exposed to pure xygen for 12 hours,  $I_{SC}$  was found to have degraded, while  $V_{OC}$  remained constant. It was suggested that formation of insulating oxide layers had caused the degradation in current density. Encapsulating the device prolonged the lifetime to more than 150days.

Jorgensen et al. provided a detailed overview of recent literatures on possible degradation mechanisms in polymer solar cells<sup>73</sup>.



Figure 44 Schematic representation of possible degradation mechanisms in polymer solar cells<sup>73</sup>

In general, the degradation mechanisms can be categorized into chemical and physical degradations<sup>73</sup>. Chemical degradation mainly arises from interactions with oxygen and water, as well as interaction of electrode materials with active polymer layer. Small amount of oxygen/water can be introduced during fabrication steps or diffuse into the finished product from the atmosphere. Oxygen is readily activated in the presence of UV illumination in the presence of organic molecules. The oxide or peroxide formed actively attacks the organic materials. It was found that the current encapsulating materials, even those complex ones, are insufficient to complete stop the diffusion process. It only impedes the process. It was also found that oxygen diffused mainly through micro-pinholes formed in the metallic electrode, which were possibly formed during vapor deposition process.

Photo-oxidation of the polymers proves to be another significant degradation mechanism<sup>73</sup>. This is induced by the formation of singlet oxygen, through energy transfer from the photoexcited polymers to the adsorbed, ground-state oxygen molecules. The singlet oxygen is believed to react with the polymers.

The electrodes have also shown to undergo chemical degradation<sup>73</sup>. It was found that inclusion of moisture and impurities in the device during processing would enhance ionic conduction and accelerate corrosion of the ITO and Al electrodes. One suggestion is that Al, with its low work function, has high reductive power and forms Al-C bond with the polymers. Alternatively, anion radicals may have been formed due to electron transfer between Al and C. Both Al-C compounds and anion radicals are highly reactive with donor materials. PCBM are highly electronegative and hence are likely to reactive with the metal electrode to form other compounds. The ITO electrodes exhibit chemical degradation as a result of its mobile indium ions<sup>73</sup>. Indium ions were found to diffuse throughout all the layers. Hole-conducting PEDOT:SS layers were shown to absorb water and increase resistivity.

Physical degradation has not been carefully studied, according to the review<sup>73</sup>. In general, it has been discussed that the performance of the OPVs relies strongly on the spatial organization of the layers, the precise thickness tailored for optimal absorption and exciton diffusion, as well as controlled nanomorphology. It is then obvious that such strictly controlled parameters are not static and fixed throughout the lifetime of the OPVs. At elevated temperature, such features could be degraded or lost.

# 5.2.1 Possible Routes to Increase Lifetime

In view of the chemical degradation mechanisms studied, a few possible routes to prolong lifetime has been suggested<sup>73</sup>. One obvious route is to synthesize polymers that are more resistant to oxidation. For instance, P3HT has been found to be more oxidation-resistant than PPVs, due to a lack of easily oxidizeable vinylene group.

The roles of oxygen and moisture in the degradation of OPVs render it imperative to encapsulate the device. When impermeable glass substrate is used, the problem is alleviated. However, in flexible OPVs deposited on polymer substrates, diffusion of these entities present a big problem. Hence, it is clear that such products as Power Plastics, cannot have desired long lifetime unless the active polymers are oxidation-resistant, or additional barrier is deposited between ITO layer and the substrate. Multilayered barrier films were shown to significantly increase product lifetime. However, encapsulation proves to be limited in achieving long lifetime. When BHJ OPVs were rigidly encapsulated between a thick layer of Al and a glass substrate, and sealed with epoxy glue, the cell performance still degraded by 25% in a year's time. This proves the intrinsic chemical and physical degradation processes that are not related to atmospheric oxygen and water.

## 6 State of the Art

To overcome the challenge of low efficiency, the state of the art today focuses on mainly on materials research and morphology optimization, which allow efficiency of >5% to be reached for mixtures of poly-3hexylthiophene (P3HT) and pheny-C61-butyric acid methyl ester ( 60-PCBM).

### 6.1 Device Structure

Recent efforts to improve device structure have been limited, for several reasons. Firstly, there has been considerable drive towards achieving record cell efficiencies. This dictates small devices and high electrode conductivity<sup>1</sup>. The back electrode is usually an evaporated metal electrode. Hence, the limiting electrode naturally becomes the transparent front electrode. The best performing transparent electrode material that combines high transparency over a broad range of wavelength and high electrical conductivity is indium tin oxide (ITO). However, the need for ITO has severely limited the evolution of device geometry and processing techniques<sup>1</sup>.

### 6.1.1 Tandem Cells

The most significant step is undoubtedly the stacking of high and low band gap materials into a tandem cell, as shown below in Figure 46, with efficiency reported as  $6.5\%^1$ . While the maximum efficiency of a single cell has been calculated to be 10%, tandem cells are calculated to have a maximum, practical efficiency of 14%, assuming EQE of 65% and a FF of 65%. The  $\Delta E_{LUMO}$  between the acceptor and donor is assumed to be 0.3eV<sup>67</sup>.



Figure 45 calculated efficiencies of an OPV tandem cell versus the bandgap of top and bottom cells<sup>67</sup>.



Figure 46 Construct of OPV tandem cells, consisting of CuPc as donor material and PTCBI as acceptor materials<sup>61</sup>.

In the device shown in figure 46, two cells were stacked together<sup>61</sup>. Indium tin oxide (ITO) was used as the transparent anode, and silver Ag as the counter-electrode. Copper phthalocyanine (CuPc) was used as donor material, 3,4,9,10-perylene tetracarboxylic-bis-benzidazole (PTCBI) as the acceptor material. They were deposited by thermal deposition. The series connection allows a  $V_{oc}$  twice that of a single device. Upon photoexcitation, excitons are generated in both cells. After dissociation at the D/A interface, holes in the front PV drifts towards ITO, while electrons in the back PV drifts towards Ag electrode. To prevent charge accumulation, electrons from the font PV and holes from the back PV diffuse towards the nanoclusters of Ag between the cells, where they recombine. The advantage of such tandem cells is that each cell is thin enough (<L<sub>D</sub>) for more exciton to reach the D/A interface to contribute to photocurrent, while ensuring greater range of the solar spectrum is absorbed by the device. The device had an efficiency of 2.5% while that of a single cell was 1.1%<sup>61</sup>. This was attributed to optical field enhancement due to Plasmon generation on the Ag nanocluster surfaces<sup>61</sup>.

The first organic tandem cell published was based on small molecules, similar to the one shown in Figure 46. Small molecules are attractive because it eliminates the risk of any interference of underlying layers as a result of solvent diffusion. Secondly, the metallic recombination layer between the cells is usually thermally evaporated<sup>67</sup>. Solution-processed tandem cells were realized much later<sup>67</sup>. The most significant breakthrough was a solution-processed recombination layer, which allowed, for the first time, for the whole tandem device to be solution processed<sup>68</sup>. This means that production of such tandem cells is now compatible to roll-to-roll processing methods. This tandem cell used a TiOx sol-gel intermediate layers as shown in Figure 47. The transparent TiOx layer serves as electron transporting and collecting layer for the bottom cell (lower bandgap PCPDTBT:PCBM film) and provides a stable foundation for upper cell (P3HT:PC<sub>70</sub>BM)<sup>68</sup>. A high efficiency of 6.5% was achieved, although uncertified.



Figure 47 Structure of the tandem cells realised by Kim et al.<sup>58</sup>

In theory, multiple cells could be stacked together, such that individual cell absorbs a separate part of the solar spectrum. This is attractive as organic materials only absorb strongly in a narrow range of wavelengths, as explained in Section 3.1. However, such tandem cells pose new challenges that are inherent to multi-layer process: the underlying layers might be affected during solution processing of the upper layers. Various means, such as vacuum processing of the entire cells and using thermocleavable materials, pose more challenges such as costs, complexity and degradation in performance<sup>1</sup>. Similarly, the need for a hole transporting layer, consisting of poly-(ethylenedioxythiophene):polystyrenesulphonic acid (PEDOT:PSS), has also limited the choice in device geometry. In addition, each cell must absorb same number of photons. This limits the number of cells that can be stacked together to achieve higher efficiency<sup>53</sup>.

