Photovoltaic Manufacturing: Present Status, Future Prospects and Research Needs

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Abstract

In May 2010 the United States National Science Foundation sponsored a two-day workshop to review the state-of-the-art and research challenges in photovoltaic (PV) manufacturing. This article summarizes the major conclusions and outcomes from this workshop, which was focused on identifying the science that needs to be done to help accelerate PV manufacturing. A significant portion of the article focuses on assessing the current status of and future opportunities in the major PV manufacturing technologies. These are solar cells based on crystalline silicon (c-Si), thin-films of cadmium telluride (CdTe), thin-films of copper indium gallium diselenide (CIGS), and thin films of hydrogenated amorphous and nanocrystalline silicon (a-Si:H or nc-Si:H). Current trends indicate that c-Si and CdTe performance are evolving beyond the constraints commonly associated with these technologies. With a focus on TW/year production capacity, the issue of materials availability is discussed along with the emerging technologies of dye-sensitized solar cells (DSC) and organic photovoltaics (OPV) that are potentially less constrained by elemental abundance. Lastly, recommendations are made for research investment, with an emphasis on those areas that are expected to have cross-cutting impact.
I. INTRODUCTION

Global power consumption currently stands at approximately 15 TW (1 TW = $10^{12}$ W), the vast majority of which is generated by the combustion of fossil fuels. The associated release of CO$_2$ from these anthropogenic sources has dramatically altered the composition of the atmosphere and may detrimentally impact global temperature, sea levels, and weather patterns. The terawatt challenge is the effort to supply up to 30 TW of carbon-free power by the mid 21st century.\textsuperscript{1} Assuming that all this power will be supplied by photovoltaics (PV) and the lifetime of solar cells is 30 years, this translates to PV production of $\sim$ 1 TW/year. While all renewable resources will be important, only solar can meet this level of demand. The practical global potential of other renewable energy sources such as wind, hydroelectric, biomass and geothermal is estimated to be less than 10 TW.\textsuperscript{2} Of the $>10^5$ TW of sunlight hitting the earth, it is estimated that harnessing up to 600 TW is technically feasible. Solar energy may be harvested through its conversion to heat (solar thermal), electrons (PV), or chemicals (solar fuels). The former is perhaps the most straightforward, with installations ranging in scale from 1 kW household water heaters to 50 MW power plants located in areas of high solar insolation.\textsuperscript{3} Common approaches to solar fuels include the photoelectrochemical splitting of water to produce H$_2$ and the reduction of CO$_2$ into liquid fuels such as methanol.\textsuperscript{4} Solar fuels remains the least developed strategy to harness solar energy, and is currently the focus of renewed efforts at the basic research level.\textsuperscript{5}

The subject of this article is solar photovoltaics, which has been growing at an average rate of $>40\%$ per year over the past decade, with annual shipments exceeding 8 GW in 2009. That number is projected to double in 2010. Moreover, the market is poised
for further expansion in the next decade as PV transitions from a subsidized commodity to one that provides outright economic advantage. Figure 1 compares the levelized cost of solar electricity with that produced by conventional sources. In 2009, the average cost of grid-supplied electricity in the United States was 9.5 C/kWhr, and this value will continue to rise due to increased demand or at potentially higher rates if measures such as carbon taxation are introduced. The current price of electricity generated using solar cells remains 2 to 3 times greater than grid-supplied electricity, but PV costs continue to decrease. A crossover, commonly called “grid-parity”, is expected sometime during the next decade. In fact, grid parity has been reached in areas such as Southern California where solar insolation and the marginal cost of electricity are high. We also note that projected grid-parity does not require any technological breakthroughs, but is simply an extrapolation of the learning curve that the PV industry has been following for several decades, along with the inevitable increase in the cost of fossil fuel derived electricity.6

Despite this amazing success, PV manufacturing must be further expanded by two orders of magnitude to TW/year production levels in order to transform our society from one that relies on burning fossil fuels to one that uses sustainable energy sources. The challenge is daunting, but the opportunities are equally boundless. The sun continuously provides power to the planet with an average flux of 1000 W/m². If one assumes 10% net conversion efficiency (generation, transportation, storage), ~10¹² square meters would be required to supply 30 TW of clean energy. Assuming 30 year panel lifetimes, this translates into the production of ~5 x 10¹⁰ m²/year. To put this number in perspective, the global production of all flat glass, which is currently dominated by the construction and automotive sectors, is about 6 x 10⁹ m²/year. Glass is an appropriate comparison since it
is common to the majority of current PV platforms, accounting for a substantial fraction of the weight and cost of PV panels.

