

Organic Solar Cells: A Review

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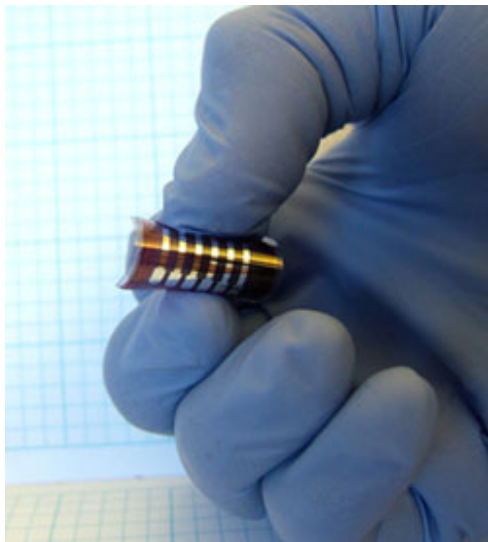


Figure 1: A flexible organic solar cell
made in Dr. M. McGehee's lab at Stanford

Submitted for partial fulfillment of EE 293a,
taken fall 2006 with Dr. Aldo da Rosa

Table of Contents

Introduction	3
Operation Principles	4
General operation principles for organic solar cells.....	4
Current Challenges	6
Current Collection and Transport.....	6
Cost effective processing.....	6
Device Design and Fabrication.....	7
Organic Solar Cell Design Overview.....	7
Current Fabrication Techniques.....	8
Applications.....	8
Economic Considerations.....	9
Solar Cells, generally.....	9
Organic Solar Cells.....	10
Final Remarks.....	11
References.....	12

Introduction

Enthusiasm for solar cell technology originates from its superior viability as a clean energy source. Society is finally starting to acknowledge the environmental damage inflicted by the current usage of nonrenewable energy sources. Former vice president Al Gore, who has been leading a global warming awareness campaign, has been nominated for the 2007 Nobel Peace Prize. The knowledge that energy needs will only increase leads researchers and investors to explore innovative, environmentally friendly energy sources such as windturbines, biogas, and solar cells. Nanotechnology-based "cleantech," as the science of environmentally responsible energy sources has been dubbed, is expected to be one of the largest sinks for venture capital in the coming decade, according to Oliver Morton, Nature's chief news and features editor [Morton].

Solar cells are an exciting cleantech technology. Analyses of cleantech efforts to reduce or eliminate use of nonrenewable energy sources such as coal and oil indicate that photovoltaic energy converters are more reasonable than windturbines and biofuels. Unlike windturbines, solar cells employ no moving parts. Such solid-state devices are noiseless, don't interfere with flight paths as wind turbines do, and require almost no maintenance once installed. To power society in the future, biofuels would require more arable land than is currently available (unless far more efficient fuel-driven technologies are invented). The lower power density of biofuels requires three to four orders of magnitude more land area than oil fields for equal power production. The environmental and socioeconomic damage from displacement of natural crops with biofuel crops and fertilizer runoff pollution could be worse than the consequences of using nonrenewable energy. The most productive solar alternative is Brazilian ethanol from sugar cane, at $0.45\text{W}/\text{m}^2$. Corn ethanol only has a power density of only $0.22\text{W}/\text{m}^2$. To provide the amount of power the United States consumed in the beginning of this century for fueled transportation alone, an area of land equal to all of the United States' arable land would have to be replaced with sugar cane, or twice the United States' total arable land would have to be utilized for corn ethanol production (12 Gha). Of course, the growing conditions in the U.S. aren't as fertile and insolated as in Brazil; biofuel crops would be grown around equator zones. Based on lessons learned in the past, it is best to supply our energy from within the borders of our countries to reduce such a fundamental dependency on other nations. If the U.S. relied instead on solar energy, without disturbing current arable land, unutilized insolated areas such as roof tops and deserts could provide all the U.S.'s power needs. Global power consumption by the year 2050 is estimated to be 30TW; the sun provides earth with 89,000TW at the surface. All the U.S.'s energy needs could be provided by installing the common commercial 15% efficient solar cells into the unused desert areas of Nevada.