### 6.1.2 Hybrid Planar-Mixed Heterojunction Design

An extension of the bulk heterojunction cell design is the hybrid planar-mixed heterojunction (PM-HJ) architecture. The BHJ design greatly increases the interface area and ensures greater availability of interface for exciton diffusion, within the diffusion length of every exciton formation site<sup>59</sup>. However, the collection efficiency could be compromised if there is no continuous pathways for electron and hole conduction. The PM-HJ design aims to overcome this limitation.

Princeton group's concept of a 'hybrid', planar-mixed heterojunction (PM-HJ) cell



Figure 48 Schematic representation of a PM-HJ cell architecture, consisting of C60, CuPc and BCP layers<sup>60</sup>.

In this cell design, an intermediate mixed layer of acceptor and donor is sandwiched between two planar layers. Because the planar layers have a thickness less than the diffusion length  $L_D$  of excitons, excitons generated throughout the structure have a high probability of reaching a D/A interface<sup>59,60</sup>. The mixed layer should have a thickness less than the characteristic carrier collection length,  $L_C$ , so that separated charges can reach the planar layers efficiently. A high power conversion efficiency of (5.0±0.3)% was achieved- the highest value at the time of publication<sup>59,60</sup>.

### 6.2 Morphology Control

The use of various mixing and annealing methods to control the morphology of the active layer is another main active area of research.

The lifetime of the excitons is short. Therefore, it is necessary to optimize exciton diffusion to the donor-acceptor interface before the excitons undergo decay. As addressed before, the bulk heterojunction design overcomes this problem by intermixing acceptor and donor materials, thus increasing D/A interface area. However, this is limited by the need for continuous conducting pathways within the two phases for charge collection at the electrodes. This is because, upon dissociation, the electrons and holes must drift to the electrodes within their lifetime. This necessitates continuous, percolated pathways. These are achieved through morphology control. Ideally, the donor and acceptor phases should self-organize into nano-domains, with dimensions comparable to the exciton diffusion length.

The impact of nanoscale morphology control on cell efficiency was discovered in P3HT-fullerene BHJ cells. It was found that upon a mild thermal annealing at  $55^{\circ}$ C, efficiency was increased from 0.82% to 2.50%. Power conversion efficiencies of more than 5% were later reported through optimized thermal annealing temperature and duration<sup>5</sup>. This improved performance was due

to an overall enhancement of the absorption intensity and a red-shift of the optical absorption. This in turn was as a result of increased crystallization of P3HT, induced by increased molecular mobility during thermal annealing. The annealing process also leads to improved transport properties of the active layer, leading to a reduced series resistance and an increased fill factor. Transmission electron microscopy revealed the formation of long crystalline P3HT fibrils upon heating, leading to a nanoscale lateral phase separation and therefore larger donor-acceptor interface area for efficient charge generation and crystalline order for improved transport properties<sup>32</sup>. Optimal nanomorphology can also be promoted at room temperature, through the control of drying time of the active layer during wet solution processing – a method known as 'solvent annealing'<sup>5</sup>. Similar results are achieved by construction of ordered precursors in the solution use for film deposition, using appropriate additives<sup>5</sup>. Mixtures of solvents, in which the donor and acceptor materials have different solubility, induce the formation of ordered aggregates in solution and eventually in deposited film.



Figure 49 Effect of thermal annealing: increased crystallization of the donor material P3HT, leading to higher external quantum efficiency<sup>32</sup>

The significance of such phase separation and crystalline domain formation on charge transport properties is illustrated below, in figure 50. Poor mixing of donor and acceptor phases or molecules lead to few continuous pathways for electron and hole conduction. Such structure suffers from charge trapping and increased recombination.



Figure 50 Conduction in BHJ OPVs. (a) ideal interpenetrating donor and acceptor layers with lateral sizes no longer than exciton diffusion lengths. (b) Poorly structured mixing of donor and acceptor. (c) Improved mixing conditions with continuous pathways<sup>56</sup>.

Another evidence that nanomorphology is critical to BHJ OPVs is that when acceptor polymer is mixed with PCBM, increasing PCBM content improves cell performance<sup>62</sup>. This is because a higher PCBM and a minimum PCBM grain size may be necessary to ensure percolated pathways for electrons. However, beyond a certain optimal PCBM grain size, the performance starts to degrade as the interface area decreases. As such, optimal nanomorphology control and stability are crucial to long-term cell performance.

Nanomorphological control proves to be so significant to the performance of OPVs that a lot of research work has been carried out in this area. Alternative methods include solvent annealing, solvent vapor annealing as well as ordered bulk heterojunction cells. These methods can be summarized in the diagram below:



Figure 51 Various methods to optimize nanomorphology of photoactive layer in OPVs<sup>5</sup>

### 6.3 In Search of New Materials

Over the past decade, most of the research focuses on active layers made of regioregular poly(3-hexylthiophene) (P3HT) and PCBM<sup>5</sup>. Recent works have also focused on the search of new donor and acceptor material, in order to achieve breakthroughs in the power conversion efficiency of OPVs. A few main properties are targeted<sup>5,26</sup>:

- 1. It is noted that Coulombic attraction of the hole-electron pair in the exciton is relatively large. It is therefore necessary to achieve large energy offsets,  $\Delta E_{LUMO}$  and  $\Delta E_{HOMO}$  as shown in Figure 52, that are larger than the binding energy to avoid recombination.
- 2. To increase the fraction of the light absorbed, low band gap materials are desired, such that red and infra-red portions of the solar spectrum can be absorbed.
- 3. As it has been shown the thermodynamic limit of the open-circuit voltage  $V_{oc}$  is proportional to the difference, LUMO (acceptor) – HOMO (donor), a large energy gap of the donor materials is desired. The objective is then to identify a D/A pair that exhibits the highest  $V_{oc}$ . In addition, respective donor and acceptor material needs to (a) exhibit efficient photo-induced charge transfer, (b) cover a broad absorption spectrum, (c) have high charge carrier mobilities and lastly, (d) able to de-mix to create 20-30nm domains for optimal nanomorphology<sup>5</sup>.
- 4. The new materials should also have high solubility in solvents and excellent processability.



Figure 52 Energy diagram for OPVs<sup>5</sup>.

### 6.3.1 Donor Materials

For the polymers (the donor materials), which is responsible for the light harvesting, there has been a lot of focus on obtaining a low band gap such that as much of the available energy from the Sun is harvested. Many materials with low band gap have been prepared, the devices obtained thereof did not yield significant improvement as compared to the previous ones with larger band gap. In many cases, the low band gap polymers are copolymers made of alternating electron-rich and electron-poor building blocks<sup>5</sup>. However, the cell efficiency achieved was only comparable to that of established P3HT:PCBM cell. This was because to achieve lower band gap, it can be done by either moving the HOMO level towards the vacuum level or the LUMO level away from the vacuum level. However, the former action reduces the V<sub>oc</sub> and therefore the overall efficiency. The latter lowers the  $\Delta E_{LUMO}$ , which needs to be large enough to optimize exciton dissociation<sup>5</sup>. This is further complicated by the fact that LUMO level of fullerene is fairly difficult to raise<sup>5</sup>.

A recent breakthrough in the search of new donor material was achieved by J. Guo et. al<sup>66</sup>. The new low bandgap polymers are co-polymer with alternating ester-substituted thieo[3,4-b]thiophene and dialkoxyl benzodithiophene units, **PTB1**.



Figure 53 Structure of the new low-bandgap donor material, PTB1, and its absorption spectrum<sup>66</sup>.