In May 2010, the United States National Science Foundation (NSF) organized a workshop on the theme of catalyzing innovation in PV manufacturing to help address the challenges described above. The workshop was co-sponsored by four divisions including Chemical, Bioengineering, Environmental, and Transport Systems, Industrial Innovation and Partnerships, Chemistry, and Materials Research. The objectives of the workshop were as follows.

- Identify the potential technologies and innovations that offer low-cost, high-conversion-efficiency and sustainable photovoltaics materials.
- Determine the current and potential technical challenges in preparation and/or manufacture of above photovoltaics materials.
- Facilitate effective and efficient collaborations between small businesses and universities or large companies in the efforts to overcome these challenges.

The event was organized and hosted by Colorado School of Mines in Golden, Colorado. To address this diverse set of goals 60 leaders were invited, with nearly equal representation between industry and academia (Fig. 2). Scientists from National laboratories including the National Renewable Energy Laboratory (NREL) and the National Institute of Standards and Technology (NIST) were also present. A full list of participants, topics, and presentations from the workshop are available online. In this article, we highlight the major outcomes of the workshop. We begin by briefly summarizing the current status of PV manufacturing, and then assess the major
challenges and opportunities with respect to the major PV manufacturing technologies. The aggressive goal of TW/year production capacity necessitated the discussion of the important issue of materials availability for existing technologies. Lastly, recommendations are made for research investment, with an emphasis on those areas that are expected to have cross-cutting impact.

II. PRESENT STATUS OF PV MANUFACTURING

This paper is not intended to provide a comprehensive review of the history of photovoltaics, but rather to update the substantial changes that have occurred since the turn of the century. This date was chosen for a couple of reasons. First, there are a number of very good reviews detailing the growth and evolution of the PV industry up to around 2003. Moreover, there have been two significant changes that have accompanied the growth experienced during the past 7 years. In 2003 various forms of silicon accounted for >99% of the PV market, and manufacturing was lead by Japan and Europe. Today crystalline silicon (c-Si) still accounts for 85% of the market, but China has become the world’s leading manufacturer. Table I lists the top 10 crystalline Si manufacturers and their output in 2009. In a very short period of time China has moved from being a negligible player to supplying 50% of the worlds PV modules. This growth was spurred by strategic government investment, access to cheap capital and has benefited from low Chinese labor costs that enables module production at lower costs than its competitors in Japan, Europe, and the US.

The second major change in the past decade has been the emergence of cadmium telluride (CdTe) thin film technology, which was a negligible contributor in 2003. Figure 3 displays the global market share held by the various PV technologies in 2008 and
A single company, First Solar, has brought CdTe to mass production. In 2009, it became the world’s first PV manufacturer to exceed 1 GW/yr production rate and captured 13% of the global market (Fig. 3). While some of this market share has come at the expense of c-Si, it has also eroded the foothold of competing thin film technologies such as amorphous silicon (a-Si:H). However, the distribution of market share continues to be very fluid, with c-Si expected to regain market share in 2010 due to continued expansion of PV manufacturing operations in China. The most important point is that the emergence of CdTe attests to the fast change the PV industry can undergo within a relatively short period of time. Such shifts are driven by innovations in manufacturing and fundamental science coupled with creative and aggressive entrepreneurship.

Figure 4 displays the champion overall power conversion efficiencies for laboratory solar cells and commercial modules for the established PV manufacturing technologies. Values are from the latest compendium by Green et al.\textsuperscript{13} with the exception of ribbon silicon.\textsuperscript{14, 15} In addition to efficiency, materials and manufacturing costs are the greatest levers controlling the cost of solar power.\textsuperscript{16} In most cases, the champion cells have seen little or no improvement over the past decade while economies of scale and advances in manufacturing science and technology have fueled the expansion of PV through cost reduction and module performance improvements. Figure 4 shows that the PV technologies are at different points in their respective learning curves when compared to the Shockley–Queisser (S-Q) limit of \textasciitilde31\% solar energy conversion efficiency for single junction devices.\textsuperscript{17} Since, the band gap energy dependence of the Shockley–Queisser limit is flat around the maximum, the theoretical efficiency limits for these technologies are only marginally different and are not a deciding factor in their
competitiveness with each other. Nevertheless, record single crystal (c-Si) cells have matured to within 90% of their S-Q limit, while commercial thin film modules harvest about 35% of their potential. The next section reviews the advantages and limitations of these competing PV technologies.

