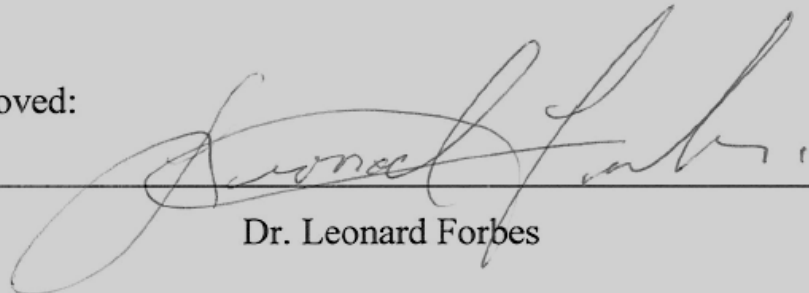AN ABSTRACT OF THE PROJECT REPORT OF

Michael Y.K. Louie for the degree of Master of Science in Electrical Engineering presented on December 11, 2009.

Title: Solar Photovoltaics : Comparisons of Different Approaches and Technologies.

Abstract approved:

_____

Dr. Leonard Forbes

Solar photovoltaic is considered one among many new alternatives to satisfy our demand for energy. Solar Cells have undergone changes in the last 50 years or so since its invention in 1954. Solar power is beginning to challenge conventional energy sources in terms of mainstream acceptance. Solar power along with other renewable energy sources could satisfy the energy needs of people in the developing and undeveloped countries (and even some state nations within the US.)

This project report will provide an overview and comparisons of current solar photovoltaics. Different approaches for solar cells include mature conventional methods using crystalline silicon to maturing methods like thin film solar cells to potentially disruptive technologies like organic based solar cells. This project report will compare and contrast the different approaches and their novel solutions.

Ultimately in order for solar photovoltaic cells to gain mainstream acceptance and compete against today's prices on conventional energy sources, solar photovoltaics needs to be efficient, stable, and economically feasible to the consumer. Solutions to improve solar photovoltaics in terms of improving efficiency and lower cost will be examined.

Solar Photovoltaics: Comparisons of Different Approaches and Technologies

by
Michael Y.K. Louie

A REPORT

submitted to

Oregon State University

in partial fulfillment of
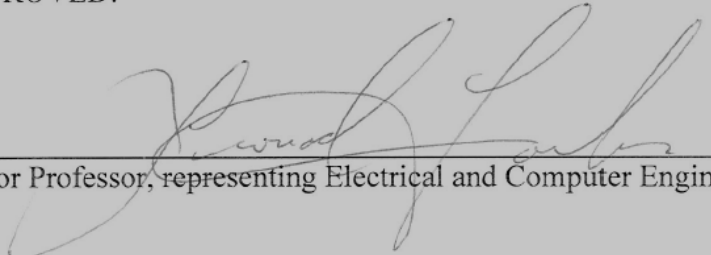the requirements for the
degree of

Master of Science

Presented December 11, 2009
Commencement June 2010

Master of Science project report of <u>Michael Y.K. Louie</u> presented on <u>December 11, 2009</u>

APPROVED:

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Director of the School of Electrical Engineering and Computer Science

_____

Dean of the Graduate School

I understand that my project report will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my report to any reader upon request.

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Michael Y.K. Louie, Author

ACKNOWLEDGEMENTS

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Solar Photovoltaics: Comparisons of Different Approaches and Technologies

1 Introduction

In the era of high and volatile fluctuation in cost of energy, such as rapid rise from forty dollars to one hundred and forty dollar per barrel of North Sea Brent Light Sweet Crude (and to lesser degree for Dubai light sweet and other sour crude) in the 2008 timeframe, world economies are dependent on energy to function. Other examples include cost of natural gas doubling from five dollars to ten dollars per million BTU. Energy is needed in industrial and agricultural production, transport, retail, and general everyday living. Pressure on energy demand only will increase as result of worldwide population growth. Availability, affordability and abundance of power were often the difference in lives of citizens between (developed,) developing and undeveloped countries.

Solar photovoltaic is considered one among many new renewable alternatives to satisfy our demand for energy. Solar photovoltaic and other renewable energies could satisfy peoples' energy needs and provide a path for citizens in the developing and undeveloped countries to improve their lives and possibly join the global economy. Solar Cells have undergone changes in the last 50 years or so since its invention in 1954 [1]. Solar power beginning to satisfy the energy needs of some state nations in the mountain west region of the US. Solar in conjunction with wind power are especially suitable in areas where previously have little or no infrastructure in terms of nearby high voltage transmission lines (used in conjunction with battery banks to store the energy.) As a side benefit, there are added benefits of no greenhouse gases, no strip mining and no particulates from certain forms of conventional energy extraction and its associated generation. Solar power is beginning to challenge conventional energy sources in terms of mainstream acceptance. One factor that speeds up photovoltaic solar cells into mainstream acceptance and to challenge conventional energy sources would be advancement of battery technologies, which will not be discussed in this report.

1.1 Motivation

This report will provide an overview and comparisons of current solar photovoltaics. Different approaches for solar cells include mature conventional methods using crystalline silicon to maturing methods like thin film solar cells to potentially disruptive technologies like organic based solar cells. This project report will compare and contrast the different approaches and their novel solutions.

Ultimately in order for solar photovoltaics to gain mainstream acceptance and compete against today's prices on conventional energy sources, solar photovoltaics needs to be efficient, stable, and economically feasible to the consumer. Solutions to improve solar photovoltaics in terms of improving efficiency and lower cost will be examined.

1.2 Report Organization

The structure of this report is as follows. Chapter 2 explores and examines photovoltaic cells made from crystalline materials, mainly from silicon. Chapter 3 explores and examines techniques and technologies used to reduce reflectance and improve conversion efficiency. Chapter 4 explores into thin film photovoltaic cell technology and issues that comes with each technology. Chapter 5 explores the different organic photovoltaic technologies. Chapter 6 concludes with a summary of this report and examines the future potential of current photovoltaic technologies.

2 Crystalline Photovoltaic Cells

Crystalline photovoltaic cells can be further broken down to subcategories: Crystalline silicon, polycrystalline silicon, amorphous and gallium arsenide photovoltaic cells.

Crystalline silicon (c-Si) based photovoltaic cells were developed by Chapin, Fuller and Person at Bell Labs in 1954 [1,6]. First gallium arsenide (GaAs) photovoltaic cell was developed by Zhores Alferov of Russia in 1970 to support their space program [31]. First dual junction photovoltaic cell made of gallium arsenide and germanium (GaAs/Ge) junctions in 1989. First triple junction photovoltaic cell were made of (GaInP/GaAs/Ge) in 2000. Dual junction photovoltaic cells using concentrators were introduced in 1983 while triple junction version using concentrators were introduced 1999 [12].

There are two main sizes of photovoltaic solar cells: research solar cell and commercial solar cells. Research solar cells are generally smaller than $100cm^2$. (10cm x 10cm) Commercial size solar cells are any cells larger than $100cm^2$.
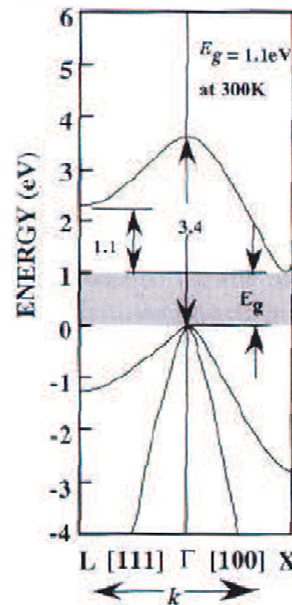
Figure 2.1 Energy Band Diagram of Silicon [Textbook, S.M. Sze]

2.1 Crystalline Silicon Photovoltaic

Crystalline silicon is an indirect bandgap material with bandgap energy of 1.11eV, any incident photons with energy below the bandgap or above 1117nm will be transmitted straight through. Silicon itself is an inefficient material given the indirect bandgap, any electron promoted to the conduction band has to take an indirect route before settling at the bottom of the conduction band. Figure 2.1 on page 3 shows energy bands of silicon. [S.M.Sze, Physics of Semiconductor Devices]
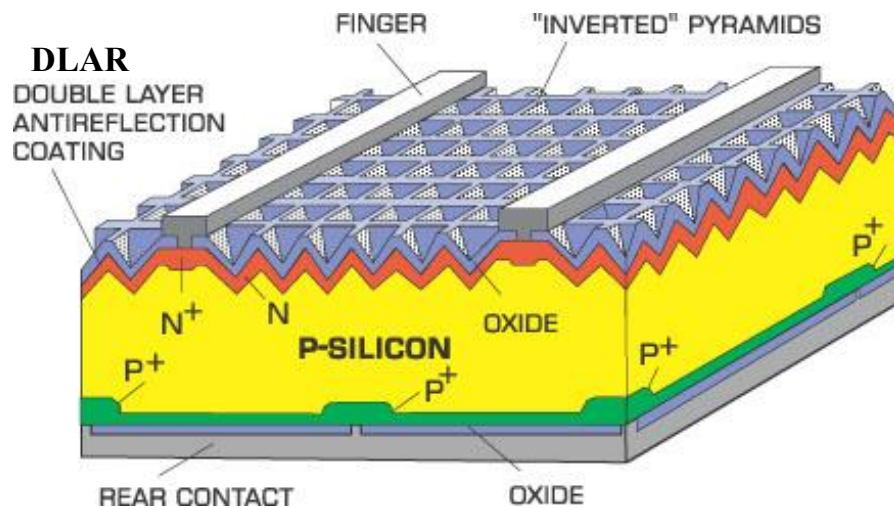
Figure 2.2 Basic Structures of Modern N-P-P+ Crystalline Silicon Solar Cell. [26]
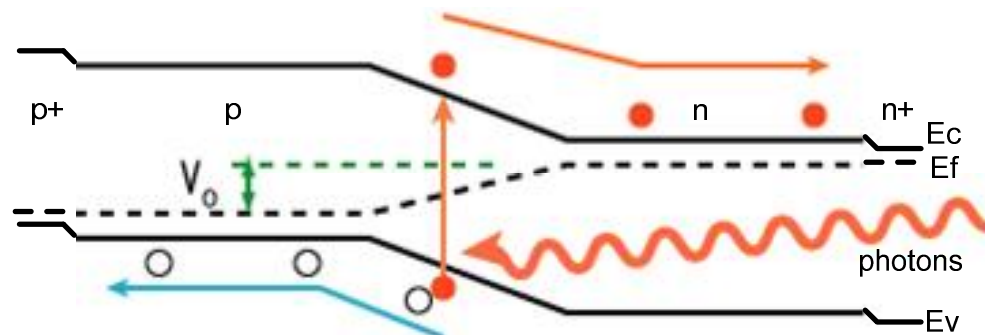
Figure 2.3 Bandgap Diagram of N-P-P+ Crystalline Silicon Cell.