OPV device based on this new donor material allows Solarmer, an OPV manufacturer, to achieve record efficiency of  $7.9\%^{33}$ . The PTB1:PCBM device achieved 30% higher photocurrent, while retaining similar V<sub>oc</sub> and fill factor as compared to the state-of-the-art P3HT:PCBM device<sup>33</sup>. This is because PTB1 films have a red-shifted absorption spectrum, broadening the overlap with the solar spectrum. It also has a higher peak absorption coefficient [ $7.5x10^4$  cm<sup>-1</sup> at 690nm as compared to  $6x10^4$  cm<sup>-1</sup> at 550nm for P3HT films]. Consequently, PTB1 films can harvest photons more effectively as compared to other polymers.

Investigations also revealed  $\pi$ -stacked polymer backbone planes of PTB1 were oriented parallel to the substrate surface, in contrast to the  $\pi$ -stacked polymer backbone planes oriented perpendicular to the substrate surface in regioregular P3HT:PCBM films. This gave rise to a higher charge carrier mobility, nearly twice as that in P3HT:PCBM films. From solar cell application point of view, this means better charge collection at the electrodes due to greater contact between the polymer backbone and the electrode surface. In addition, the photoinduced charge separation rate was twice as that in the annealed P3HT:PCBM films. These three factors yielded significantly higher efficiency.

Annealing the PTB1:PCBM films reduced the efficiency from 5.24% to 1.92%. TEM imaging revealed that annealing resulted in PCBM-enriched, large phase-separated domains, suggesting reduced interface boundaries between PTB1 donor and PCBM acceptor. This suggests further complexity for future search of new materials: each new material seems to have different behavior and hence requires another long progression of optimization.

A recent review by Dennler et. al highlights new classes of donor materials that exhibit potential carbazole-, and thiophene-, fluorene-, are: OPVs. These for high-efficiency cyclopentadithiophene-based co-polymers. These materials are said to have potential to achieve 7-10% efficiency, while already achieving ~6% efficiency at the time of publication (2009). Two of these are worth mentioning. The fluorene-based copolymers offer sufficiently large variability in the position of the HOMO/LUMO levels and are also low-bandgap materials. Device based on such materials achieved 5.4% efficiency, albeit uncertified<sup>67</sup>. Another class of new material is cyclopentadithiophene-based copolymers, with PCPDTBT as the most promising candidate of this class. This copolymer exhibits true low-band gap of 1.45eV, and high hole mobility. However, when blended with currently most effective acceptor PCBM, an unfavourable nanomorphology resulted, leading to short carrier lifetimes and high recombination rate. Intensive research into appropriate additives by Konarka Technologies produced an efficiency of 5.2%. However, PCPDTBT suffers from the drawback of high flying HOMO level, resulting in limited  $V_{\text{oc}}$  of 600-700mV when mixed with PCBM. Again, this highlights the complexity of new material research: a new donor necessarily means a need for a new complementary acceptor material and a new optimization route.

### 6.3.2 Acceptor Materials

The most successful acceptor materials are derivatives of PCBM, a derivative of fullerene. PCBM was first used in solar cell applications in 1995, and since then no better acceptor has been found, according to Dennler et. al<sup>67</sup>. Fullerene derivatives have unique advantages such as high electron affinity and high electron mobility that render them very good acceptor component in BHJ solar cells<sup>5</sup>. However, they are not the most ideal acceptor in terms of optical absorption range and HOMO/LUMO levels.

In spite of intensive research for better fullerene derivatives, there have been no derivatives that perform as well as 60-PCBM<sup>5</sup>. 60-PCBM shows an adequate solubility hat leads to desired nanomorphology. The exceptions are trimetallic nitride endohedral fullerenes, such as  $I_{h^-}$  Sc<sub>3</sub>N@C<sub>80</sub> and Lu<sub>3</sub>N@C<sub>80</sub>, which show potential for further increase in efficiency.

It was suggested that an optimized  $\Delta E_{LUMO}$ ~0.3eV, a power conversion efficiency of 10% could be achieved<sup>5,67</sup>. Hence there had been efforts to increase the LUMO level of the PCBM (acceptor), by adding electron-donating moieties to the PCBM phenyl ring. However, a dismal shift <100meV was achieved.

# 7 Key Patents

The IP landscape of the OPV industry is a rather peculiar one. Since the bulk heterojunction design was introduced in the early 1990s, the device structure and materials have not changed significantly<sup>1</sup>. This is mainly due to the fact changing either of the donor or acceptor materials necessitates the change of the other material, due to solution processing and energy level matching requirements. In addition, the need for ITO as the most ideal transparent electrode materials has significantly limited the evolution of device geometry and processing methods<sup>1</sup>.

Most of the recent patents disclose new tandem cell designs and synthesis of new low-bandgap materials, since these are the two main strategies to overcome low efficiencies in OPVs.

# 7.1 US Patent 4,164,431<sup>76</sup>

This patent was filed in 1979 by Ching W. Tang from Eastman Kodak Company. It laid claims to the invention of a multi-layered OPV as shown below.



Figure 54 Basic construct of a multilayered OPV designed by C. W. Tang<sup>76</sup>

This invention laid the foundation to modern OPVs. Previously, conventional OPVs consisted of a single organic layer sandwiched between two electrodes. Tang showed that the use of bilayered donor/acceptor elements created a rectifying behavior at the interface, which allowed effective charge separation, due to the difference in work functions of the donor/acceptor materials.

# 7.2 US Patent 2007/0295400A127

The patent, titled 'roll to roll manufacturing of organic solar modules, was filed on July 20, 2007, assigned by Konarka. It laid primary claims on the manufacturing process of solid-state organic photovoltaics using roll-to-roll printing methods. It also laid claims to the use of 'sacrificial layer', such as photoresist, oil or wax, which is the evaporated or removed to separate the individual cells in order to produce series-connected photovoltaics in a module. Various potential printing methods are covered, such as inkjet printing, slot-die printing and wet lithography.

The patent was filed before Konarka launched its large scale production of OPVs in late 2008. It was the first time disclosure of using roll-to-roll printing methods in the OPV industry, although

similar methods have already been used in other organic electronic industry. It was novel in achieving minimal damage to the photoactive layer throughout the process, by preventing contact between the photoactive layer and solution/vapor.

# 7.3 US Patent 2010/0032018A134

The patent, titled 'Novel Photoactive Polymer', was filed in 2009 by Konarka. The primary claims include the composition of the novel copolymer that can absorb photons in the range of IR. The copolymer comprise 3 monomer units: silacyclopenta-dithiophene, cyclopentathiophene, and benzothiadiazole. It also lays claims to the construction of a tandem cell using such a copolymer, with the upper cell absorbing in the blue and green range. High efficiency of more than 6% can be achieved.

This is a fairly significant patent, in view of the research into new low-bandgap donor materials. Konarka Technologies, being one of the leaders in the industry, had realized the potential of tandem cells in achieving desired efficiency of OPVs for commercialization. Such low-bandgap materials allow OPVs to absorb lights in red and infra-red regions of the solar spectrum and hence increase the overall efficiency. Unlike inorganic PVs, such as Si, tandem cell processing proves to be more feasible, since all the layers can be solution-processed, without the need for high-temperature vacuum deposition as for the case of inorganic PVs.

# 7.4 International Patent: PCT/US2009/04436435

The patent, titled 'Semiconducting Polymers', was filed in 2009 by the inventors Luping Yu and Yongye Liang of University of Chicago. However, the rights were later licensed to Solarmer Energy. It lays claims to the synthesis of the novel polymer dubbed as'PTB1' [synthesized via the Stille polycondensation between an ester substituted 2,5-dibromothieno[3,4-b]thiophene and dialkoxyl benzodithiophene distannane monomers] and the use of such a polymer and its conjugates in semiconducting devices, including photovoltaic cells.

This is a very significant patent, especially to Solarmer Energy who has acquired the licensing rights. Solarmer started off its business with its invention on translucent OPVs. However, the efficiencies achieved have been moderate at 3-4%. By acquiring the rights to this new donor polymer, Solarmer has since then achieved the highest cell efficiency in the industry, at 7.9%, significantly higher than that achieved by Konarka and other OPV suppliers. This gives Solarmer very strong competitive advantage over its competitors. It has aimed to launch commercial products by 2011.