By these figures, one might deduce that the ultimate advantage of solar cells amongst other cleantech options is that solar energy is solely capable of providing all human society's energy needs (if we are to eventually convert to 100% renewable energy). Windturbines and biofuels could not provide global energy needs without serious environmental impact (such as displacing all of our cities and arable land with biofuel crops). Solar cells remain too expensive to commercially replace other technologies except in the cases where they are greatly subsidized (as in California). Solar cells today span three generations of technology. First generation solar cells are those seen as flat silicon panels on rooftops; these comprise 87% of the current solar cell market today. First generation solar cells operate using a single P-N junction. Second generation solar

cells operate using multiple (tandem) P-N junctions that cover a wider spectrum for better efficiencies; but because of the high cost of these additional photolithographic steps, the first generation technology remains more practical when weighing both efficiency and cost. Finally, everything else that does not rely on P-N junctions is (at least for the time being) considered third generation solar cell technology. According to [Wikipedia], this includes photoelectrochemical cells, polymer cells, and nanocrystalline material cells. All three could describe organic solar cells.

Having set the case for solar cells, I now postulate that amongst solar cell technologies, organic solar cells (a member of the 3rd generation solar cell class) have the potential to supersede the current inorganic semiconductor solar cells, and hence become the most important source of power for society by the end of this century. This may seem counterintuitive since the best production-scale organic solar cell ($\eta=3\%$) is still four times less efficient than the cost-effective inorganic cell used for 87% of rooftop applications ($\eta=12\%$). The best performer of current solar cell technology, rated at nearly 41% efficiency, is based on first-generation, photolithography-intensive, cleanroom-fabricated inorganic semiconductor heterostructures. These heterostructures are made from silicon to take advantage of the existing silicon-CMOS infrastructure for cost savings and throughput. Silicon, being the second most abundant element (after oxygen) in the earth's crust, would seem to be the ideal material for solar cells; however, the electronic grade silicon wafer substrate necessary for fabricating inorganic solar cells is expensive. The optimism and investment in organic materials research is due to the unique properties of organic materials. These include the potential for self-assembling nanostructures, resulting in cost effective fabrication and high structural efficiency, and the ability to be fabricated in thin, flexible films. Organic films can be printed onto flexible sheet rolls. This allows organic solar cells, unlike the current inorganic solar cells, to be commercially printed without need for expensive cleanroom environments and lithographic tools. Additionally, such thin films require less material. In addition to reducing material costs, this ensures that there is enough Indium (In) and other rarer materials to meet the world's energy needs using organic solar cells. (As will be discussed in the Device Design and Fabrication section, Indium is one of the most common organic solar cell ingredients.) For perspective, Indium is about as abundant as silver. Researchers at Stanford's February 24th Solar Cell workshop working with inorganics claim that Indium is in too short of a supply to build enough organic solar cells to meet society's energy needs. Researchers working with organics claim that there is enough Indium provided we use thin film or alternate organic cell technologies.

The scope of this paper will attempt to describe organic solar cells in terms of operational principles, device fabrication, examples of more promising devices, and more practical economic considerations.

Operation Principles

General operation principles for organic solar cells

The following operation principles apply to most organic solar cells. Photons (sunlight) must be absorbed in the active region of the device. Other regions of the device facing insolation must be transparent; this can be accomplished by use of a transparent substrate (usually glass) and a diffuse cathode matrix to allow sunlight to penetrate into the active region. The external quantum efficiency, η_{EQE} (1), is this ability to couple light

into the active region, and is affected by the reflectivity of the layers adjacent to the active region R and the internal quantum efficiency η_{IQE} .

$$\eta_{EQE} = (1 - R)\eta_{IQE} \quad (1)$$

The active region must efficiently absorb photons (maximize absorption efficiency, η_A), generating photocurrent when an electron-hole exciton pair are broken apart between P and N type materials (exciton dissociation efficiency = η_{CT}). The diffusion lengths of excitons are short, on the order of 10-30 nanometers. Therefore it is important for the bulk heterostructure material to consist of nanostructures that, in addition to increasing the surface area between P and N regions, provide conductive channels every 10-30 nanometers (maximizing exciton diffusion efficiency, η_{ED} , to a dissociation site). This can be accomplished, for example, by extremely conductive nanorods (increasing charge collection efficiency, η_{CC}). With bandgap matching coatings, nanorods can provide both current transport mechanism and donor material interfacing with an acceptor fill matrix.