Figure 2.2 shows the basic structure of modern N-P-P+ crystalline silicon cell. [26]   Double layer of anti-reflection coating (DLAR) sits on top of textured N-type surface.   Incoming photons (light) hit the side of the inverted pyramids and thru the

DLAR and into the P-silicon. Figure 2.3 on the page 4 shows the bandgap diagram of the N-P-P+ crystalline silicon cell. Incoming photons with energy greater than the material bandgap (in this case P-type silicon) creates an electron-hole pair in the valence band. Given it doesn't take much energy, like a few millivolts, to dissociate a electron and hole pair. The incoming photon through photo excitation transfers photons energy to the free electron, the free electron with enough energy promoted to the conduction band. Both electron and hole are collected via drift current at the top 'finger' and rear contacts, respectively. Photons with excess energy above the material bandgap that isn't reflected still generate electron hole pairs. The free electron releases phonons (heat) as it heads back down to bottom of the conduction band after absorbing the incoming photon's energy.
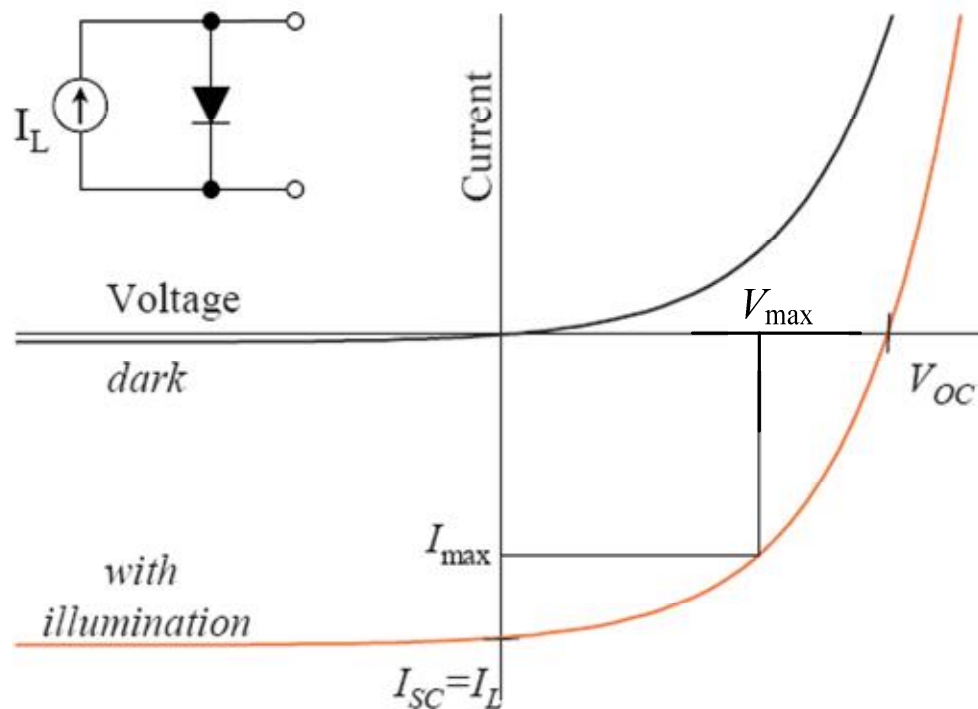
Figure 2.4 Ideal Model and I-V Characteristic of Solar Cell [27]

Model of the photovoltaic solar cell is similar to standard p-n junction diode with a few minor exceptions. Figure 2.4 shows the ideal model of the solar cell itself and its associated current-voltage (I-V) characteristics. [27] Under darkness, the

photovoltaic solar cell characteristics are almost identical to the p-n junction diode.
Current of the photovoltaic solar cell is given in the equation 2.1 below.

$$I = I_0 (e^{qV/kBT} - 1) - I_{SC} \tag{2.1}$$

$$P_{MAX} = V_{MAX} * I_{MAX} = FF * V_{OC} * I_{SC} \tag{2.2}$$

$$FF = P_{MAX} / (V_{OC} * I_{SC}) \tag{2.3}$$

$$\eta = P_{OUT}/P_{IN} \tag{2.4}$$

I_0 is the saturation current of the solar cell under darkness. I_{SC} and V_{OC} is the
short circuit current and open circuit voltage of the solar cell. Maximum power P_{MAX}
is given by equation 2.2 above equaling to maximum voltage and maximum current.
In turn (shown by equation 2.3,) maximum power equals to the fill factor multiplied
by I_{SC} and V_{OC}. Fill factor (FF) is how close your solar cell can perform to the
maximum output. Conversion efficiency (η) is stated in equation 2.4 as output
power over incident power. Incident power given by equation 2.5 as the input
irradiance as a function of wavelength multiplied by the area of the solar cell. Output
power (shown by equation 2.6) is given by fill factor multiplied by short circuit
current and open circuit voltage. Conversion efficiency is given (in equation 2.7) as
follows: fill factor multiplied by I_{SC} and V_{OC} divided by (Input Irradiance * Area).

$$P_{in} = A\int_{0}^{\infty} F(\lambda)\frac{hc}{\lambda}d\lambda \tag{2.5}$$

$$P_{OUT} = FF*V_{OC}*I_{SC} \tag{2.6}$$

$$\eta = I_{SC} * V_{OC} * FF / (\text{Input Irradiance} * A) \tag{2.7}$$

Most efficient solar cells made using crystalline silicon measured at 24.7%
efficient in 1999 by J. Zhao, albeit only in research sizes. [7] Currently most efficient
commercial size solar cells without using concentrators are 23.0% from Sanyo in
May 2009. [21] SunPower achieved 23.4% cell efficiency on a 5-in wafer. [1]
Around 28% (27.6%) efficiency is achieved when using small scale concentrators
(92.3x) with crystalline silicon in 2003 from Amonix. [9]

Most efficient multiple junction solar cells today can achieve efficiency in the low 40% range when used in conjunction with concentrators and for small research size solar cells. All were triple junction tandem solar cells using type III and V semiconductor materials, in 3 absorber layers comprising of gallium-indium-phosphide, gallium-indium-arsenide, and germanium (GaInP/GaInAs/Ge.)   Cells from National Renewable Energy Lab (NREL) achieved 40.8% efficiency back in August 2008 using 326x solar concentrator. [24] Cells from Fraunhofer Institute for Solar Energy Systems in Germany (FhG-ISE) achieved 41.1% efficiency in January 2009 using 454x solar concentrator. [23] Cells from University of Delaware achieved 42.8% efficiency in July 2007 using simulated large scale 500x solar concentrators. Their cell (Univ. of Delaware) uses are concentrating lens the size of a table (say 2 foot on each side) and thickness of more than 30cm, or about 1 foot thick focusing on a 1cm2 device. [25]

Currently solar photovoltaic technology is competing against conventional and other renewable energy sources en route to reach 'grid parity,' a few percentages in efficiency gains matters when it translates to lower overhead and operating cost.

2.2 Theoretical Limits on Conversion Efficiency

Shockley and Queisser back in 1961 did a detailed balance limit to determine the maximum efficiency of p-n junction based solar cells. They determined the theoretical maximum efficiency for single junction crystalline silicon solar cell at 30% without using a concentrator. [8] They arrived to theoretical maximum based on two conditions. Those incident photons with energy above the bandgap will be absorbed to produce power. And any photons (i.e. blue light) with energy above and beyond the bandgap energy still gets absorbed but the excess energy is lost as heat as the photo excited free electron drops back down to bottom of the conduction band. This single junction theoretical limit can be sidestepped in two ways. One involves using a solar concentrator. The other involves using multiple junction (tandem) solar cells.

Concentrators consist of large scale lens and/or parabolic mirrors focusing on the solar cell target, which may require more expensive solar tracking (i.e. with parabolic mirrors) and possible cooling. Using concentrators on a single junction crystalline silicon solar cell increases the theoretical maximum efficiency to 37%. [27] Concentrators were able to increase the conversion efficiency by massively increasing the amount of incident photons. Overall photo excitation rate is slightly higher when compared to non-concentrator case. This leads to an increase in output power via an increase in open circuit voltage (V_{OC}), which in turn increases slightly the conversion efficiency of the solar cell using a concentrator. Reason overall photo excitation rate is not massively higher using the concentrator is that despite the massive increase in incident photons, some of the extra electrons recombine with the already photo excited site.

Multiple junction (tandem) cells got around the original 30% theoretical limit by using multiple junctions in tandem with different bandgap for each junction specifically target certain wavelength of light. Typical configuration of tandem cells involve top layer with wider bandgap targeting blue photons with subsequent layers with smaller and smaller bandgap targeting longer wavelength photons, like green (or yellow) and red photons.

Unfortunately, some light absorbed gets reemitted within the other cells in the tandem stack. DeVos in 1981 estimated dual junction cells only get about 42% efficiency ideally, while you get 49% and 53% in theory for a triple and quad junction tandem cell, respectively. [27] You can in theory reach 68% efficiency (or close) with infinite (or large) amount of tandem junctions. C.H. Henry estimated in 1980 in conjunction with a large scale concentrator system (providing 1000x Air Mass 1.5 standard input irradiance) with cooling, a triple tandem junction could in theory achieve 56% efficiency (50% for dual junction using solar concentrators.) [10]

2.3 Heterojunction Intrinsic Thin Layer Solar Cell

Heterojunction intrinsic thin-layer (HIT) solar cell is an example of crystalline silicon based photovoltaics. HIT solar cell was introduced commercially in 1997 by Sanyo Electric Company, Ltd. Figure 2.5 shows schematic of the HIT solar cell. [3]

Ag Collector Electrodes

FSF

Transparent Electrode (TCO)

p/i amorphous hydrogenated Si (a-Si:H) [<20 nm]

Textured N-Type Crystalline Si (c-Si)
(200 um)

i/n amorphous hydogenated Si (a-Si:H) [<20 nm]

Transparent Electrode (TCO)

BSF
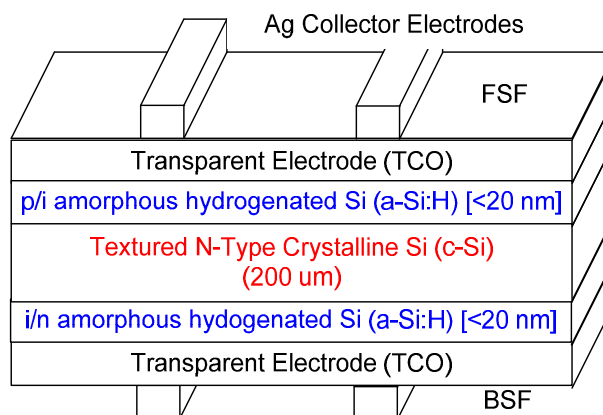
Figure 2.5 Schematic of Heterojunction Intrinsic Thin Layer Solar Cell. [3]

Performance of the HIT solar cell in terms of conversion efficiency at 21.3% was comparable to other commercial crystalline silicon solar cells at 2003 timeframe. HIT solar cell is cost competitive when compared against other conventional crystalline-silicon solar cells (with silicon substrate thickness of 250-400um compared to HIT ~200um in 2003) and thin-film solar cells in 2003 timeframe. [3] Sanyo announced in May 2009 achieving 23.0% efficiency using their HIT solar cell based on ~180nm textured N-type crystalline silicon substrate. [21] This leads to increased conversion efficiency at a reduce cost (from using less substrate material.) Hydrogenated amorphous silicon film deposited on both sides of the doped textured crystalline silicon substrate via plasma enhanced chemical vapor deposition (PECVD) and the transparent electrodes sputtered on top of the hydrogenated amorphous silicon films. Main advantages of HIT solar cell are low temperature process at 200 C and less degradation in conversion efficiency with increasing temperature. Typically solar cells generate less power with increases in temperature, leading to lower conversion efficiency.