### 7.5 US Patent 6,933,436 B272

The patent, titled 'Photovoltaic Cell', was filed on 23 Aug 2005 by Shaheen et al.



Figure 55 Construct of the novel OPV: 1. Substrate 2. ITO electrode 3. PEDOT 4. Photoactive layer 5. LiF or other insulating salt (a few nm) 6. Counterelectrode<sup>72</sup>

The patent presents one of the recent efforts to improve the efficiency of OPVs by improving charge collection efficiency at the electrode. The patent lays claims to the use of a very thin layer of insulating alkali halogenide, such as LiF, of 2-5nm thick. In conventional cells without this insulating layer, indirect reactions between the electrode surface and the active layer may lead significant resistance to charge transportation and collection at the electrode/active layer interface. The nm-thick layer of insulating salt suppresses such reaction. In addition, as such ultra-thin layer is necessarily non-continuous, charge carrier transportation across the layer is possible. As such, overall cell efficiency can be improved by 20%-25%, as compared to a similar cell without the insulating layer.

# 7.6 US Patent 2004/0113546 A174

The patent was filed in 2004 by Forrest et al. from Princeton University.



Figure 56 Detailed construct of a tandem cell based on organic molecules<sup>74</sup>

The patent lays claims to the fabrication method of organic tandem cells, comprising uniquely a recombination layer made of ultra-thin Ag layer, as well as exciton blocking layer (BCP). Forrest et al. demonstrated the significance of having such a recombination layer between the subcells, as discussed in Section 6.1.1.

### 7.7 US Patent 5,331,18375

This patent was filed in 1994 by Sariciftci et al. from University of California. It laid claims to the invention of heterojunction devices based on conjugated polymers and fullerene blends. Assynthesized conjugated polymers are usually p-type materials. While previous efforts tried to dope the polymer to render it n-type, such n-type materials are often environmentally unstable.

This invention laid claims to the unique use of fullerene, in particular C60 derivative, in creating a donor-polymer/acceptor-fullerene blend. This novel donor/acceptor mix exhibits photoinduced charge transfer to the fullerene, results in photoinduced spectral changes and leads to charge separation at the interface. Fullerene proved to be such effective acceptor material that it has been widely used as the acceptor material since then. This patent was followed by a publication years later in 1986. Only then did this bilayered design gain much attention.

### 7.8 US Patent 2005/0039792 A177

This patent was filed in 2005 by Takahashi et al. which laid claims to the invention of diffused heterojunction design.



Figure 57 Diffused heterojunction design<sup>77</sup>

In this novel design, a liquid film of donor material is first deposited, followed by second liquid film of acceptor material. Diffusion causes mingling of the two layers. While the mingled layer acts as active layer for charge separation, the unmingled parts act as efficient charge transporting route to the contacts. Thus, the problem of poor charge transporting properties in bulk heterojunction design is resolved.

#### 7.9 EP 1,855,323 A178



Figure 58 Construct of a tandem cell, with an oxide layer (3) separating the two subcells<sup>78</sup>

The patent was filed in 2005 by Kawano et. al. It laid claims to the invention of a novel processing method for organic tandem cells. In this method, an ultra-thin oxide layer is introduced between the two sub-layers. The transparent oxide layer, of 5-250nm thick, can be introduced by various evaporation growth methods, while the other organic layers can be solution processed. The oxide layer acts to prevent damages to the underlying subcell, when a second subcell is being deposited on top. This allows organic tandem cells to be solution processed and hence are compatible to roll-to-roll processing.

# 7.10 WO 2005/106965 A179

This patent was filed in 2005 by Dastoor et al. It laid claims to the invention of a multiple component OPV design. This represents another novel approach to solving the fundamental problem in OPVs- that the organic materials only absorb a limited range of the solar spectrum. This cell design incorporates an additional absorbing dye, which can be organic or inorganic, into the photoactive layer. The dye helps to absorb light in the red and infra-red region of the solar spectrum. However, such multiple component device may prove to be more difficult to process and its nanomorphology control more complex.

# 8 Market Analysis

# 8.1 General Applications of PVs

The first practical application of solar cells was developed for aerospace applications. The US satellite 'Vanguard' was equipped with dual power systems: chemical batteries and silicon solar cells<sup>26</sup>. The batteries failed after a week while the silicon solar cells continued to keep the satellite alive. Ever since, solar cells continue to play a crucial role in powering satellites and hence making telecommunications possible.

The first market for solar cells was developed in the early 1970s, when Exxon Corporation financed a significantly cheaper solar cell, by using lower grade silicon wafer and cheaper packaging materials. The price was brought down from \$100 per watt to \$20 per watt<sup>26</sup>. Currently, the price of silicon PVs is around \$4 per watt peak<sup>44</sup>.

Solar cells are now used in situations where people need electricity distant from power lines. Offshore oil rigs, for example, use solar powered warning lights and horns to prevent ships from running into them. I.T.O. Navaids company manufactures solar power LED buoys for marine navigation<sup>45</sup>. Many gas and oil fields far inland and distant from power lines also utilize solar cells to combat corrosion in piping<sup>26</sup>. Such stand-alone photovoltaic applications represent 90% of PV applications today<sup>26</sup>. They provide power when and where it is needed, without the need for utility grid. Batteries are used to store energy, so that the devices continue to operate during cloudy days and during the nights. Another main market for stand-alone photovoltaic systems is providing alternative electricity in rural areas, where people lack access to grid electricity. Instead of relying o costly and hazardous solutions to light their homes, such as kerosene lamps, the people can now use clean solar power for electrical lighting. Recently, a \$7.6M initiative by United Nations Environment Programme aimed to enable 18,000 households in Karnataka of India to access solar powered electricity to light their homes<sup>46</sup>. By 2007 alone, more than 2.5 million households in developing countries were receiving electricity from solar home systems<sup>26</sup>. China has been the largest market, with over 400,000 systems installed. This followed by Bangladesh, with 150,000 systems installed. Outside Asia, markets include Kenya, Mexico and Morocco<sup>26</sup>.

Directly connected systems do not utilize batteries. Solar modules produce DC current that is directly used to power DC motors<sup>26</sup>. The current and voltage vary with sunlight intensity. Such applications include solar powered water pumps used in Sahara<sup>46</sup>.

### 8.2 PV Market<sup>6</sup>

The 2008 Solar Technologies Market Report by DOE<sup>6</sup> shows that the global cumulative PV installation has increased exponentially since early 1990s. During the 1990s, the silicon-based PVs established a market as decentralized power sources and the market expanded at 15-20% annually<sup>26</sup>. Grid-connected applications dominate the market currently, primarily due to government incentives for grid-connected PVs in the top global markets. Such grid-

connected PV installations including rooftops, large PV power plants as well as PVs for distributed generation. Major markets are Germany, Spain and Italy. Those who install such PV systems on their roofs can sell the electricity back to their local utility during the day when there is sunlight, and buy back electricity at night – also known as Net Metering Arrangement<sup>26</sup>.



Figure 59 Global cumulative installed capacity<sup>26</sup>

Similar trend can be seen in US, as shown in the figure below.



Figure 60 Cumulative installed PV capacity in US<sup>26</sup>

The global PV production has seen a similar trend, with total production reaching 6.9 GW in 2008. The top producers are Europe, China and Japan. Most of the top 10 PV producers in 2008 remain as crystalline Si PV, as shown in the figure below.



Figure 61 Top global PV cell/module producers in 2008<sup>26</sup>



Figure 62 Top US PV cell/module producers in 2008<sup>26</sup>

For the first time, First Solar, a predominantly thin-film CdTe PV producer, entered the top 10 list, laying claim to the lowest manufacturing cost per module in the PV industry. In the US PV industry, thin-film PVs (TFPVs) remain the top producers. First Solar, CdTe PV producer, captured 36% of the market, followed by United Solar (a-Si) at 27%. Global Solar, CIGS producer, was also amongst the top 10 PV producers.