The cumulative internal quantum efficiency of the solar cell, η_{IQE} , (2) is given in terms of the absorption efficiency of light within the active region of the solar cell (η_A), the exciton diffusion efficiency to a dissociation site (η_{ED}), the charge transfer efficiency (efficiency of dissociation of an exciton into a free electron and hole pair, η_{CT}), and the charge collection efficiency (η_{CC}).

$$\eta_{IQE} = \eta_A \eta_{ED} \eta_{CT} \eta_{CC} \quad (2)$$

The power conversion efficiency, η_P (3), is given by the fill factor (FF), open circuit voltage (V_{OC}), the short circuit current density (I_{SC}), and the incident power density (P_{INC}).

$$\eta_P = \frac{V_{OC} J_{SC} FF}{P_{INC}} \quad (3)$$

A process called “photodoping” can enhance the charge transfer efficiency. Molecules such as buckminsterfullerene (a.k.a. buckyballs/ C_{60}) increase photocurrent with increasing light intensity (Fig.2). This enhancement is best used with light concentrators to maximize this effect while reducing expensive chip area.

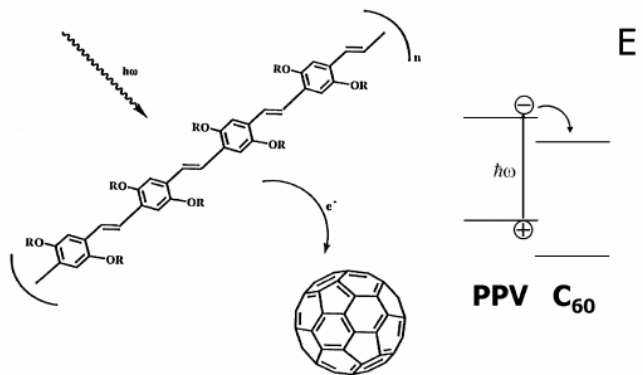


FIG. 2. Illustration of the photoinduced charge transfer (left) with a sketch of the energy level scheme (right). After excitation in the PPV polymer, the electron is transferred to the C_{60} due to its higher electron affinity. J. Mater. Res., Vol. 19, No. 7, Jul 2004

Current Challenges

It was stated earlier that organic solar cell technology could supersede first and second generation solar cells (inorganic/ PN junction based technologies). However, in the current state, inorganic technology outperforms organics; the best efficiencies for commercial production organic and inorganic cells are 3% and 12%, respectively. In fact, organic solar cell technology was dormant for the first 30 years; only with recent advances during the last decade in nanoscience has it become interesting. Fundamentally, organics make excellent absorbers (usually two orders of magnitude more absorption than inorganic counterparts) that are hindered by poor current transport. Therefore, the most critical research advances will be concerning current transport and cost effective fabrication before organic solar cells become competitive functionally and economically.

Current Collection and Transport

Current transport is the primary weakness of organic materials. New nanostructures are in development to alleviate this. As described in the Operation Principles section, current transport relies on organic bonds. This can be enhanced by “photodoping” with molecules that increase photocurrent with increasing light intensity. These are best used with light concentrators to maximize this effect while reducing expensive chip area. Additionally, the splitting of excitons by incident light to generate current (electron/hole pairs split into independent current carriers) is the primary mechanism of energy transfer from light to electricity. The excitons must be harvested within a diffusion length or they will recombine before any useful current can be extracted. These diffusion lengths are extremely short and so devices must have an exciton generation site, which can be formed by the interface between a p and n type material, every ten or twenty nanometers. Such a low-dimensional material interface structure is critical to current collection efficiency. Researchers are using nanostructured materials to accomplish such high surface area between P and N type bulk heterojunctions.