III. Opportunities and Challenges in Current PV Manufacturing Technologies

A. Crystalline Silicon

Silicon is the most developed and well-understood semiconductor in the world, benefiting from decades of development by the integrated circuit (IC) industry. Techniques to control and manipulate its properties are well established. Silicon has proven field stability, and it is the most abundant semiconductor in the world. Multi-crystalline silicon (mc-Si) remains the leading PV product (Fig. 3), though its market share has ebbed from values as high as 65% earlier in the decade. The combination of higher efficiency, lower polysilicon prices, and improvements in wire cutting technology has reduced wafer thicknesses and kept single crystal (c-Si) silicon competitive. The issues that limit the c-Si technology today remain quite similar to those described by Goetzberger et al.,\(^8\) in their detailed 2003 review article. The cost of the silicon feedstock remains the biggest lever impacting manufacturing costs. Reducing the cost of silicon is being pursued through a number of avenues including improving the feedstock, production of kerfless wafers, and the development of ultrathin silicon, as well as the use of bifacial cells. These strategies are briefly reviewed below as well as efforts to further improve module efficiency.
1. **Silicon feedstock**

To date, purification techniques for silicon have been dictated by the IC industry, which employs electronic grade silicon with purity levels of less than 1 ppb. A significant shift occurred a few years ago when the PV industry surpassed the IC industry as the largest consumer of refined silicon. Despite decades of steady growth, this transition apparently caught silicon suppliers by surprise, leading to short-term shortages and price spikes in 2008. However silicon foundries have responded to their leading client by both increasing capacity and examining strategies to develop “solar grade” silicon. Electronic grade silicon is produced primarily using the energy intensive (>120 kWh/kg) Siemens process.\(^\text{18}\) New production strategies such as fluidized bed technology are being investigated to upgrade metallurgical grade silicon, potentially reducing these energy requirements by up to a factor of five.\(^\text{19}\) Though less expensive, these techniques often retain higher levels of metals such as Fe and Al than electronic grade silicon. While these impurities would be catastrophic in IC manufacturing, such low levels may be tolerable in solar cells. An active area of research is focused on establishing the impurity levels, which can be tolerated by solar cells, as well as devising processing strategies to mitigate and/or passivate these defects. Such improvements should reduce both the energy payback time and ecotoxicity associated with silicon production.\(^\text{20}\)

2. **Kerfless wafers**

Improvements in wire-saw technology have enabled the reduction of wafer thicknesses to 180 \(\mu\)m at present. However, over 50% of the silicon is lost as silicon sawdust or Kerf. While this material can be recycled, it would be desirable if the wire-
Sawing step could be eliminated all together. Kerfless wafer could potentially reduce Si use from an industry average of about 6 g/W to 3 g/W at current wafer thicknesses. Techniques for the direct production of wafers from the melt were invented in the 1970s, and after decades of development they have now reached the market. The two closely related techniques are edge-defined, film-fed growth (EFG) and string ribbon silicon technologies. In the EFG process the Si wafers are pulled out from the melt through a graphite die using capillary action. This process was developed extensively by ASE Americas and is now employed by Schott Solar. Ribbon silicon is produced by pulling a pair of high-temperature strings through a crucible of molten Si, and this technology has been promoted and implemented by Evergreen Solar. These two growth techniques produce vertical sheets of mc-Si approximately 300 µm thick and up to a 100 mm wide. The elimination of wafer sawing makes this the most energy efficient mode to produce c-Si, and companies using these methods claim that energy payback times have been reduced to one year. The quality of the material produced by these techniques is somewhat inferior to standard block-cast mc-Si, but is continuously improving with champion laboratory cells now reaching power conversion efficiencies over 18% and 14.5% efficient modules already on the market. Passivation of surface and bulk defects is critical to achieving high efficiency, and this is usually achieved through the deposition of a hydrogen-rich silicon nitride layer, which also serves as an anti-reflection (AR) coating. These technologies are expected to become more cost-competitive as energy costs continue to rise, but improvements in manufacturing are needed to compete with conventional c-Si technology (Fig. 3). In particular, further reductions in wafer thickness coupled to improvements in throughput are viewed as the most important tasks.
for scaling these technologies to TW levels. Increasing the grain size and crystal quality will also be important for further improvements in efficiency.