Thus, it can be seen that the potential market for TFPVs is very large. This is primarily due increasing efficiency and much lower manufacturing costs as compared to traditional Si solar cells. Given this context, the eventual market potential for OPVs is large, if they can compete successfully with other TFPVs. A market report on OPVs, by Nanomarkets<sup>25</sup>, projected a total market size of \$915M for OPVs and DSSCs by 2015, as shown below.



Figure 63 Potential OPV market size projected by Nanomarkets<sup>2</sup>

Another report by GTM Research<sup>2</sup> even projected 5MW OPV production capacity by 2010 and a huge jump to 1025 MW by 2012. Although the reliability and accuracy of such projections are yet verifiable, they certainly reflect the recent hype surrounding OPVs.

# 8.3 Competitors: Thin-film Photovoltaics (TFPVs)

Thus far, it has been shown the potential market for OPVs as a thin-film photovoltaic is large. Furthermore, roll-to-roll printing yields significant cost reduction and other advantages as compared to other PV types, including TFPVs. However, to gain any significant share of the PV market, OPVs must be able to compete with the main players in the thin-film PVs in the near term. Comparison with the Si solar cells does not yield any significance, since they are vastly different technologies at current stage and in the near term.

As compared to traditional wafer-based Si technologies, TFPVs yield comparable performance but with significant advantages in manufacturing<sup>27</sup>:

- Lower consumption of direct and indirect materials
- Independence from Si supply shortage
- Fewer and automated processing steps
- Potential to be utilize flexible substrates

There are four main competing thin film technologies currently. They are, namely, amorphous Si thin films (a-Si), CIGS thin films on metal foil, dye-sensitized solar cells and CdTe thin films. This section will provide a broad overview of these technologies.

### 8.3.1 Amorphous Silicon PV

Amorphous silicon alloy thin film technology absorbs light more efficiently than its crystalline (c-Si) counterpart. Thus a-Si TFPVs can be made up to 100 times thinner than that of c-Si, and thereby reducing the materials cost significantly<sup>27</sup>. The ability to deposit a-Si thin films on flexible stainless steel substrate using low-temperature vapor deposition, the product is relatively light-weight, flexible and durable. The energy payback time is also significantly shorter.

A significant development took place in 1997 when Uni-Solar developed a triple junction cell, as shown below.



Figure 64 Construct of a triple junction a-Si cell<sup>28</sup>

In the triple junction cell, different layers have different band gaps, utilizing band gap engineering between Si and Ge<sup>27</sup>. Ge is alloyed with Si in different compositions, such that the first layer has a band gap of ~1.8eV and absorbs blue photons. The middle layer has an optical gap of 1.6eV and absorbs green photons. The bottom layer has optical gap of 1.4eV and absorbs IR photons. A back reflector is also utilized to trap light. This construct enables absorption over larger wavelength range and thus higher efficiency, especially at low irradiation levels and under diffused light conditions. Roll-to-roll production methods are employed. United Solar Ovonic employs steel substrate, whereas Flexcell uses plastic substrate. The production process is highly automated and high throughput can be achieved. Currently, average a-Si cell efficiency stands at around 12% and has a life of 20 years.

### 8.3.2 CIGS PV

Since the mid-1970s, copper indium gallium diselenide (CIGS) has been at the forefront of TFPV industry with respect to cell efficiency<sup>26,29</sup>. CIGS solar cells and modules have achieved 19.5% and 13% efficiency respectively. The best efficiency could rival that of polycrystalline silicon solar cells.



Figure 65 CIGS thin-film PVs have been leading the TFPV industry in terms of efficiency<sup>29</sup>

A wide range of band gaps can be achieved in CIGS PVs, by changing the compositions of the compounds, rendering the required versatility to the solar cells. In addition, CIGS modules are extremely stable and have a lifetime of 25 years, as there is no intrinsic mechanism that damages cell performance<sup>26</sup>.



Figure 66 Basic Construct of a CIGS TFPV<sup>30</sup>

The basic construct of a CIGS cell is shown above. The structure is very similar to that of a CdTe thin-film PV. CIGS thin films are now also available on flexible substrate, manufactured by Global Solar Energy in the US. Roll-to-roll processing can be employed using CIGS ink, which is the proprietary right of Nanosolar<sup>26</sup>. Nanosolar employs AI substrate, onto which a layer of solar-absorbing nano-ink can be printed. The AI foil substrate is cheap and highly conductive. Thus it allows cost saving by doing away an expensive electrode layer found on non-conductive glass/plastic substrates.

However, despite its high performance, CIGS TFPVs face several main obstacles to large-scale production and commercialization. This is mainly due to complexity of the materials. The multi-

components used in the semiconducting layer necessitate complicated and slow manufacturing methods and leads to poorer quality control.

### 8.3.3 Dye-sensitized Solar Cell (DSSC)

DSSCs, or Gratzel cells, was invented in the 1990s. DSSCs entered the market in 2003<sup>26</sup>. They are low-weight, flexible and share the low cost of production using roll-to-roll manufacturing. Currently about 10% efficiency can be achieved. They work well in dim and diffuse light conditions. The panels can come in various colors to increase aesthetics. This allows potential applications in building-integrated PV (BIPV) domain. A schematic representation of DSSC is shown below.



Figure 67 Schematic representation of a DSSC<sup>31</sup>

The functional layer contains a mesoporous oxide layer of nanoparticles which have been sintered together to allow for electron conduction<sup>31</sup>. This layer typically consists of TiO<sub>2</sub>. A monolayer of organic dye is deposited on the nanoparticles, such that photon exciton of the dye results in electron transfer to the oxide. A series of regeneration by the electrolyte and the cathode restores the state of the dye and completes the circuit. The main problems associated with DSSCs are the use of liquid electrolyte and hence the need for more stringent packaging. Secondly, DSSCs suffer serious degradation issues over time.

### 8.3.4 CdTe PV

The energy bandgap of CdTe is 1.45eV, which is a good match to the solar spectrum and thus allows it to convert wider range of the solar spectrum, as compared to silicon (1.20eV). Thus, CdTe is able to achieve comparable efficiency with only about 1% of the semiconductor material requirement<sup>26</sup>.

The basic structure of a CdTe PV cell is shown as follows:



Figure 68 Basic construct of a CdTe TFPV<sup>30</sup>

As shown, the basic construct is very similar to that of an OPV, comprising a substrate, two electrodes and a semiconductor layer sandwiched in between. The main distinctions are the inorganic semiconductor layer is significantly thicker than OPV, and a glass substrate is used instead of plastic substrate. CdTe also absorbs low a diffuse light more efficiently and thus works better in cloudy weather than its Si counterparts.

The most common deposition methods for CdTe TFPVs involves acquiring commercial SnO<sub>2</sub>coated glass, followed by chemical bath deposition of CdS. Various methods can be used to deposit the CdTe thin film: closed-space sublimation (usually at laboratory level), vaportransport deposition (First Solar), or electrodeposition<sup>26</sup>. This is followed by CdCl<sub>2</sub> treatment, by eliminating small grains at grain boundaries and recombination centers<sup>13</sup>. The deposition process occurs at high temperature (~500°C). Currently, First Solar claims the lowest manufacturing cost in the PV industry at <\$1/Wp.

However, CdTe has its own limitations. There is an issue of interdiffusion at CdS/CdTe interface, which will degrade performance. Also, CdTe does not absorb short wavelength photons efficiently.

# 9 Supply Chain

A schematic representation of the supply chain for OPVs is shown below.



# 9.1 Suppliers: Materials, Chemicals & Equipment

The suppliers of semiconductor materials (i.e. conjugated polymers and fullerene derivatives) and chemicals are limited at current stage. This is because OPVs production has not been scaled up. It can be expected that, however, the semiconductor materials will be produced in-house by the OPVs manufacturers. This is because there are great incentives for them to protect the trade secrets related to the chemical composition and optimized processing parameters for the semiconductor materials. It is ultimately the material-specific IP and trade secrets that are going to provide them with the efficiency edge over their competitors. In addition, there are incentives to integrate the start-to-end materials processing to achieve high throughput and flexibility in changing processing parameters.