In addition to current collection, high-surface area bulk heterojunctions can be tailored to enhance conduction of the collected current to device anodes/cathodes. Conduction in organic materials relies is limited by distributed pi bonds. To increase transport to the anode and cathode, inherently conductive nanostructures are being explored, such as nanorods. These aligned structures conduct excellently, decreasing resistive losses and boosting efficiency. Disordered structures such as nanoporous materials provide less direct and therefore more resistive current paths, but can be filled with complementary polymers to achieve high-surface area P-N heterojunctions without as much processing complexity.

Cost effective processing

Silicon-based CMOS has garnered over 90% percent of today’s semiconductor market (up from 50% in 1980) because although electronic-grade silicon and other materials are very expensive, monolithically integrated device processing has become refined and high-throughput. There is enormous infrastructure build upon silicon-CMOS processing, including chip fabrication plants, design tools, and research. Organic solar cell devices generally cannot take advantage of the cost and throughput advantages of this mainstream fabrication. Organic solar cells often require materials incompatible with silicon-CMOS processing. These materials are either banned in silicon-CMOS processing areas due to threat of contamination, or require unique processing due to

nanostructure designs. This usually includes processing steps to fabricate and incorporate nanostructures such as nanorods, nanoporous materials, or nanocrystals. Screen printing methods promise to fulfill both high-volume production and cost requirements (see next section).

Device Design and Fabrication

Organic Solar Cell Design Overview

Organic solar cells can be generally described in five layers as shown in Fig. 3. The first layer, the solar cell substrate, can be made of a heat-resistant transparent substrate such as glass, or flexible materials such as polyester.

Whereas conventional solar cells allow light to enter through a conductive grid anode on the opposite end as the substrate, organic devices generally admit light through a transparent substrate top layer coated with Indium Tin Oxide (ITO), for example, which forms the cathode and second layer. ITO is a commercially available glass coating and is widely used as the conductive electrode second layer of organic solar cells because of its transparency in thin films and carrier injection properties that can be enhanced using film treatments. ITO allows for carrier injection into the organic layer of the solar cell. After deposition, oxygen plasma treatment using RF or microwave sources is one of the most effective methods to effectively increase the ITO work function [Hashimoto], which allows an increase in hole injection between ITO and the hole transport layer (HTL). One of the challenges for researchers today is to quantitatively understand the effect of the plasma electrons and oxygen ions affect on the electrode-organic layer interface electronic properties.

Between the cathode material and active layer, a layer of poly (3, 4-ethylenedioxythiophene)-poly (styrenesulfonate) (PEDOT-PSS) can be deposited to form the third layer. PEDOT-PSS forms a hole transporting, exciton-blocking, and smoothing layer. Additionally it prevents oxygen and cathode material from diffusing into the active region. Any unwanted material in the active region could form device-degrading trap sites. The fourth layer of organic solar cells is a donor/acceptor-blend active layer. A dye-sensitized solar cell (DSSC) could be chosen to exemplify organic solar cell active layer structure because it is currently the most efficient [Nazeeruddin] and stable excitonic solar cell. Other types of organic solar cells, including organic and hybrid organic-inorganic types, use the same general device structure but with a different active layer scheme. Active layers usually employ some sort of nanomaterial to maximize surface area between donor and acceptor regions; nanoporous materials, nanocrystals, and aligned nanorods are all variations to suit this purpose. All variations