3. Ultrathin silicon

In this article, ultrathin silicon (ut-Si) refers to solar cell technology where the photon absorbing silicon layer is on the order of 5 – 50 µm thick. Because silicon has an indirect band gap, it is often assumed that silicon must be thicker than 100 µm to effectively absorb light. However simulation studies have shown that ~40 µm is ideal for obtaining maximum performance. Green’s calculations showed that a 19.8% efficient device could be obtained with only 1 µm of single crystal silicon with state of the art surface passivation. If one could produce such materials using a Kerfless process, it would result in an order of magnitude reduction in materials cost with respect to today’s state-of-the-art wafers: thus, ut-Si would merge the benefits of crystalline silicon with those of thin film solar cells. Thin silicon is also amenable to use of bifacial architectures, which harvest light from both directions.

There are a few general approaches to the fabrication of ut-Si. The first strategy employs heteroepitaxial growth followed by lift off or removal of a sacrificial substrate. Material grown at high rates is typically polycrystalline, necessitating the use of post-processing techniques such as laser annealing or rapid thermal processing to produce the desired material quality.

One complication is identifying low cost substrates with appropriate properties for these types of processes. A related approach involves deposition a-Si directly on glass followed by thermal re-crystallization. The third approach involves “peeling”
ultrathin silicon layers off of silicon ingots using techniques such as stress-induced liftoff.\textsuperscript{34} The startup company Silicon Genesis has recently introduced a process where this is achieved through a combination of ion implantation and thermal treatment, producing Kerf-free wafers as thin as 25 microns.\textsuperscript{35}

Substantial challenges remain once ut-Si is produced. Achieving high efficiency will require the use of the most advanced technologies for both surface passivation\textsuperscript{36, 37} and light trapping.\textsuperscript{38, 39} However, results to date are encouraging. The University of Stuttgart has fabricated a 16.7\% solar cell from 45 $\mu$m thick Si produced by lift off, while 8.2\% modules have been fabricated using 2 $\mu$m polycrystalline Si.\textsuperscript{13} Commercialization of such efforts will need to address the nontrivial challenge of mechanically handling these ultrathin wafers while maintaining high throughput and low cost. While ut-Si offers tantalizing benefits with respect to materials utilization, time will tell if process technologies can be developed that can capitalize on this opportunity.

4. Module Efficiency

While crystalline silicon solar cell science and technology is considered to be mature, there remains room to further enhance its efficiency, particularly at the module level. Typical modules fall ~20\% short of record values with respect to both $V_{oc}$ and $J_{sc}$. Efforts to address this include improvements in front side texturing, integration of back side reflectors, and the use of advanced AR coatings.\textsuperscript{40} Another strategy is to reduce the level of shadowing associated with front contacts by either reducing the linewidths or by completely eliminating them using back side contacting schemes such as those employed in Sunpower’s high efficiency modules.\textsuperscript{41} Another problem is that the quantum efficiency in the blue region of the spectrum is limited by high absorption and associated
recombination in the vicinity of the front emitter. This issue is being addressed through the use of selective emitter designs and improved passivation strategies. Crystalline Si is also adopting some of the advanced photon management techniques discussed later in this article in the context of other PV technologies. Through a combination of the strategies discussed above it is expected that mc-Si modules will exceed 20% within the next decade, with c-Si modules approaching 25%, the record in laboratory scale cells.

B. Cadmium Telluride (CdTe)

The first reports of CdTe-related PV devices appeared in the 1960s. However, the development of this technology was fitful, with many stops and starts. The early 90s saw a flurry of improvement that brought efficiencies to levels that began to attract commercial interest. CdTe has a number of intrinsic advantages as a light absorber. First, its band gap of 1.45 eV is well positioned to harness solar radiation. Its high optical absorption coefficient allows light to be fully captured using only two microns of material. Like many II-VI compounds, CdTe sublimes congruently: it vaporizes homogeneously and the compound’s thermodynamic stability makes it is nearly impossible to produce anything other than stoichiometric CdTe. Thus, simple evaporation processes may be used for film deposition. Close-space sublimation employs diffusion as the transport mechanism, while very high rates (>20 µm/min) may be obtained using convective vapor transport deposition.