Other materials suppliers include those for electrical contacts, transparent conducting electrode, metal paste, sealants, protective covers, specialty materials (to stabilize the organic materials that can be easily oxidized when exposed to air), as well as packaging materials. Such materials will constitute bulk of the total materials costs. Also, for these materials, OPVs will likely share similar suppliers with other organic electronics and TFPVs manufacturers. It is envisioned that purchasing the materials from specialized suppliers will be more cost effective than producing them in-house. This is mainly because these materials bear no significant impact on the competitive advantage of the OPVs manufacturers.

As abovementioned, the capital equipment for OPV roll-to-roll printing can be modified from existing photographic film or newspaper printing facilities. Indeed this was Konarka's strategy to first commercialize its OPV, by purchasing the former Polaroid plant, a photographic film producer. However, there are currently very few commercially available printing inks for polymer solar cell, although inks optimized for PEDOT:PSS and silver pastes are available for flexible electronics<sup>1</sup>. This may entail potential supplier power during the initial commercialization of OPVs.

### 9.2 OPVs Manufacturers

Currently there are three main start-up companies that manufacture OPVs in the US. They are, namely, Konarka Technologies Inc., Plextronics and Solarmer. All three companies were spin-offs from universities. Solarmer specializes in OPV panel production and announced to launch product by 2011<sup>19</sup>. Konarka was founded in 2002 and started off by manufacturing DSSCs. Later,
it diversified into solid-state OPVs and was the first to demonstrate large-scale production of OPV using roll-to-roll printing, and claimed an annual production capacity of 1GW<sup>18</sup>. Its main proprietary product is the Power Plastic panels<sup>20</sup>. By partnering with various consumer product manufacturers, Konarka has released several consumer products, such as solar bag panel, solar charger, and portable battery charger for mobile phones<sup>20</sup>.



Figure 69 Examples of envisioned consumer products by Konarka<sup>20</sup>

Plextronics Inc. has a much more diversified portfolio. Its products and services range from OPVs, to other organic electronics, such as organic LEDs, processing inks and technologies related to organic electronics<sup>80</sup>. Unlike Konarka and Solarmer, Plextronics' core business is solution-processable inks for printed electronics. It focuses on polymer design and ink formulation.

Solarmer Energy Inc. currently holds the world's record efficiency for OPVs, at 7.9%, although the test conditions were debatable<sup>33</sup>. Solarmer's success is mainly derived from its ownership of rights over a novel donor material, PTB1. As compared to other state-of-the-art donor materials such as P3HT, PTB1 proves to have higher charge carrier mobility, results in higher charge separation rate and thus higher cell efficiency. Solarmer aims to achieve 10% efficiency by the end of 2010. Its main target applications are portable electronics, smart fabrics and building-integrated photovoltaics. Similar to Konarka, it claims to have produce lifetime of 1-3 years.

All three companies have substantial financing by venture capital and received significant research funding from the government. Konarka, for instance, has received over \$150M in funding<sup>21</sup>. At the same time, they are seeking active partnership with consumer product manufacturers and organic electronics producers, to promote their product. However, market penetration for these products seems limited currently<sup>21</sup>. This is mainly due to low module efficiency (2-5% for Konarka) and low lifetime (1-3 years).

Other organic electronics manufacturers, especially OLED producers, are also keen to enter OPV production<sup>22</sup>. This is because the roll-to-roll processing for OPVs is very similar to that of OLEDs. There is great potential synergy between the two producers. Thus, if the efficiency and lifetime of OPVs are improved to a baseline level for commercialization, there will be a significant and widespread increase in OPV suppliers.

#### 9.3 Consumer Products

The current niche market for OPVs is too small for OPV suppliers to produce consumer products themselves. Most of the products are portables and consumer products, released through

partnership with established consumer product manufacturers. Given the limitations of OPVs, it is unlikely that this business model will change significantly in the near term.

Some of the main consumer products are outdoor solar chargers, solar panel bags, and tents. Another potential application is mobile phone industry, where thin PVs have been integrated onto mobile phones, such as Sumsung's Blue Earth phone<sup>23</sup>. However, currently silicon PVs are used, mainly due to their high efficiency and therefore lower charging time. Another main customer now is the military, who is interested in fabric-integrated OPVs, OPV tents, and portable chargers etc<sup>4</sup>.



Figure 70 Sumsung's solar cell mobile phone, using Si  $\mathrm{PV}^{23}$ 

## **10 Cost Analysis**

Thus far, it has been shown that the seemingly potential market for OPVs is very large, given the exponential growth in thin-film PVs for the past decade. Furthermore, the relatively low materials costs and ability to mass produce OPVs using low-capital roll-to-roll printing methods seem to suggest potential large cost savings, which could compensate its lower efficiency and shorter lifetime as compared to other TFPVs. These are the arguments put forward by OPV enthusiasts who describe OPVs as 'third-generation thin film PVs'<sup>2</sup>. It is therefore crucial to compare and contrast OPVs with other TFPVs, on the basis of cost-efficiency-lifetime, through the means of a detailed cost modeling. This is to provide a quantitative assessment of the abovementioned arguments. If such arguments can be validated through quantitative assessment, the cost model will provide a baseline cost-efficiency-lifetime value that enables OPVs to compete successfully with other TFPVs.

### 10.1 First Solar: CdTe PV

This section also aims to compare the module costs of OPVs to TFPVs, using First Solar's CdTe PVs as a baseline for comparison. First Solar is chosen because it is currently the largest TFPV manufacturer in the US. It is therefore the largest competitor for OPV should it ever enter the market. Therefore, this section will first provide a detailed perspective on First Solar production and costs.

### 10.1.1 Corporate History

First Solar started its CdTe PV manufacturing with very modest production volume and efficiency, at less than 6MW and around 6% efficiency<sup>7</sup>. Since then, the production volume and module efficiency have increased steadily over the years. Data on its production capacity, cost per Wp, and efficiency have been compiled from various sources<sup>7,8,9,10</sup>, and tabulated as follows:

Year	Capacity / MW	Module Cost/Wp	Efficiency	Cost/m2
2004	10	\$2.94	6.75%	\$ 198.45
2005	25	\$1.59	9.01%	\$ 143.26
2006	99	\$1.40	9.46%	\$ 132.44
2007	308	\$1.23	10.30%	\$ 126.69
2008	716	\$1.08	10.80%	\$ 116.64
2009	1228	\$0.87	11.10%	\$ 96.57
2010	1282	\$0.81	11.30%	\$ 91.53

Table 2 First Solar's production capacity, module cost per watt, efficiency and cost per square meter since 2004



Figure 71 Recent trend of First Solar's production capacity and cost per Wp

As shown above, the module cost per Wp has decreased steadily over the years, and First Solar aims to achieve \$0.52-\$0.63/Wp by 2014. Such cost reduction has been achieved mainly through increased efficiency and production volume.

First Solar has been able to achieve high volume throughput using its proprietary production method, known as the High Rate Vapor Transport Deposition<sup>11,12</sup>.



Figure 72 Schematic representation of the high-rate vapor transport deposition method used by First Solar<sup>7</sup>

High quality soda-lime glass is first produced by pouring molten glass over a bath of molten tin. The ITO electrode is then sputtered onto the glass. The glass substrate is then fed into a vacuum deposition chamber, where a layer of CdTe is deposited on the glass, followed by a layer of CdS. The deposition occurs at a temperature range of 500°C to 600°C. The modules are then laser-scribed, metalized, and encapsulated in ethy vinyl acetate, and then another layer of glass. The entire production duration for a module is less than 2.5 hours<sup>8</sup>. Typical module efficiency stands at 11.1% currently and has a lifetime warranty of 25 years<sup>14</sup>. It hopes to achieve 15% efficiency by 2014.