2.4 Outlook on Crystalline Photovoltaic Solar Cells

Photovoltaic Solar Cells made from crystalline materials remains popular today and still dominated the overall solar renewable market. Some of the reasons include manufacturing, research & development and production engineering infrastructures are already in place and optimized. Despite the higher material cost in the thicker crystalline (silicon) substrate and its energy intensiveness of substrate manufacturing, photovoltaic solar cell made from crystalline materials are still cheaper than thin film solar cells giving its optimized yield and manufacturing efficiency. Recent research efforts are focused on cost reduction by using a thinner crystalline (silicon) substrate in attempt to bring cost down to grid parity.

3 Photovoltaic Cell Texturing

Bare silicon by itself inherently reflects about 40% of the incoming photons. Every percentage in terms of conversion efficiency are critical for photovoltaic solar cells when every percentage in reduction of reflectance could potentially translates into additional power output for the same incident power into the solar cell. Purpose is to maximize absorption by minimize reflectance and transmission. There are two main thrusts to reduce reflection, shown by figure 3.1: using anti-reflection coating and texture the silicon surface. [15] Anti-reflection coatings use index-matching and destructive interference to minimize reflection. Texturing surfaces reduce reflectance by giving reflected photons additional chances to get trapped in the solar cell itself. These texturing techniques are not only limited at the solar cell level, but applied on the module level as well. These texturing technologies are equally applicable in silicon based solar cells and thin film based solar cells.
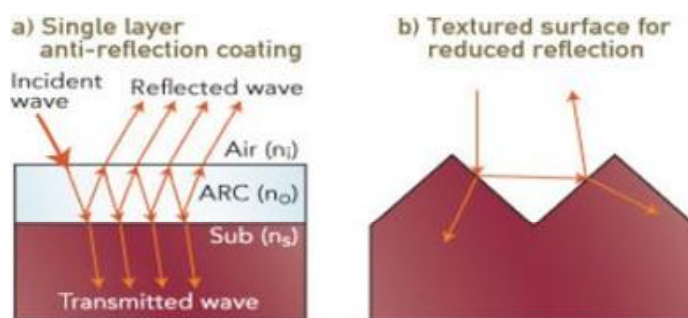
Figure 3.1 Reflection reductions by a) anti-reflection coatings b) textured surfaces.

3.1 Anti-Reflection Coatings

Anti-reflection coatings to minimize reflection rely on index matching, destructive interference when reflected incoming photons, and constructive interference for transmitted photons. An example of anti-reflective coating (AR, or ARC) is tantalum pentoxide (Ta_2O_5.) [2] Other examples of ARC are silicon nitride, titanium dioxide (TiO_2), and zinc sulfide magnesium fluoride (ZnS/MgF_2) combination serving as double layer ARC. [17]

Anti-reflection coatings are applied both on the top side and on the backside of the solar cell. ARC generally comes with a higher-refractive index than air but lower than silicon. Dielectric based anti-reflective coatings are popular in backside reflective as well as top side applications. Downsides of anti-reflections coatings are they are targeted for maximum reflectance at a single (or very narrow band of) wavelength known as a blaze wavelength. To minimize reflections from the anti-reflection coating, the anti-reflection coating thickness needs to be one quarter of wavelength of incident light and when refractive index of the coating layer is equation 3.1 below.

$$(n_I * n_S)^{1/2} \qquad\qquad (3.1)$$

3.2 Surface Texturing

Texturing surfaces reduce reflectance by giving reflected photons additional chances to get trapped in the solar cell itself, increasing efficiency by increases in short circuit current and output power. Figure 3.2 shows a side view figure of ideal pyramid surface texturing. [2]
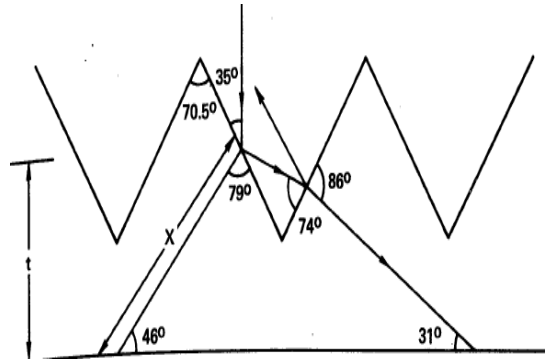
Figure 3.2 Ideal Pyramid Surface Texturing [2]

Initial efforts attempts to texturing surfaces from the top side includes controllable parallel V-grooves, regular pyramids layout, and random pyramids layout, distribution of pyramids of various sizes and spacing.[11] All of them are geometrically based. More advance geometric based texturing schemes were applied on the top absorber surface to reduce reflectance. That eventually leads to texturing

of the bottom absorber surface as well. More recent attempts in reducing reflectance includes micro-texturing of the absorber surface and using bio-mimicry like moth's eye structure.
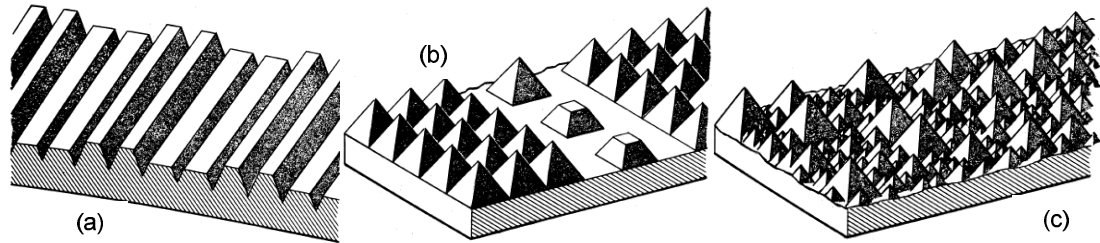
Figure 3.3 Early Geometric Texturing Schemes: (a) Parallel V-Grooves (b) Uniform Regular Pyramids Layout (c) Textured Random Pyramids Layout. [11]

3.2.1 Early Texturing Techniques

Most of the texturing techniques are aiming to reproduce an ideal Lambertian surface where incoming light once trapped stayed trapped via internal reflections. [18] Early attempts in reducing reflectance involve texturing surfaces from the top side includes controllable parallel V-grooves, regular pyramids layout, and random pyramids layout, distribution of pyramids of various sizes and spacing.[11] Figure 3.3 shows a schematic of these early geometric texturing schemes. All of them are geometrically based. Regular pyramids layout consists of uniformly distributed pyramids of equal size and spacing. Random pyramids layout consists of pyramids with distribution of pyramid sizes and/or sizing, sometimes at random spatial locations.   Randomness varies from distributed pyramid sizes with random spatial locations to distributed pyramid sizes with distributed spacing between them. These pyramids are formed by anisotropically etch with potassium hydroxide (KOH) on (100) oriented silicon to expose (111) planes in the silicon. [2,11] Other anisotropic etches use hydrazine hydrate (N_2H_4), sometimes in conjunction or in combination with KOH in solution. Concentrations of etchant are adjusted to create the desired pyramids. Reflectance for silicon with top side texturing only was reduced from 30% to 9%, in the visible wavelengths and up to middle of the near-infrared range.

More advance geometrically based texturing schemes like brickwork pyramid layout, modified brickwork layout, and "Tiler's pattern."[18] Brickwork pyramids layout involves row of uniform pyramids with similar spacing with each row shifted by half the distance of the pyramid base. Modified brickwork layout involves shifting sections of brickwork pyramids by half the pyramid base distance in the other direction. Tiler's pattern involve shifting square sections of uniformly distributed of uniform pyramids by half distance of the pyramid base in the other direction (vertically if going horizontally and vice versa.) Figure 3.4 shows a schematic of these later geometric texturing schemes. [18]
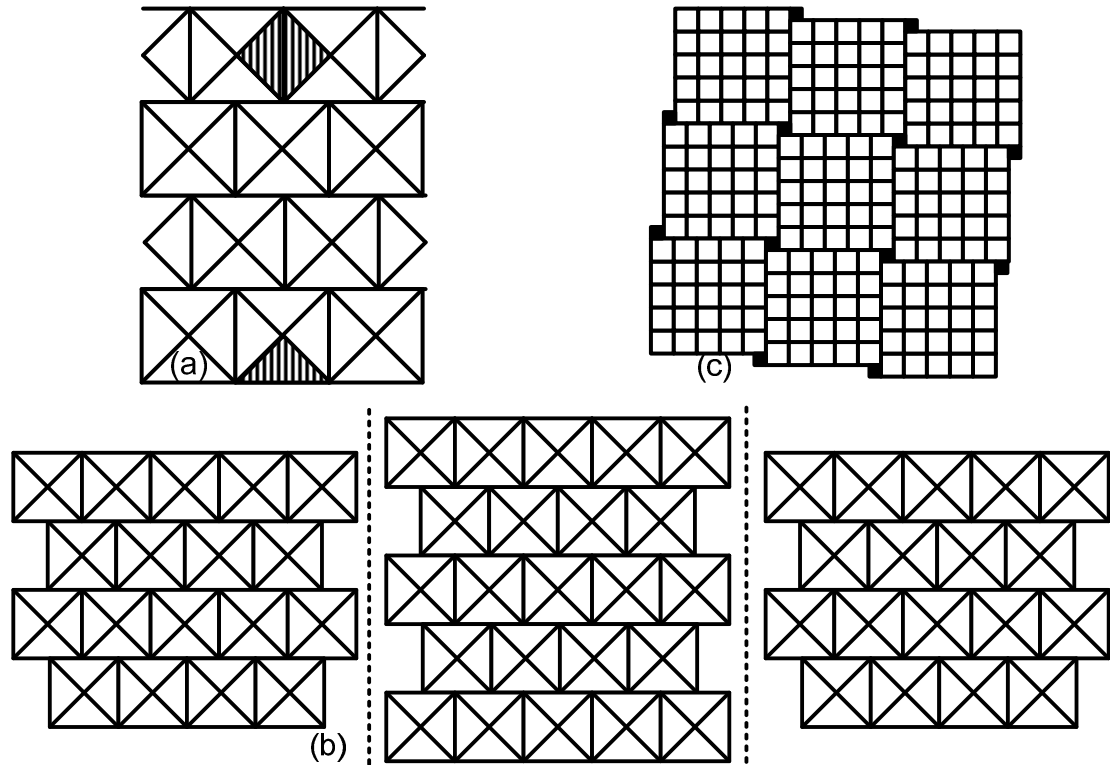
Figure 3.4 Geometric Texturing Schemes: (a) Brickwork Layout (b) Modified Brickwork Layout (c) Tiler's Pattern. [18]

Natural progression in attempting to reduce reflectance leads to the similar geometric texturing on the bottom surface of the absorber as well, sometimes in combination with the top surface texturing. Simple example of double sided texturing is the perpendicular slat approach. Distributed V-grooves texturing on the

top while distributed V-grooves running perpendicularly in the bottom. Different types of geometric texturing were use today to texture silicon based solar cells.