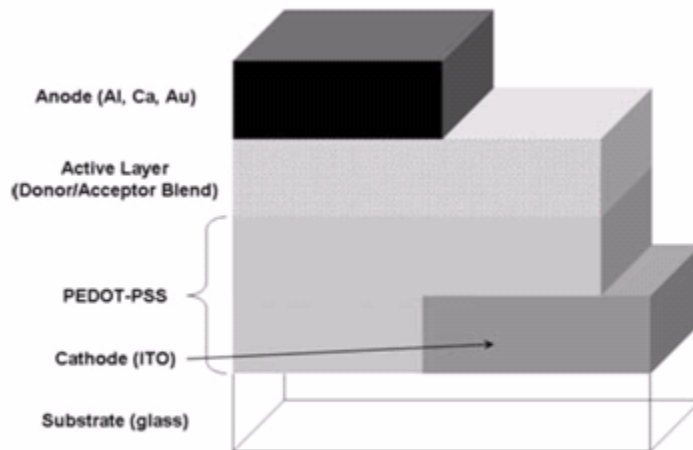


Figure 3: General organic solar cell structure

have been attempted by many researchers and can be tuned for different enhancements. After this layer, the anodic fifth layer is deposited. The anode can be made from any conducting material; aluminum, gold, silver, and even calcium can be employed. In practice, a layer of lithium fluoride can serve as a protective barrier between the active and anodic layers.

Current Fabrication Techniques

The most economically promising way to fabricate organic solar cells is screen printing. Silicon Valley startup companies such as Nanosolar have popularized this technique by demonstrating the high throughput and cost savings benefits of printing devices roll-to-roll. Screen printing (Fig.4) utilizes wetprocessing rather than traditional deposition/photolithography. Other wetprocessing techniques include any solution processing. Organic molecules, monomers or polymers, must often be processed in solvent. Unlike other wetprocessing techniques such as doctor-blading, inkjet printing, and spin-coating, screenprinting allows cost savings by tapping into existing printing infrastructure. Wetprocessing is important to organic treatment because the active layers of organic devices are usually made of large molecules that cannot be deposited by vacuum deposition (as in traditional monolithically fabricated solar cell production). However, this is not a disadvantage. Unlike silicon-CMOS processing that is used to make the existing, inorganic semiconductor solar cells, organic solar cells which can be fabricated by printing techniques do not require expensive vacuum-environments, depositions, various lithography steps, high heat environments, and other energy-expensive steps. The reduced amount of energy necessary to produce inorganic solar cells decreases the amount of time inorganic solar cells must be used before installation costs and production energy usages are recouped.

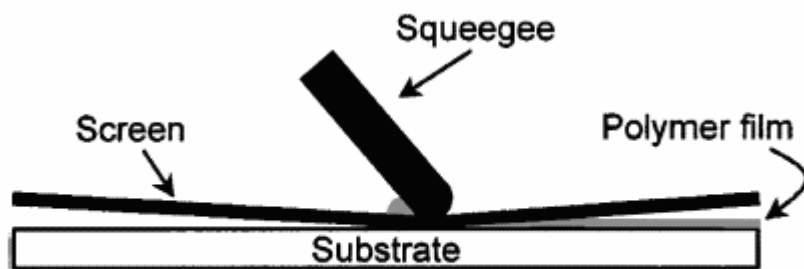


Figure 4: Screen printing

Applications

Flexible screen printed devices can be laid over large surface areas. They are durable and because they are printed in mass using cheaper materials and processing, low efficiency could be compensated for by inexpensively increasing light collection area.

Lithographically produced devices can be used with concentrators to increase efficiency. Concentrators have a twofold function: to reduce the necessary area of solar cells, which are far more expensive than plastic light condensers, and to boost efficiency (Fig.5). Efficiency of organic solar cells can be boosted by increasing light intensity with condensers due to a photodoping effect. For example, buckminsterfullerene (C_{60}), mixed with other organic materials, will increase photoconductivity when illuminated. The more

concentrated the light that reaches the solar cell, the better the quantum efficiency due to this effect. Therefore, concentrators can help reduce the overall cost and increase efficiency (and can also be applied to inorganic solar cells).