## 10.2 Cost Model for First Solar<sup>17</sup>

A cost model was done for CdTe thin-film PV, based on data provided by First Solar. This was summarized as follows:

	First Solar Cost/m <sup>2</sup> @20MW	Comments
Materials (all)	\$48	(only \$5 are due to semiconductor); mostly packaging
Capital (all)	\$10	Semiconductor only about \$5
Labor	\$12	
Overhead	\$20	
Total	\$90	

Table 3 Cost structure of First Solar's CdTe PV

The estimated manufacturing cost of \$90 is significantly lower than the actual value of \$143.26/m<sup>2</sup> realized in 2005 at the production capacity of 25MW. However, the relative values revealed that CdTe manufacturing requires relatively low capital costs. Furthermore, the semiconductor material cost is relatively low at \$5. Most of the costs are due to packaging materials.

#### **10.3 Key Assumptions**

As OPVs are yet to be fully commercialized, and much of the related manufacturing details remain proprietary to their parent start-up companies, the detailed cost structure of OPVs is not publicly available. To get a first-order estimate of the manufacturing costs, the cost model assumes that the cost structure is similar to that of dye-sensitized solar cells (DSSC). This assumption is valid, because DSSCs are essentially hybrid OPVs. The main distinction is that DSSC utilizes liquid electrolyte for the photoactive layer and thus requires more stringent packaging<sup>15</sup>.

In addition, a fixed production capacity of 25MW is chosen. This is because most of the values available for DSSC and TFVPs, that can be applied to OPVs, occur in the range of 10-25MW. The calculated module cost for OPV can then be compared to that of First Solar, when its capacity was at 25MW. This allows a fair comparison between OPVs and CdTe based on cost-efficiency-lifetime matrix, without taking into account the impact of economies of scale.

Other key assumptions made include OPV module efficiency of 5% and 5-year lifetime. The capital cost is assumed to be \$20M. This value has the highest uncertainty, as it is not available in public domain. The \$20M value is the estimated cost for a thin-film start up company<sup>16</sup>. Other assumptions such as device parameters, materials costs, labour costs, accounting parameters, and overhead are detailed in the Appendix A.

#### **10.4 Results**

The summary of the manufacturing cost of OPV module is tabulated as follows:

Cost Summary		Cost / m <sup>2</sup>		
Materials	\$	25.45		
Capital	\$	8.22		
Labour	\$	7.14		
Overhead	\$	27.18		
Total Manufacturing Cost	\$	67.99		
Cell Yield	95%			
Total Manufacturing Cost with Cell Yield	\$	71.39		
Module Efficiency	5.00	%		
Module Yield	98%			
Module Cost	\$	1.46 / Wp		

Table 4 Cost summary of an OPV module

The module cost is calculated to be \$1.46/Wp. This is lower than that of First Solar's CdTe module at \$1.59, produced at 25MW capacity and having 9.01% efficiency. The lower manufacturing cost is deemed reasonable, because the OPVs have lower materials costs and capital costs than that of CdTe.

However, this value is derived based on cost-efficiency comparison. For a fair comparison with CdTe, the much shorter lifetime of OPVs must be taken into account. In another words, the module cost must be based on a cost-efficiency-lifetime comparison matrix.



A lifetime of 20 years is assumed for CdTe PV. Taking into account the replacement costs of OPVs that occurs every 5 years, and taking a net present value (NPV) of the total costs, the effective module cost is tabulated as follows. It is significantly higher than that of CdTe PV.

Table 5 Effective	module cost	of OPVs,	accounting for	replacement costs
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Cost Summary		Cost/m <sup>2</sup>		
Materials	\$	25.45		
Capital	\$	8.22		
Labour	\$	7.14		
Overhead	\$	27.18		
Total Manufacturing Cost	\$	67.99		
Cell Yield	0.95			
Total Manufacturing Cost with Cell Yield	\$	71.39		
Module Efficiency	5.00%	6		
Module Yield	0.98			
Module Cost		5/Wp		
Effective Module Cost		\$3.27/Wp		

## **10.5 Sensitivity Analysis**

### 10.5.1 Capital Costs

To assess the impact of the uncertainty of capital costs, the module costs and effective module costs for OPVs are calculated at various capital costs, from \$0-\$20M, as shown below. 5% efficiency and 5-year lifetime are assumed.



Figure 73 Module costs per Wp versus Captical Cost of OPVs

Thus, it can be seen that for the capital costs range assumed, the module cost per Wp remains lower than that of CdTe. However, taking into account the short lifetime of OPVs, the effective module cost per Wp remains significantly higher than that of CdTe, due to the replacements cost over the years.

#### 10.5.2 Efficiency

If the capital cost is assumed to be at a moderate value of \$5M, the efficiency value is varied from 4% to 15%. The result is shown as follows:



Figure 74 Sensitivity analysis on OPV module efficiency

It can be seen that the module cost is very sensitive to module efficiency. At low efficiency of 4% the difference between module cost and effective module cost is as high as \$2/Wp. Hence, in order for OPVs to compete with CdTe PVs, it has to overcome the barrier of low efficiency. At a capital cost of \$5M, a lifetime of 5 years and a production capacity of 25MW, OPVs have to achieve 11% efficiency in order to make up for its significantly shorter lifetime.

#### 10.5.3 Lifetime

If an efficiency of 10% and a capital cost of \$5M are assumed, the impact of lifetime on effective module cost can be shown as follows:

Lifetime	Module Cost	\$ 0.76
5 year	Effective Module Cost	\$ 1.71
10 year	Effective Module Cost*	\$ 1.06

Table 6 Impact of OPV lifetime on effective module cost

It can be seen that at 5-year lifetime, the effective module cost is still higher than \$1.59 of First Solar's CdTe PV. Only when OPVs achieve 10-year lifetime does it have cost advantage over CdTe PV. However, to achieve such longer lifetime, the additional costs due to more stringent packaging requirements are not taken into account in this model.

# **11 Business Strategy**

## **11.1 Key Considerations**

As discussed in details, low efficiency and short lifetime pose great challenges to the widespread commercialization of OPVs, despite its potential for ultra-low costs.

It seems that nanomorphology control cannot lead to significant efficiency improvement. In addition, it was shown that the highest efficiency that can be realistically achieved is 10% for single junction cells and 14% for tandem cells. The best strategies are then to find novel materials or/and to use tandem cell construct. However, efforts to find novel materials prove to be not easy. Tandem cells, then, seem to be a potential option to allow OPVs to compete with other TFPVs. While tandem cells are difficult to process in other TFPVs, as a result of high temperature deposition requirements, solution processing renders organic tandem cells more realistically achievable.

Recent research places greater emphasis on efficiency improvement than on stability improvement. Faiman<sup>81</sup> set realistic benchmarks for OPVs, based on the efficiency, stability and cost of inorganic PVs. The average module efficiency for inorganic PVs was found to be ~14% (higher than the calculated maximum efficiency of single-junction OPVs), while degradation rate was 1.5% per year (i.e. 20-25 years lifetime, as compared 1-3 years of OPVs). Faiman also rightly pointed out that the stability issue is more significant than the efficiency issue, as there will always be a market for low-cost, low-efficiency cells if they are stable. Current encapsulation methods, however, can only yield 1-3 year product lifetime.

Very likely, it will take at least another 5-10 years for OPVs to achieve 10% module efficiency, from current 3-5%. Assuming a capital cost of \$5M for 25MW production capacity, OPVs will only have potential cost advantage over CdTe if it achieves 10 year lifetime. Given the current focus on efficiency improvements and lack of potential methods to prolong lifetime of OPVs beyond 5 years, OPVs cannot compete with other TFPVs in the next 5-10 years.