3.2.2 Black Silicon Towers

More recent attempt in reducing reflectance includes micro-texturing of the absorber surface. Silicon is micro-textured by exposing it using a short 100fs 800nm laser pulses (10 kJ/m^2) in SF_6 with the height controlled by the time (in swept speed and number of pulses in one location) the silicon swept by the laser. [5] Micro-texturing creates these silicon spikes, or towers. Figure 3.5 shows SEM of the micro-texturing spikes in silicon.[5] Reflectance is reduced when the incoming photon either gets trapped inside the towers or bounce between faces of the towers before being trapped either in the towers or silicon itself. Reflectance for silicon using micro-texturing reduced to 5% from the visible up to the middle of the near-infrared range. One side benefit of using micro-structuring in silicon is the reduced reflectance of photons
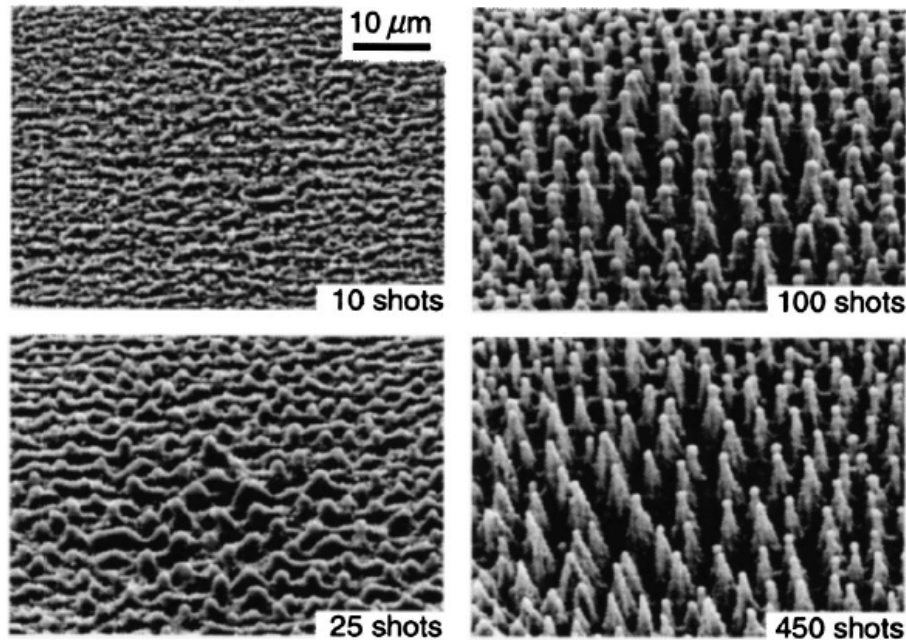
Figure 3.5 SEM of micro-texturing spikes in Silicon. [5]
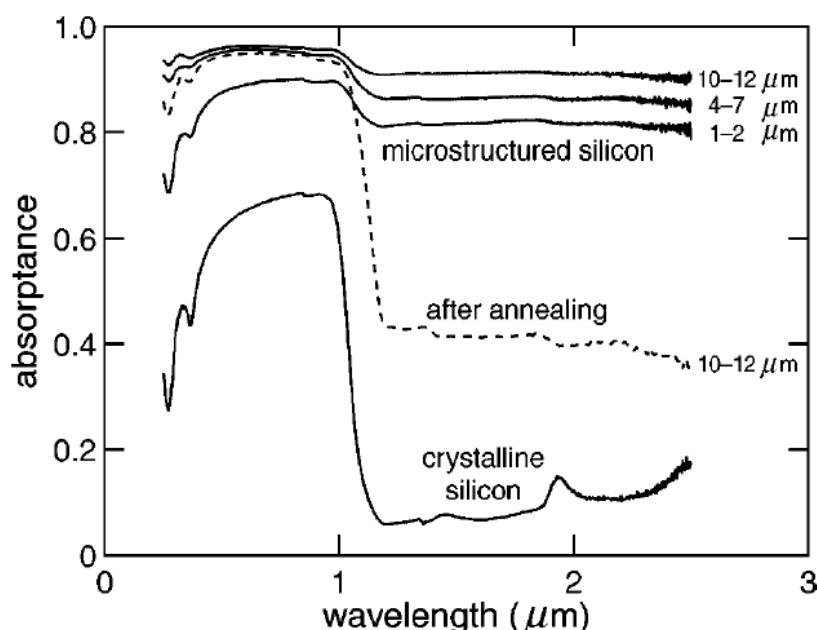
Figure 3.6 Absorption of Silicon with Micro-Texturing Silicon Towers [5]
below the silicon bandgap. Figure 3.6 shows the absorption of the silicon for device
sample size of 1 cm^2. Reflectance beyond near infrared (below the bandgap) is
reduced down to 20% from ~90% crystalline silicon, mainly from the sulfur sitting in
defect sites in the silicon reacting to infrared photons. [5] These defects account for
50% of the reflectance since reflectance below the bandgap is about 60% after
annealing the micro-textured silicon in vacuum for 3 hours at 1200K. Despite the
promise of the micro-texturing, this technique may be cost-prohibitive and horribly
slow in large scale production situations in solar cell production. [5]

3.2.3 Using Bio-Mimicry

In a quest to further reduced reflectance for photovoltaic industry, scientists
and engineers look at nature for ideas. They found the moth's eye structure have very
minimal reflectance, as the moth needs to hunt at night and maintain stealth from
predators and prey by reducing reflectance. Moth's eye structure consists of arrays of
cones of sizes below the wavelength of light. Incoming photons hit the pillars, and
gets trapped inside the pillars or reflects onto another pillar and gets trapped by
internal reflections. These cone structures acts like 'coating' with graded refractive

index. Equation 3.2 shows effective refractive index of moth-eye structure.[4] Other structures trying to mimic moth's eye structure include the honeycomb towers/cones from Univ. of New South Wales, Australia.

$$n_{eff} = \sqrt{f\, n_{Si}^2 + (1\text{-}f)\, n_{air}}$$

(3.2)

Moth-eye structures on silicon are developed initially using electron beam to create the pattern of valleys between the sub- (visible) wavelength arrays. [4] Anisotropic silicon etching (using HBr/Cl$_2$) transfers the pattern to the silicon substrate. Thin layer of oxide are deposited via dry oxidation and later removed to repair the etch damage to minimize surface recombination, and create the tapped profile to moth-eye structure. Variation on anisotropic etch controls the tower depth while the e-beam dose controls the spacing between each pillars. [4] Reflectance reduced down to about 3% over the visible light spectrum and 5-10% from the visible up to the near-infrared range. However, using e-beam is very impractical, horribly slow (taking hours to cover each 1cm^2 area) and cost-prohibitive in large scale situations such as solar cell manufacturing. Figure 3.7 shows the reflectance reduction and SEM of the e-beam moth-eye structure. [4]
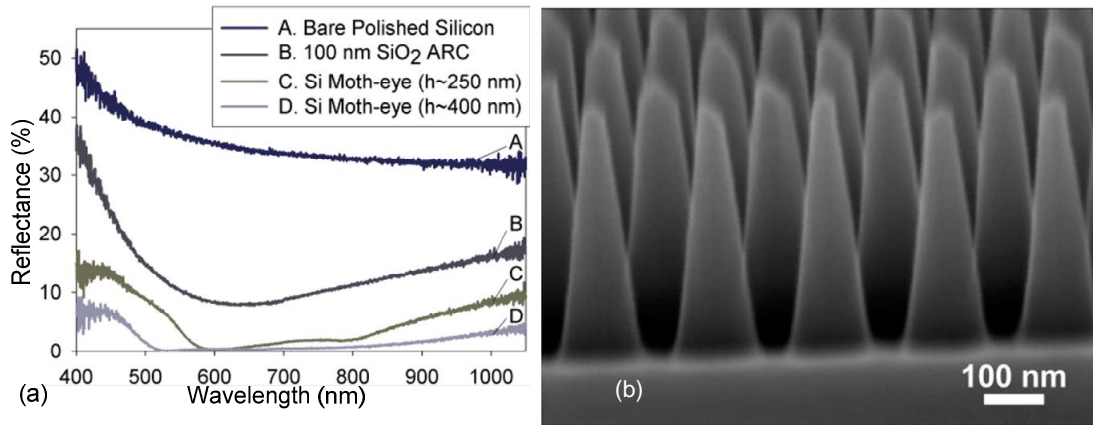
Figure 3.7 (a) Reflectance versus wavelength plot for e-beam moth-eye structures. (b) SEM of e-beam moth-eye structure. [4]

Second approach to reduce cost and complexity in create the moth-eye structure involve e-beaming a stamp and use nano-imprinting to pattern the moth-eye

structure onto the final silicon. The e-beam patterns the stamp and deposit 15nm of aluminum to create the positive pattern. Using anisotropic dry etch using SF_6/C_4F_8 to create the pillars on the stamp. Anti-adhesion coating is applied after using more isotropic reactive ion etching (RIE using $SF_6/CHF_3/O_2$) to remove the aluminum mask and shape/taper the pillars.[4]
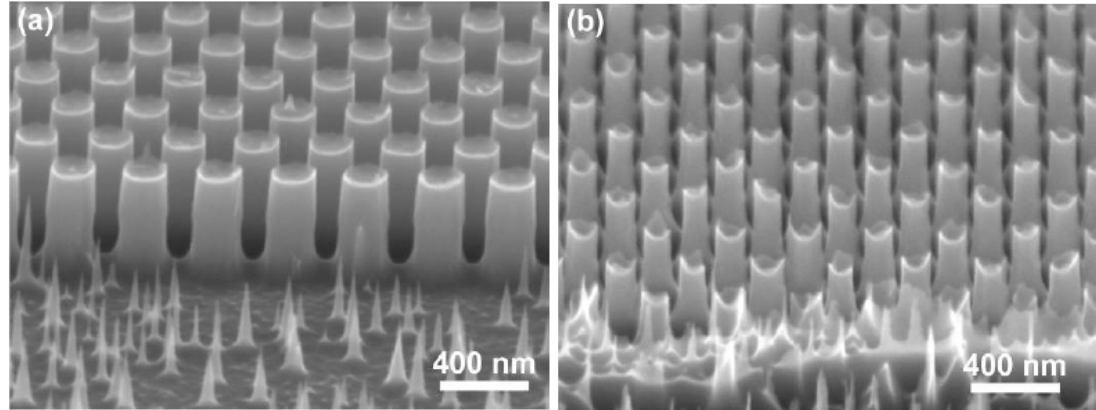
Figure 3.8 SEM of Final Moth-Eye Structures on Silicon using Nano-Imprinting (a) Square Tapered Pillars. (b) More Rounded Pillars [4]