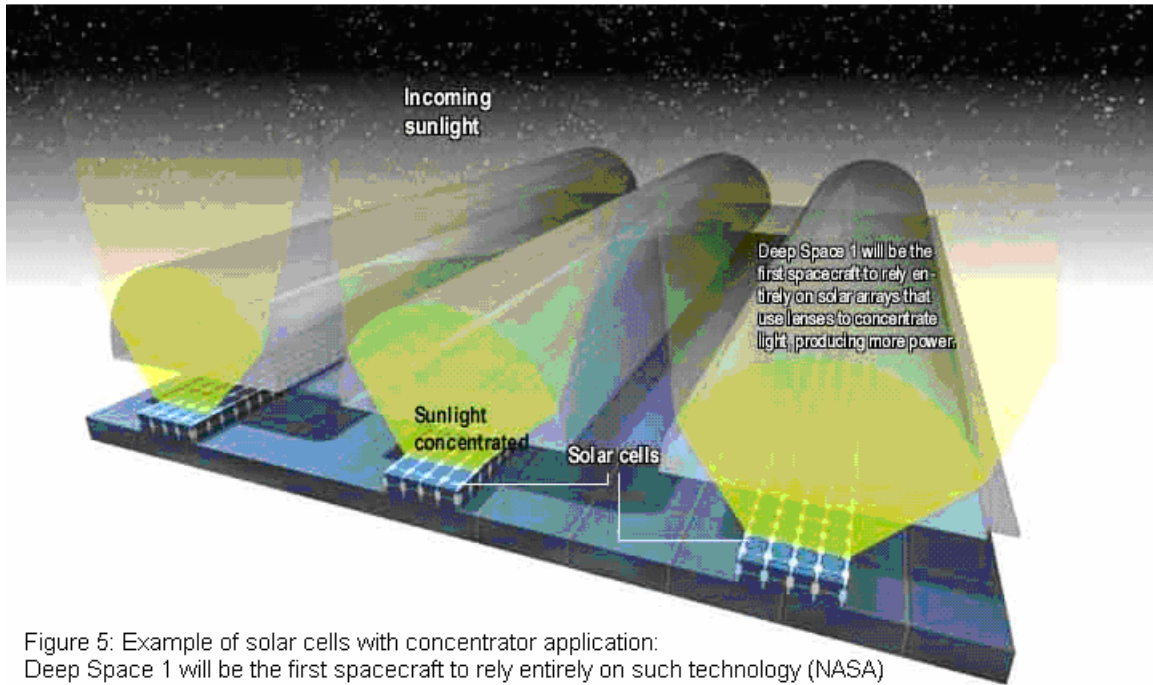


Figure 5: Example of solar cells with concentrator application: Deep Space 1 will be the first spacecraft to rely entirely on such technology (NASA)

Economic Considerations

Solar Cells, generally

The following was prepared by Dr. Mike McGehee of Stanford (Fig.5) and shows why people in California who are not installing solar cells are actually losing money on electricity costs! This is currently true because solar cells are so heavily subsidized, at least in the state of California. A 40% rebate is now being given, resulting in a backorder of solar panels for homes. The solar cell industry is in fact growing at a fast pace of over 30% a year, with over 300 million invested by venture capitalists last year alone. This tremendous growth will need to accelerate this growth in order to supply the 30TW required by 2050 if solar panels are to meet all the projected power needs of society.

Multicrystalline silicon solar cells: today's most popular technology

12 % efficiency
\$420/m²

	Cost (\$/W)
Cell	\$2.50
Making the module	\$1.00
Inverter	\$0.50
Retro fit installation	\$4-5.00
TOTAL	\$8-9.00



Average cost over 30 yrs of PV cell electricity in CA including 6 % interest payments:	\$0.34/kW-hr	actually lower if the interest is deducted from taxes
Average grid electricity in CA:	\$0.13/kW-hr	will rise over 30 years
Peak rates in CA:	\$0.29/kW-hr	

Figure 5: Dr. M. McGehee of Stanford has calculated that it is less expensive for California homeowners to use solar cell than power plant electricity due to deep subsidies given today