### **11.2 Market Segmentation**



Figure 75 Main PV market segments

The flow chart above illustrates the key market segments for photovoltaics. It is clear from OPV's near-term limitations that it cannot compete successfully with TFPVs or ms-Si PV in applications where high power consumption or long lifetime is required. Therefore, it is foreseeable that OPVs will only have significant market value in niche applications where lower lifetime is expected for the consumer products. In such niche applications, the customers do not require a PV that can sustain more than 3-5 years. Therefore, the lifetime criterion can be taken out of the cost-efficiency-lifetime matrix. Under such circumstances, OPVs will have cost-efficiency advantage over TFPVs. However, even to achieve such moderate lifetime of 3-5 years and reasonable efficiency of 7-10%, as compared to current standards of 1-3 years and 5% efficiency, it will take several years to realize. Some of the potential applications are illustrated below.

# 11.2.1 Portable Consumer Products



Figure 76 Charger for mobile phones<sup>4</sup>



Figure 77 OPV bags to charge portable electronic devices<sup>4</sup>



Figure 78 OPV-power toys<sup>20</sup>

## 11.2.2 Smart Fabrics

Smart fabrics are textile materials integrated with OPV materials for additional functionality. Applications include: tents, clothing and military uniforms.



Figure 79 OPV tents<sup>33</sup>



Figure 80 OPV fibres woven into textiles, such as military uniform<sup>4</sup>

# 11.2.3 Building-Integrated PVs

It is hoped that the ability to dye the OPVs with different colours and with reasonable efficiency/lifetime, future OPVs can be used for its aesthetic appeal.



Figure 81 Shades outside restaurants, cafes etc<sup>20</sup>

#### **11.3 Forward Strategy**

Such niche applications include portables and consumer products, already mentioned above. However, even entering such niche market entails certain degree of risks. Firstly, niche applications mean that the potential market is small. Secondly, there is no reason why other TFPVs cannot compete in the same applications. In fact, for solar mobile phones, only ms-Si are used currently as they meet the power requirement. Thirdly, many of such potential niche applications necessitate some degree of change on consumer behavior. For instance, although Konarka has released its solar bag, it has not received popular reception up to date. This is most likely because the customers do not see a need for a bag that is more expensive and yet does not fulfill its function fully realistically. Solar chargers in general assume that the consumers will stay outdoor long enough for the electrical appliances to be charged. This is certainly not the case. Secondly, given the convenience, low costs and speed of charging using grid power, there is little reason for most consumers to change their behavior overnight.

Therefore, the sensible way forward for OPVs manufacturers is not to indulge in low-cost, large scale production in the near-term. The 'ultra-low cost' does not justify its shortfall of low efficiency and short lifetime in many applications. The phrase 'low cost production' is deceptive when applied to OPVs in absolute terms, without taking into account its efficiency and lifetime. It took First Solar nearly 15 years to reach an efficiency of 9% and production capacity of 25MW in 2005<sup>24</sup>. Even then, it did not face the serious issue of short lifetime. It is uncertain how long it will take for OPVs to even match up to the standards of CdTe in 2005. Thus, it is a wrong strategy to launch mass production without ascertaining consumer needs, and anticipating mass adoption based on low costs only. A more reasonable way forward is illustrated as follows:



Figure 82 Proposed roadmap for OPV commercialization

#### 11.3.1 2010-2015

In the near term, it is more realistic that OPVs will improve the module efficiency from current 2-3% to 5-7%. In addition, a slightly prolonged lifetime of 3 years is possible, if more expensive packaging and specialty chemicals (to stabilize the organics) are used. Hence, it is more likely that OPVs will strive to achieve significant consumer adoption in the niche market they have been targeting, anchoring on such incremental improvements in device performance. To generate revenue and stay on business, it may be necessary for them to diversify their business while focusing on OPV R&D. Possible diversification include partnership with other organic electronics producers, catering special needs of the military (OPVs for tents and solar fabrics) and specialties in inks and organic compounds processing for OPVs and organic electronics. At the same time, the need to improve device performance demands novel materials and cell configurations, and thus sees closer corporations between OPVs suppliers and research institutions, such as universities, corporate and national research laboratories.

#### 11.3.2 2015-2020

It may be possible to achieve 10% module efficiency and 5-7 years of lifetime in the longer term. When such parameters are achieved, then OPVs will have significant cost advantage over TFPVs in niche applications where the consumers do not expect product lifetime more than 3-5 years. Such products include solar cells for mobile phones, laptops, indoor OPV panels for recharging purposes, commercial umbrellas that can charge laptops for customers etc. In such cases, the suppliers will launch mass production, to drive the costs down further. The corporate value could increase further by multiple injections across the supply chain, instead of just supplying

OPV modules. Examples include organic compound designing, for OPVs, specialty chemicals, organic electronic packaging, commercial inks for organic printing etc.

#### 11.3.3 2020 and beyond

Long term R&D may yield >10% efficiency and 10-year lifetime for OPVs. Based on the sensitivity analysis, under such circumstances, OPVs may have significant cost-efficiency-lifetime advantage over TFPVs, assuming that TFPVs will only improve moderately over the years to around 15% efficiency and further cost reduction due to mass production is limited. Under such circumstances, OPVs application will spill over to off-grid and on-grid domains. Its market share will increase significantly. OPVs manufacturers could increase its value to the supply chain by launching their own consumer products, if it is cost-effective. However, significant competitions amongst the OPVs manufacturers will start limit the profit margins.

## **12 Conclusion**

Organic photovoltaics will have great potential to dominate the market and expand the PV market share, if they can achieve significant improvements on their efficiency and lifetime. However, till then, it is unlikely that OPVs will gain significant market adoption in the next 5-10 years. It is also unlikely that OPVs can compete with other thin-film photovoltaics, in terms of cost-efficiency-lifetime comparison matrix. Low cost of production does not give OPVs sufficient advantage to overcome its other limitations. Hence, in the near-term, OPVs should not go into large-volume production. In addition, it is necessary for OPVs suppliers to diversify their business, increase partnership with other organic electronics and research institutions to address the dire need for novel OPV materials and design.

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## Appendix A

# Assumptions in the cost model

Device Parameters		
thickness	0.000001	m
area	1	m2
volume of active material	0.000001	m2
	1	cm3
mass of active material	1	g/cm2
	1	g/cm2
material utilization	75%	
material required	1.33	g/cm2

<b>Production Capacity</b>	25	MW	
Module Efficiency	5.00%		
Solar Resource	1000	W/m2	
Area of PV required	500,000	m2	

Matariala Casta			
Waterials Costs			
Semiconductor Material			
	C-60	\$ 1.00	per g
	CuPc	\$ 1.00	per g
	SnPc	\$ 0.50	per g
		\$ 2.50	per g
	Total	\$ 3.33	per m2
Electrical Interconnections		\$ 3.42	per m2
Elexible Substrate with ITO			
	Flexible Plastic Substrate	\$ 5.00	per m2
	ITO	\$ 2.40	per m2
	Coating Substrate with ITO	\$ 0.50	per m2
	Total	\$ 7.90	
Protective Cover		\$ 2.90	per m2
Sealant		\$ 2.90	per m2
Packaging Material		\$ 3.00	per m2
Specialty Materials		\$ 2.00	per m2
Total		\$ 25.45	per m2

Processes			
<b>Capital Cost</b>			
	Capital Equipment Cost	\$	20,000,000
	Interest Rate	10%	ó
	No. of Years of Amortization	7	
	Annuity	\$	4,108,110
	Capital Cost per m2	\$	8.22
Labour			
	no of shifts per day	3	
	no of operator per shift	25	
	Total no of operators	75	
	no of hours per shift	8	
	Wage Rate	\$	17.00
	Total Wage Per Year	\$	3,570,000.00
	Average Labour Cost	\$	7.14

	1		
Rent and Overhead			
Facilities (Rent)	\$	17.40	per m2
Utilities	\$	3.27	per m2
Maintenance (4% of Capital Cost)	\$	0.33	per m2
Miscellaneous (5% of manufacturing Cost)	\$	3.09	per m2
Customer Warranty (5% of total manufacturing cost)	\$	3.09	per m2
Total	\$	27.18	per m2