The moth-eye stamp stamps the pattern on the final silicon and deposit thin 15nm aluminum to serve as a mask during anisotropic etches using SF_6/C_4F_8 to create the pillars on the final silicon. [4] Isotropic shaping/tapering etches using RIE to remove the aluminum mask. Again like e-beaming the moth-eye structure, thin layer dry oxidation oxide repairs damage and smooth out the final moth-eye structure on silicon. Figure 3.8 shows the SEM of the final silicon using e-beam to pattern the final silicon instead of stamping the pattern.[4] Challenges remain in terms of developing this process to small scale fabrication of moth-eye structure on silicon. These challenges include section to section variation during stamping the pattern [4] onto final silicon and ability to fully transfer the pattern to the target silicon. Even longer term issue with this technology includes the durability of the stamp and the costs of e-beam to create the stamps needed for nano-imprinting in large scale production situations. Figure 3.9 shows the reflectance of the final silicon with moth-eye structure.[4] Reflectance variations are significant with wafer A (solid lines)

employing square tapered pillars while reflectance variation is less with more rounded pillars of wafer B (dashed lines.) Overall reflectance at single digits in the visible and middle of near-infrared range begin to approach roughly moth-eye structure via e-beaming. [4]
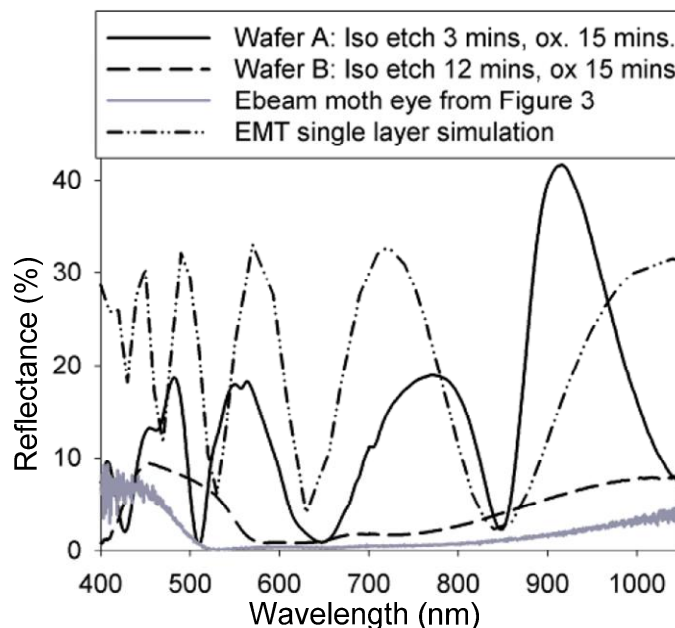
Figure 3.9 Reflectance of Moth-Eye Structure using Nano-Imprinting. [4]

3.3 Developments in Surface Texturing

More recent attempts in reducing reflectance includes micro-texturing of the absorber surface and using bio-mimicry like moth's eye structure. However these recent endeavors may still be in development and probably cost prohibitive and slow in their current form. Challenges such as the ability to consistently transfer the moth-eye pattern from the stamp to target silicon, the durability of the stamp itself, the cost in creating the moth-eye structure stamp, and ability to using lasers to create micro-texturing structures en masse could be barriers for these technologies to succeed. That also explains why geometric based texturing technology will continue to dominate until a future disruptive texturing technology takes over to help reduce a cost-effective way to reflectance in solar cells.

4 Thin-Film Photovoltaic Cells

Thin film photovoltaic cells can be further broken down to subcategories: Cadmium telluride (CdTe), Copper indium gallium diselenide (CIGS), and amorphous silicon (a-Si) photovoltaic cells. [6]

Thin film photovoltaic research cells were developed around 1976 by three separate groups each using different absorber material. Panasonic Matsushita developed the first cadmium telluride photovoltaic cells at 9% efficiency. University of Maine developed the first CIGS photovoltaic cells at 6% efficiency. RCA developed the first photovoltaic cell using thin film amorphous silicon with 1% efficiency. [6]

Some of the drawbacks of crystalline silicon solar cells lead to the development of thin film solar cells. Why bother developing thin film solar cells? Thin film solar cells uses less material and less energy to produce given less silicon is needed and low temperature process. Silicon wafer manufacturing is energy intensive to begin with. Thin film solar cells are thinner, hence offers flexibility in terms of more options in manufacturing, more options in terms of installation, more options in base materials. Obviously thin film solar cells translate into lighter solar modules for installation. Since majority of the cost in crystalline solar cells is the silicon substrate base itself, thin film solar cells obviously have a cost advantage. This will become reality eventually. But there are some issues associated with thin film solar cells. [6] First thin film solar cells are new technology and there isn't much in production infrastructure and poor supply chain. Overhead cost is prohibitive in mass production, mainly in material and capital costs in terms of thin film solar manufacturing equipment. Thin film solar cell manufacturing also have problems like part to part consistency and yield issues, very understandable given it is a new process compared to history in terms of silicon manufacturing. In addition, there are other issues involving the long term (or lack thereof) stability of photovoltaic absorber, heavy metal toxicity and deadliness of absorber material when exposed

even in small amounts (i.e. CdTe and Cu2S/CdS in any form, especially re-crystallize as CdCl,) and base material rarity (i.e. Tellurium, Indium, Gallium) that could be subject to commodity price swings in absorber and base materials when thin film solar cells ramps up to full global production scale.

4.1 Common Structures

Each thin film solar cells have these common structures. They are the substrate, the transparent conductive oxide, window layer, the absorber itself and the back contact. Thin film solar cells can be in substrate and super substrate configurations. [6]

Substrate is there for handling and for rigidity. Substrates generally composed of boron silicate glass (BSG) or Soda-Lime Glass (SLG). The substrate in super substrate configuration are transparent and the ohmic contact made by applying a conducting oxide coating on the clear substrate. Transparent conductive oxide (TCO) are generally low resistance and clear in order to transmit most (if not all) of the incoming photons to the absorber. Generally the TCO are index-matched. Windowing layer are generally very thin to admit the maximum incident photons into the absorber. This layer usually made from high bandgap material. Windowing layer are chosen to minimize any conduction band discontinuities (i.e. spikes) for better minority carrier transport and to ensure low dark current. Back contact materials are chosen for the ability to make an ohmic contact and usually have a work function higher than applied target, critical for p-type semiconductor absorbers (i.e. CIGS, CdTe.) [6]

4.2 Copper Indium Gallium Diselenide (CIGS)

Developed by the University of Maine in 1977 achieve around 6% conversion efficiency. Currently the best research CIGS solar cell is 20% efficient by the NREL in 2004. NanoSolar announced in 2006 they achieved 14.6% efficiency on a commercial size CIGS solar cell, best so far. Figure 4.1 on page 22 shows a typical

CIGS solar cell structure. [6] This structure takes advantage of dual layer TCO structure: a highly conductive TCO (ITO, indium tin oxide, 90% indium oxide [In_2O_3] doped with 10% tin oxide[SnO_2]) for low contact resistance and great lateral current collection, and a thin high resistance zinc oxide (ZnO) layer to minimize forward current working in conjunction with holes in the windowing layer. CIGS have to thin down cadmium sulfide (CdS) window layer (via chemical bath deposition) to ensure a good blue response since thick CdS layer deteriorates the blue response. Thin CdS windowing layer is achievable because CdS provides good surface coverage on a rough copper poor absorber layer.

↓ Incoming Photons ↓

TCO (ITO) 1.8um

Hi-R Buffer (ZnO) 200nm

Window Layer (n-CdS) < 50nm

Absorber [p-Cu(InGa)Se$_2$] 1um

(Contact) Mo[Molybdenum] 350nm

Glass Substrate 2mm
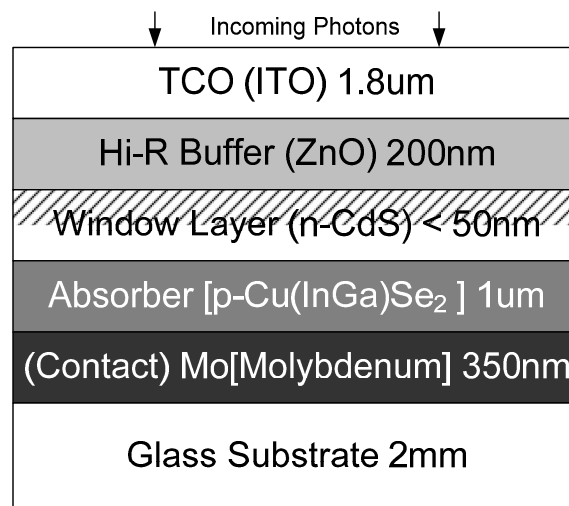
Figure 4.1   Schematic of CIGS Solar Cell Structure [6]

CIGS absorber is a type I-III-VI direct bandgap chalcopyrite where its bandgap can be customized from 1.0 to 1.7 eV by changing the ratio of the indium to gallium. Bandgap for $Cu(InGa)Se_2$ is 1.34 eV, therefore any photon having wavelength longer than 926nm (therefore below the absorber bandgap) would not see the CIGS absorber. CIGS absorber is most absorbing material that can easily be doped n or p-type to low resistivity via introduction of native defects. [6] CIGS is a very forgiving material since defects are benign electrically and fairly insensitive to impurities and grain sizes. Even better that bandgap of CIGS can be adjusted up by alloying with gallium and aluminum. Increasing the bandgap voltage leading to an

increase in open circuit voltage (V_{OC}) having some additional advantages. [6] These include reduction in the number of metal (scribe) lines during module integration, thinner electrode thickness, smaller temperature coefficient (heats up slower, pushing back output power drop off) and less variation in power output from fluctuations in photon intensity. Plus ability to vacuum deposited or printed molybdenum sheets should help manufacturing but at an extra expense. [6]

There are unfortunately some challenges in CIGS solar cell, the absorber suffers from degradation from sunlight over time and tight indium supply could slow adoption. Given CIGS solar cells are somewhat comparable in terms of conversion efficiency, current research are focused on driving production costs down.

4.3 Cadmium Telluride

Cadmium telluride (CdTe) is a direct bandgap material with a bandgap of 1.49eV. Matsushita introduced the CdTe solar cell in 1976 with efficiency of 9%. Currently the best research CdTe solar cell is ~ 16 % efficient by NREL in 2001. First Solar announced in 2009 their CdTe commercial scale solar cell achieved 12.3% efficient, best so far.[6] Figure 4.2 on page 24 shows an example structure of CdTe solar cell. This structure is similar to the CIGS solar cell that takes advantage of the dual layer TCO structure, but using a thin tin dioxide (SnO_2) instead of zinc oxide. CdTe cell uses the same windowing layer material (CdS) as the CIGS cell for response, but even 60% thinner (<20nm vs. 50nm for CIGS) than the case of CIGS solar cell. Using this dual TCO structure (versus using ITO alone as TCO) allows for a thinner CdS layer to improve the blue response of the CdTe solar cell. This dual TCO structure works in conjunction window layer provide additional benefit of low dark (reverse saturation) current.