Organic Solar Cells

Organic solar cells have the ability to become less expensive than silicon-based cells. By using screen printing and other innovative techniques, start-up companies are giving first-generation (silicon tandem cells) and second-generation (thin-film tandem cells) serious competition. Nanosolar attributes the economic success of screen printed organic cells to the following key innovations: nanostructured components, printable semiconductors and electrodes, rapid thermal processing, low-cost thin-film substrate, and fast assembly through roll-to-roll processing. Although silicon solar cells may leverage the infrastructure of silicon-CMOS technology for cost benefits, poly- and single-crystalline silicon substrates are very expensive and will not be economical in the future for solar cell use. This is because the prices of silicon is skyrocketing; the price of polysilicon increased by a factor of 5 between 2004 and 2007 (present time). Part of the culprit is, surprisingly, silicon solar cells. The International Technology Roadmap for Semiconductors predicts that in the next few years, more silicon will be allocated to the solar cell industry than the chip industry. The growth of the silicon solar cell industry is due in part to the European Commission's stipulation that 20% of European Union energy usage come from solar cells. Countries such as Germany and Japan are huge proponents of solar cell technology; these countries and the U.S. heavily subsidize solar cell development and sales. Actual production costs for organic solar cells were not available to the author at this time; but it is predicted that, given these factors and the

development of inexpensive organic solar cell thin-film printing technology, organic solar cells will be more economical in the future.

Final Remarks

Before attending the Stanford Solar Cell Workshop on February 24, 2007, I imagined the solution to enable solar cells to become cost competitive with nonrenewable energies would be to increase the efficiency of the current silicon P-N junction based technology. This could be accomplished by adding more layers to these commercially available, monolithically integrated devices which are based on silicon technology. These cascading layers of differing material bandgaps would absorb sunlight from shorter to longer wavelengths as they propagated through the device. There is a fundamental limit to how many layers can be added however. Adding more layers increases processing cost and limits device applications (thicker chips are more prone to breakage and cannot be fabricated on films).

Since attending this workshop and spending time reading various research journals and review articles, I have formed the opinion that by the year 2100, society will be powered primarily by organic solar cells. Rather than eeking more efficiency from the current, silicon P-N junction commercial technology, innovative new organic semiconductor devices can reduce material and production costs so much that efficiency is no longer the important figure of merit. Although efficiencies can further improve and possibly match that of the inorganic counterpart, organic solar cell area in the future will be far less expensive than silicon solar cells and so efficiency could be compensated by increasing area while the devices remain cost competitive with nonrenewable energy sources. Of course, as society realizes that oil and coal stores on this earth are not infinite, we start amortizing incidentals surrounding the cost of oil (e.g. wars in the middle east), and add in the exponentially increasing costs of carbon sequestering and other expenses of repairing the damage of using nonrenewable energy sources, the cost benefits of solar cells in general will appear even more reasonable. Researchers are currently developing such inexpensive and high-throughput fabrication techniques, such as screen printing. Device efficiencies are being increased by use of high-surface area/conduction enhancing P-N bulk heterostructures such as nanorods (ordered schemes) and nanoporous materials (disordered schemes). Less innovative schemes emulating the silicon technology will not suffice (thin film organic tandem cells [Forrest]) as they must employ more expensive structures to eek further efficiency (more expensive photolithography layers, light path increasing structures).

References

- S. Forrest and J. Xue, "Strategies for solar energy power conversion using thin film organic photovoltaic cells" IEEE (2005)
- Y. Hashimoto and M. Hamagaki, "Effect of oxygen plasma treatment on Indium Tin Oxide for organic solar cell" Elec. Eng. In Japan 154, No.4 (2006)
- H. Hoppe and N. Sariciftci, "Organic solar cells: an overview" J. Mat. Res. 19, No.7 (2004)
- O. Morton, "Solar energy: A new day dawning?: Silicon Valley sunrise" Nature 443, 19-22 (2006)
- Nasa, Deep Space 1 project; more information available at <http://nmp.nasa.gov/ds1>
- M.K. Nazeeruddin et al, "Engineering of efficient panchromatic sensitizers for nanocrystalline TiO₂-based solar cells" Journal of Amer. Chem. Soc. 123, 1613-1624 (2001)
- S.E. Shaheen et al, "Fabrication of bulk heterojunction plastic solar cells by screen printing" Appl. Phys. Lett. 79, 2996 (2001)
- V. Smil, "Background notes for a presentation at the Global Science Forum Conference on Scientific Challenges for Energy Research," Paris, May 17-18, (2006)
- Wikipedia, website: www.wikipedia.com; definition of "solar cell"