CdTe absorber is a direct bandgap material that captures incident photons shorter than 833nm (which is above its bandgap.) Its high absorption allows CdTe absorber to be thin. Higher chemical and higher thermal stability made CdTe a candidate for thin film solar cells by giving it different deposition options. Contact is

made by applying a layer of conducting oxide coating on the substrate. Ohmic contact in the back is done with metal alloy of nickel and aluminum.

```
            ↓   Incoming Photons   ↓
    ┌─────────────────────────────────────┐
    │      Glass (Super)Substrate         │
    ├─────────────────────────────────────┤
    │            TCO (ITO)                │
    ├─────────────────────────────────────┤
    │   Hi-Resistivity (SnO₂) 50nm        │
    ├─────────────────────────────────────┤
    │   Window Layer (n-CdS) <20nm        │
    ├─────────────────────────────────────┤
    │    Absorber [p-CdTe] 3-10um         │
    ├─────────────────────────────────────┤
    │   (Contact) Ni-Al metal contact     │
    └─────────────────────────────────────┘
```
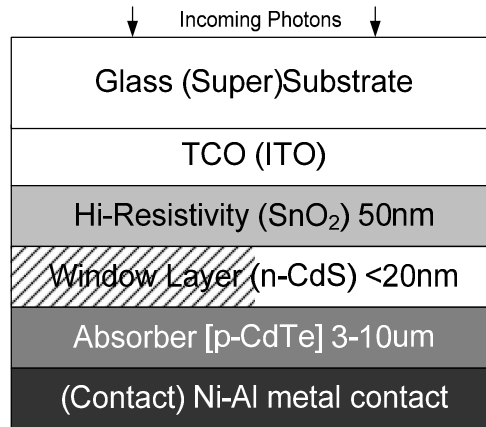
Figure 4.2   Structure of Cadmium Telluride Solar Cell, Super-substrate Config [6]

Some challenges still exist with the CdTe solar cell, the absorber suffers from degradation from sunlight over time and tight tellurium supply could slow adoption. Tellurium is only available as a byproduct of copper production. Another challenge is the cadmium toxicity and reactiveness in CdTe particles, possibly re-crystallizing as cadmium chloride (CdCl.)   Current research is finding an alternative to using cadmium sulfide as a windowing layer to cut down the toxicity issue and driving down production costs (to 75 USD/m^2) in order to be competitive against other photovoltaic technologies.[6] Today production costs are at 111 USD/m^2 resulting at 1.04 USD/watt, at 10.7% conversion efficiency [FirstSolar].

4.4 Amorphous Silicon

Amorphous silicon (a-Si) can be treated as direct bandgap material. Amorphous silicon has significant number of dangling bonds ($\sim 10^{19}$ cm^{-3}) that serve can serve as recombination sites. Hydrogenating amorphous silicon (a-Si:H) ties up some of these dangling bonds cutting down the 'concentration' (to $\sim 10^{16}$ cm^{-3}) of the recombination sites.[6] Alloying hydrogenated amorphous silicon (i.e. with carbon becoming silicon carbide, a-SiC:H) widens the bandgap allowing for customization of your solar cell, plus yielding a transparent material suitable for solar photovoltaic

applications. For example, hydrogenated amorphous silicon alloying with carbon at 50% produces silicon carbide (a-SiC:H) have a bandgap of 1.7eV, hence transparent to photons longer than 730nm.

RCA introduced the hydrogenated amorphous silicon solar cell in 1976, achieving 1% efficiency, initially targeted for low power and/or low cost applications. Hydrogenated amorphous silicon like its crystalline silicon cousin could be doped once it is laid down on a substrate.[6] Using amorphous silicon as an absorber in thin film solar cell is a significant cost advantage over conventional crystalline silicon substrate solar cells. Plus it is a low temperature process and some infrastructure used in normal silicon processing can be leveraged for amorphous silicon solar cells. However, conversion efficiency of amorphous silicon solar cells significantly lags behind their crystalline silicon substrate version. This leads to using amorphous silicon solar cells in tandem.

Incoming Photons

TCO (ITO)
Window Layer (p+a:SiC:H-3) 10nm
Absorber [i 3 a Si alloy (:H)]
Window Layer (n+aSiC:H-3) 10nm
Window Layer (p+a:SiC:H-2) 10nm
Absorber [i 2 a Si alloy (:H)]
Window Layer (n+aSiC:H-2) 10nm
Window Layer (p+a:SiC:H-1) 10nm
Absorber [i 1 a Si alloy (:H)]
Window Layer (n+aSiC:H-1) 10nm
Hi-R Buffer (ZnO)
(Contact) Silver
Glass (Super)Substrate

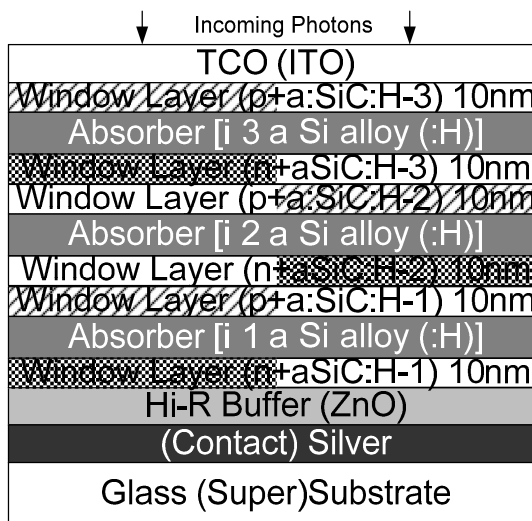Figure 4.3 Schematic of Tandem Amorphous Silicon Solar Cell, Super-Substrate Configuration [6]

Figure 4.3 shows a schematic of tandem amorphous silicon solar cell. It consists three stacks of thin window layers sandwiching the absorber allowing maximum photon transmission to the amorphous silicon carbide absorber. Top absorber layer heavily alloyed with carbon (possibly with bandgap >= 2.7 eV) to

produce a wide bandgap to absorb higher energy (i.e. blue) photons. Middle and bottom absorber layers alloyed to target green/yellow and red photons (with bandgap of 2.2 and 1.5eV), respectively. Contact made to the module level by a conductive oxide coating on the glass substrate. Despite the savings from material cost and its high optical absorption coefficient, using a-SiC:H as an absorber still have its problems. There exist dangling bonds ($\sim 10^{16}$ cm^{-3}) that serve as recombination centers. Like its crystalline silicon cousin but to a greater degree, amorphous silicon suffers from light induced defects (Staebler Wronski; increasing e- recombination centers) over time.[6]   Additional manufacturing complexity associated with depositing the tandem structure relegates the technology to niche uses where flexibility and thinness are desirable. United Solar has the best research amorphous silicon cell at ~12% in 1999. Current research is into reducing the induced defects by using nano-crystalline or micro-crystalline hydrogenated silicon as absorber material.

4.5 Outlook on Thin Film Photovoltaics

Thin film photovoltaic solar cells are beginning to carve out its share of the solar cell market dominated by crystalline silicon solar cells. Thin film solar cells have the potential of equal footing with crystalline silicon. Advantages include material and energy savings from not having the absorber material performing double duty as a substrate. Manufacturing options opens up and ability to adjust bandgap energy makes up for the slight disadvantage in conversion efficiency (compared to crystalline silicon solar cells.) However there is cost issues that needs to be worked out (i.e. tandem thin film and CIGS) in order for these thin film solar cells to be successful. Capital investment in thin film production and engineering infrastructure as well as thin film manufacturing is a necessarily in order to drive cost toward grid parity (cheaper than conventional energy sources) and for thin film to be successful. Other material issues involving base material availability and toxicity may limit the amount of solar cell market share thin film can take due to full production ramping issues.

5 Organic Pigment Based Photovoltaics

Organic based photovoltaic solar cells are little different compared to their crystalline and thin film counterparts. Organic based solar cells can be split into 3 categories: Insoluble, Soluble, and Liquid crystalline. Those organic based solar cell uses monomers (i.e. dyes and pigments) and polymers (i.e. p-conjugated polymers.)
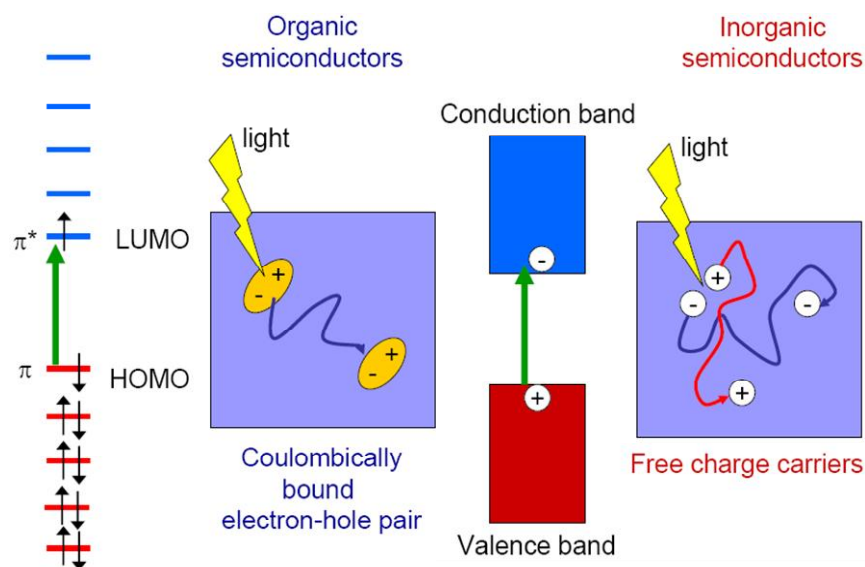
Figure 5.1   Comparing Concept of Energy Bands between Organic and Inorganic Semiconductors. [28]

Organic based solar cells work differently compared to other types of solar cells. Unlike having distribution like energy bands in inorganic semiconductors, organic semiconductors work on distinct molecular orbitals. Figure 5.1 shows an example of distinct molecular orbitals. Lowest Unoccupied Molecular Orbital (LUMO) is analogous to the bottom of conduction band while Highest Occupied Molecular Orbital (HOMO) is analogous to the top of the valence band.[28] Carriers in inorganic semiconductors moves within the 'fluid' conduction band while the carriers move in distinct orbitals, jumping from one orbital to the one above or below it. Unlike inorganic semiconductors where binding energy is only a few millivolts, it doesn't take much energy to dissociate electron hole pair into free electrons and

holes. Organic semiconductors having binding energy close to half a volt, freeing an electron isn't easy. Incident photons still generate excitons if the photon energy is above the bandgap of the organic absorber, however the organic absorber tend to have a short absorption bandwidth. Photo excitation in organic semiconductors from incident photons doesn't generate a free electron hole pair, but rather induce a coulombically bounded electron-hole pair, called an exciton. Dissociation occurs via charge transfer at the electron donor-acceptor interfaces between two organic materials. Recently freed electron and holes collect toward their contacts via charge transport. Figure 5.2 shows a schematic of this process. [29]
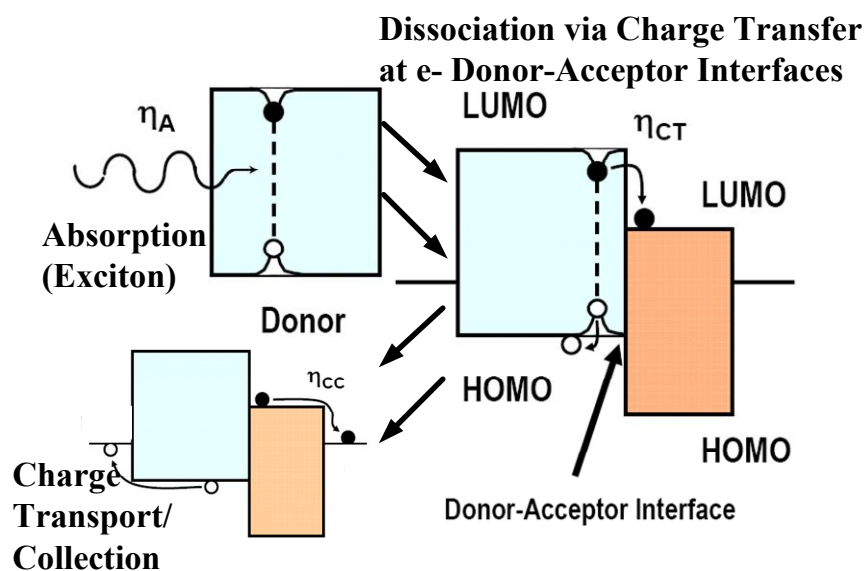
Figure 5.2   Schematic of Organic Semiconductors in Absorption, Dissociation and Charge Transport and Collection. [29]

5.1 Dye Sensitive Solar Cells

Dye Sensitive solar cell is synonymous as Grätzel solar cells. Grätzel solar cells were discovered by Michael Grätzel and Brian O'Regan of Swiss Federal Institute of Technology in Lausanne (EPFL, Lausanne Federal Polytechnic University, Switzerland) in 1991. Best commercial organic based solar cells at ~5 %

efficiency in 2005. Research small size Grätzel solar cell is at 11% efficiency in 2005. [28] Figure 5.3 shows the anatomy of a Grätzel solar cell. [12]
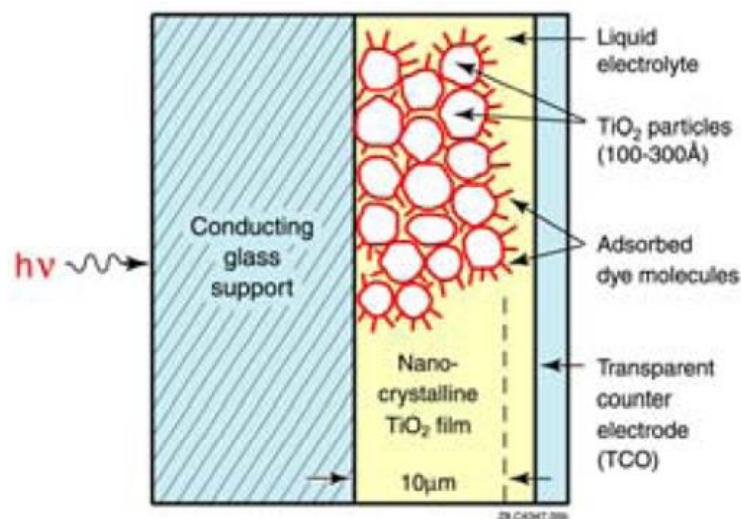

Figure 5.3 Anatomy of Grätzel Solar Cell. [12]

Grätzel solar cell consists of organic absorber dye, liquid electrolyte, a couple of transparent conductive plates, and a substrate. Organic absorber dye generally composted of Ruthenium-complex, coats the surface of TiO_2 particles in nano-crystalline TiO_2 film. Liquid electrolyte composts of either iodine or ethanol, sometimes with a mediator like tri-iodine. This electrolyte serves to exchange charge via oxidation and reduction-oxidation reactions. Two transparent conductive plates serve as transparent electrodes, with the counter electrode coated with catalyst that catalyzes reactions at electrolyte and electrode interface. Diffusion length in organic semiconductors are very short, somewhere around 10nm before requiring a large electric field to move the exciton any further than 10nm to the donor-acceptance interface of two organic materials with different orbital energy levels.
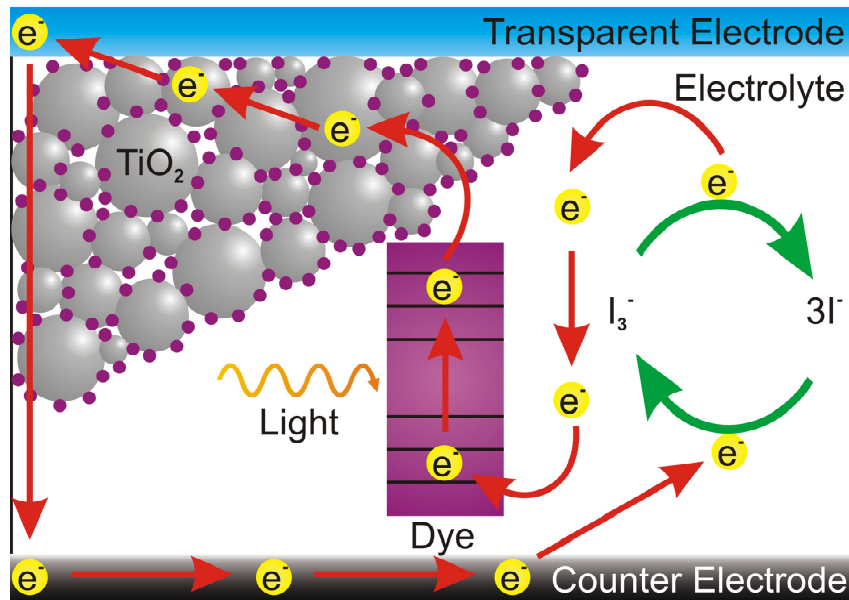
Figure 5.4 Operation of Grätzel Solar Cell [30]

Figure 5.4 shows the operation of a Grätzel solar cell. Incident photon with energy above the bandgap generates an exciton, bounded electron-hole pair in the organic absorber dye. Exciton reaches the electron donor-acceptance interface (Dye-TiO_2) and dissociates into electrons and holes (Dye*.) Liquid electrolyte sometimes with a mediator quickly oxidizes, gives up a couple electrons to replenish the couple electrons dissociated (and 2 holes already in the electrolyte. $2 \text{ Dye*} + 3 \text{ I}^- \rightarrow 2 \text{ Dye} + I_3^-$.) The electrons hop onto the conduction band of the TiO_2 particles and diffused to the anode. Liquid electrolyte flows over to the counter electrode wants its two electrons back from the counter electrode via reduction reaction ($I_3^- + 2 \text{ e-} \rightarrow 3 \text{ I}^-$.)

5.2 Polymer-Polymer Solar Cells

Polymer-polymer solar cells are based on two different polymers; one is electron donor and another electron acceptor. Polymer-polymer solar cells also known as plastic solar cells. Conjugated polymers have bandgap voltages from 1.0 to 3.0 electron volts (eV.) Photo-excitation in polymers absorber operates similar to organic absorber dyes. Figure 5.5 shows the schematic and photo of the polymer-

polymer solar cell.[28] Absorber material consists of two polymers: MDMO-PPV and PCBM (poly-{2-methyl-oxy, 5-(3,7-dimethyloctyloxy)}-p-phenylene-vinylene and fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester.) MDMO-PPV is the electron donor with a bandgap of 2.1eV with absorption of 400-600nm peaking at510nm. PCBM is an electron acceptor and a fullerene derivative of a carbon-60 (known as buckeyball) with bandgap of 2.4eV and peak absorption of 670nm.) ITO is used as TCO with aluminum used as the back metal contact.   [28]
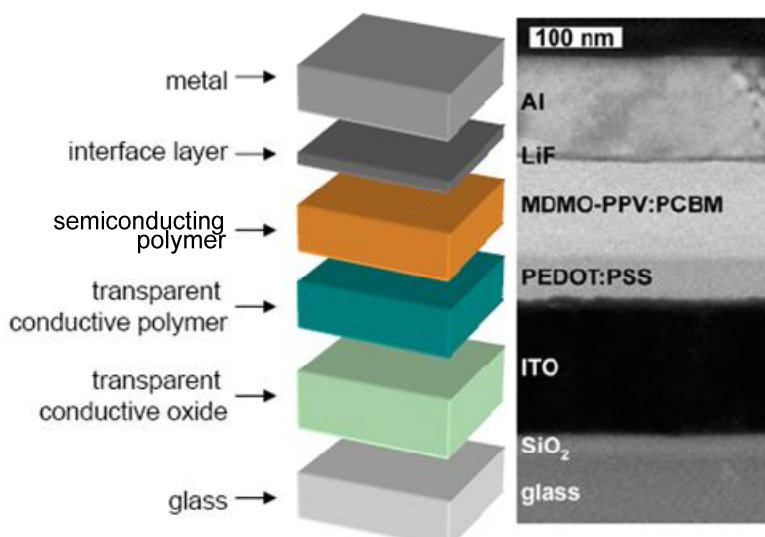
Figure 5.5   Schematic and Photo of Polymer-Polymer Solar Cell. [28]

Difference in LUMO (Bottom of conduction band) and HOMO (Top of the valence band) between MDMO-PPV and PCBM is 1.1 and 1.2 electron volts, respectively. MDMO-PPV absorbs a (i.e. blue) photon with the dissociate electron. PCBM ionizes with the dissociate electron, later recombine with the free hole in MDMO-PPV. Separately, PCBM absorbs a red photon; photo excites and dissociates a free electron. MDMO-PPV gives up an electron to the PCBM. The free electron recombines with the MDMO-PPV. Best research organic plastic solar cells have 2.5% conversion efficiency in 2001 by separately Sean Shaheen, Wienk and J. van Duren. This specific class of plastic solar cells has the best performance so far with high electron mobility and processing is easier than others but hurdles include absorber stability and lower absorption. [28]

Advantages of polymer solar cells are the absorbers) can be made by solution, and only need low temperature processing. Hurdles for polymer-polymer solar cells to succeed include (low) single digit conversion efficiency, absorber instability and ability to produce in commercial size and ramp up to production scale.

5.3 Potentials of Organic Solar Cells

Organic based solar cells are still at its infancy with conversion efficiency so far in the single digits. However, organic based solar cells have great potential becoming a disruptive technology to the current photovoltaic landscape. Organic solar cells can be custom tailored and be manufactured cheaply like printing. Light absorption can be optimized in parallel with charge carrier transport given they are not dependent in organic solar cells. However, there are a lot of challenges to organic solar cells. Absorber stability issues under strong UV exposure and long term absorber degradation, especially troubling for conjugated organic polymers up to 50% and to lesser degree for dye based organic solar cells. Lifetimes for organic absorbers are very short with the absorber sensitive to moisture and breaks down when exposed to air. Given the narrow absorption wavelength and short diffusion length of the single organic absorber, tandem organic cells is natural for organic solar cells to cover wider range of wavelengths (i.e. visible light, Air Mass 1.5 Irradiance, etc.) Tandem organic solar cells were made by mixing 2 or more polymers, with side benefit of overcoming the limited diffusion length (10nm/side.) by creating more 'junction' areas. [28]

Current research in organic solar cells is to find a solid state electrolyte to replace the unstable liquid electrolyte and to improve conversion efficiency by finding new absorber dyes and different nano-materials. Organic solar cells needs to develop the techniques, production methods, engineering infrastructure to produce commercial size and eventually ramp up to production scale. Organic solar cells are the potentially disruptive technology and could compete against conventional energy if all the challenges were resolved and able to scale up to production scale.

6 Conclusion

Demands for energy won't stop increasing, as long as world population is increasing and more people move up the social economic ladder. There are over 6 billion people on earth and the number is still climbing, with over 2.3 billion of them beginning to join the developed world with another billion or two in the undeveloped world beginning to develop. Energy demands will increase as they need places to live, transportation, food, lights, etc. The difference between the lives of citizens between developed, developing and undeveloped countries is the availability, affordability and the abundance of power. Aside from global warming concerns, there is only limited supply of conventional energy (non-renewable) sources on earth and no matter the advances in technologies to bring these conventional energy sources onto market, energy and commodity prices over time will increase. One of many ways to get out of this positive feedback loop on energy demand is to generate enough energy from renewable energy sources such as solar cells. Personally I think other ways to slow down increasing energy demand may be unnatural and excessively bloody.

In order for solar technologies to satisfy a portion of the renewable energy supply to meet increasing worldwide energy demands, energy from solar photovoltaic has to be cost competitive or cheaper than conventional energy sources, known as grid parity. Solar energy will approach grid parity eventually within the next decade as conventional energy costs will only increase. Solar energy from crystalline silicon will continue to dominate for the next 5 years, maybe a decade or longer given the mature, optimized infrastructure and current advances in thinner substrate in crystalline silicon solar cells. Thin-film solar cells have the potential to dominate the amount of solar cells producing energy. Capital spending into thin film solar cell infrastructure, supply chain and technologies is needed in order for thin film solar cells to be successful. Or thin film research can taken advantage of the established infrastructure to drive production costs down so thin film solar energy can reach grid

parity. Organic and/or plastic solar cells have potential but would take time to overcomes challenges and achieve the conversion efficiency and costs of crystalline silicon. Figure 6.1 shows the Air Mass 1.5 Spectrum and various absorber curves from various solar cell technologies. CIGS solar cells have the best match to absorb the air mass 1.5 spectrum. [1] However, in the solar renewable energy game, cost in the solar cell, solar energy production costs competing against conventional energy sources to grid parity is the key to success in meeting energy needs of the world.
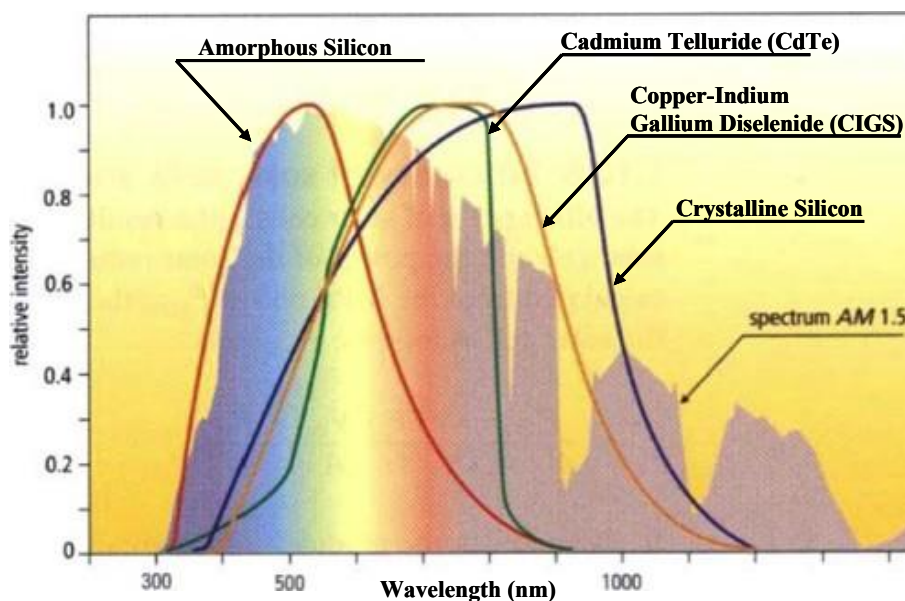

Figure 6.1   Air Mass 1.5 Spectrum and Absorption Curves of Various Solar Cell
Technologies. [1]

Bibliography

1. Haavind, Bob., "Industry execs hears about bright days ahead in energy," Solid State Technology, January 2009.

2. Arndt, R.A., Allison, J.F., Haynos, J.G., and A. Meulenberg, Jr., "Optical Properties of the COMSAT Non-Reflective Cell," Conf. Rec. 11th IEEE Photovoltaic Specialist Conf., IEEE, New York, 1975, p. 40-43.

3. Tanaka, Makoto et al., "Development of HIT solar cells with more than 21% conversion efficiency and commercialization of highest performance HIT modules," 3rd World Conference on Photovoltaic Energy Conversion, May 11-18, 2003, Osaka, Japan.

4. Boden, Stuart A. and Bagnall, Darren M., "Nanoimprinting for Antireflective Moth-Eye Surfaces," 4th Photovoltaic Science, Applications and Technology Conf. C89(PVSAT-4_008), University of Bath, April 2-4, 2008.

5. Mazur, E. et. al., "Near Unity Below-Band Gap Absorption By Microstructured Silicon," Appl. Physics Lett., vol. 78, no. 13, pp. 1850-1852, March 26, 2001.

6. Chopra, K.L, Paulson, P.D., Dutta, V., "Thin-Film Solar Cells: An Overview," Progress in Photovoltaics: Research and Applications, vol. 12, no. 2-3, pp. 69-92, 2004.

7. Zhao, J., Wang, A., Green, M. A., "High-efficiency silicon solar cells on FZ, MCZ and CZ substrate," Technical Digest of the International PVSEC-11 (Hokkaido, 1999) p.557

8. Shockley, W. and Queisser, H. J., "Detailed Balance Limit of Efficiency of p-n Junction Solar Cells," J. Appl. Phys., 32, pp. 510-519 (1961).

9. Slade, A. and Garboushian, V., "27.6% Efficient Silicon Concentrator Solar Cells for Mass Production," Proc. 15th Int'l Photovoltaic Science and Engineering Conf., Beijing, Oct. 2005.

Bibliography (cont'd)

10. Henry, C.H., "Limiting efficiencies of ideal single and multiple energy gap terrestrial solar cells," J. Appl. Physics, vol. 51, p. 4494 (1980).

11. Baraona, C.R, and Brandhorst, H.W., "V-Grooved Silicon Solar Cells," Conf. Rec. 11th IEEE Photovoltaic Specialist Conf., IEEE, New York, 1975, p. 44-48.

12. "Basic Research Needs for Solar Energy Utilization," DOE Workshop Report, April 2005.

13. Goetzberger, A. et. al., "Light Trapping, a new approach to spectrum splitting," Solar Energy Materials & Solar Cells, vol. 92, pp. 1570-1578 (2008)

14. Vallejo, B. et. al., "On the texturization of monocrystalline silicon with sodium carbonate solutions," Solar Energy, vol. 81, pp. 565-569 (2007)

15. Doble, Dan M.J. and Graff, John w., "Mimization of reflected light in photovoltaic modules," Photovoltaics World, March 2009.

16. Cotter, Jeffrey E., "Optical intensity of light in layers of silicon with rear diffuse reflectors," J. Appl. Phys., vol. 84, no. 1, pp. 618-624 (1998)

17. Green, M.A. and Blakers, A.W., "Characterization of high-efficiency silicon solar cells," J. Appl. Phys., vol. 58, no. 11, pp. 4402-4408 (1985)

18. Campbell, Patrick and Green, M.A., "Light trapping properties of pyramidally textured surfaces," J. Appl. Phys., vol. 62, no. 1, pp. 243-249 (1987)

19. Keevers, M.J., Green, M.A., "Absorption edge of silicon from solar cell spectral response measurements," J. Appl. Phys., vol. 66, no. 2, pp. 174-176 (1995)

20. Yablonovitch, Eli and Cody, George D., 'Intensity Enhancement in Textured Optical Sheets for Solar Cells," IEEE Trans. Electron Devices, vol. ED-29, pp. 300-305 (1982).

21. Sanyo Electric Co., Ltd. News Release "SANYO Develops HIT Solar Cells with World's Highest Energy Conversion Efficiency of 23.0%," May 22, 2009,

Bibliography (cont'd)

http://us.sanyo.com/News/SANYO-Develops-HIT-Solar-Cells-with-World-s-Highest-Energy-Conversion-Efficiency-of-23-0-

22. "Feature of HIT Solar Cell," http://www.technosun.com/es/principal/descargas/varios/53701006_Cell_features.pdf

23. Fraunhofer Institute for Solar Energy Systems ISE Press Release "World Record: 41.1% Efficiency reached for multi-junction solar cels at Fraunhofer ISE," January 14, 2009, http://www.ise.fraunhofer.de/press-and-media/pdfs-zu-presseinfos-englisch/2009/press-release-world-record-41.1-efficiency-reached-for-multi-junction-solar-cells-at-fraunhofer-ise-pdf-file

24. NREL Press Release, "NREL Solar Cell Sets World Efficiency Record at 40.8 Percent, " June 25, 2008, http://www.nrel.gov/news/press/2008/625.html

25. Univ. of Delware Press Release, "UD-led team sets solar cell record, joins DuPont on $100 million project," July 23, 2007, http://www.udel.edu/PR/UDaily/2008/jul/solar072307.html

26. Centre for Photovoltaic Engineering of Univ. of New South Wales, "High Efficieincy Solar Cell on N-Type Silicon Substrates," 2002, http://www.pv.unsw.edu.au/Research/heeg_High_Eff_N.asp

27. Harry Atwater, CA Inst. Of Technology , "Photovoltaics: Meeting the Terawatt Challenge," June 24, 2006, http://web.mit.edu/nanoengineering/ENIC06/ENIC2006PVTutorialHAA.pdf

28. René Janssen, Eindhoven Univ. of Technology, "Organic and polymer solar cells 3Y280," April 3, 2008, http://user.chem.tue.nl/janssen/SolarCells/Organic%20%20Solar%20Cells%202008.pdf

Bibliography (cont'd)

29. Helen Gerardi, Princeton University, "Improving Organic Photovoltaic Cells," August 1, 2005, http://www.princeton.edu/~pccm/outreach/REU2005/REU2005Presentations/gerardi.pdf

30. Delft Univ. of Technology, "Delft Outlook: Nano Particles play with electrons," http://www.delftoutlook.tudelft.nl/info/index21fd.html?hoofdstuk=Article&ArtID=2243

31. Alferov, Zhores I., "The double heterostructure concept and its applications in physics, electronics and technology," Nobel Prize Lecture 2000, December 8, 2000, http://nobelprize.org/nobel_prizes/physics/laureates/2000/alferov-lecture.pdf

32. Netherland Research Platform for Sustainable Energy Supply, "New Concepts," http://www.energyresearch.nl/energy-options/solar-cells/research/ru-nijmegen/new-concepts/

33. Layton, Julia. HowStuffWorks, "HowStuffWorks: Squeeze the Light," http://science.howstuffworks.com/luminescent-solar-concentrator1.htm

Appendices