Standard CdTe-based devices employ a superstrate configuration: production begins with a glass substrate followed by the successive deposition of the transparent conducting oxide (TCO, SnO₂:F), the n-type window layer (CdS), the p-type CdTe absorber, and finally the back contact (ZnTe/Cu/C). As pointed out by Meyers and
Albright, CdTe PV manufacturing is uniquely equipped to be integrated with the production of float line glass. Glass exits a float line at ~600 °C, which happens to be an optimal temperature for vapor-phase deposition of the SnO₂:F (FTO), CdS, and CdTe. Part of First Solar’s success has been due to their ability to integrate these various process steps into an in-line manufacturing process. Several other companies including Abound, Calyxo, and PrimeStar hope to soon join them as major manufacturers.

With low manufacturing costs established, the biggest opportunities for CdTe lie in the improvement of device efficiency. Champion cells (Fig. 4) convert just over 50% of their S-Q potential, while commercial modules are at ~11% power conversion efficiency. Improving efficiency will require enhancements in both current and voltage. The former is perhaps the most straightforward route, as much of the blue region of the solar spectrum is absorbed in the TCO and CdS layers that make up the front contact. Top laboratory cells have replaced the FTO with advanced TCOs such as cadmium stannate and ITO. Likewise, the CdS window layer (2.6 eV) absorbs a significant fraction of the blue light. Integration of advanced front contacts into manufacturing appears to be the near term strategy. This will not be trivial because ITO is expensive and cadmium stannate is a complex material. Furthermore it is not clear what might be used to substitute for CdS though sulfides of zinc and indium have attracted significant interest. Oxygenated CdS is another option.

The more daunting challenge is improving the voltage. The open-circuit voltage (Voc) of champion CdTe cells is well below that of similar band-gap PV materials. For example, the best Voc obtained in CdTe is 230 mV short of GaAs devices, which has a similar band gap. Short carrier lifetimes are at the root of this limitation. The combined
effect of defects and grain boundaries limits minority carrier lifetimes in polycrystalline CdTe to a few nS, even in the best devices. These lifetimes are very short compared to almost 1 µs for epitaxial CdTe or hundreds of ns for CIGS. Sites and Pan showed through simulation that increasing the carrier lifetime or the use of a $p-i-n$ device structures may be two viable routes to increase the efficiency to above 20%. The short term goal of commercial manufacturers is to raise module efficiencies from current levels to >15% by 2014 through a combination of process integration, research, and development. However a recent analysis suggests that this target is overly optimistic, as the current learning curve would put the value near 12%.

A number of fundamental questions must be solved for CdTe PV to move beyond current records and approach 20% efficiency. At present, the issue of extending carrier lifetime is partially addressed by chemical passivation. Examples include the introduction of O$_2$ during CdTe growth, post-deposition CdCl$_2$ treatments, and controlled diffusion of Cu from the back contact. The empirical recipes associated with these processes constitute the “black art” of CdTe manufacturing. Clearly a preferable route would be to understand the nature of the defects states so one could prevent their formation in the first place or develop alternative and perhaps better passivation strategies. Fundamental research in understanding these defects and how to passivate them would be transformative leading to improvements in one of the most promising solar cell technologies. Another fundamental question concerns the role of grain boundaries in these devices. CdTe is an interesting and unusual material in that solar cells based on polycrystalline CdTe outperform devices made using single crystal CdTe. It is thought that grain boundaries can have both positive and detrimental impacts on charge transport,
but the current level of understanding is not sufficient to suggest how one might engineer a desired morphology. The use of $p$-$i$-$n$ structures to create high-efficiency devices requires deliberate control of the sample free carrier density, which is not yet fully understood or achieved. A final area that deserves attention is the back contact. It is difficult to contact CdTe because it has low conductivity. Moreover, the back contact has been implicated as a potential contributor to degradation.\textsuperscript{63, 64} The issues discussed above are non-trivial and will require substantial investment and fundamental research to resolve.

A final issue to be mentioned with respect to large-scale CdTe manufacturing is perceptions with respect to both cadmium toxicity and tellurium availability. The toxicity issue appears to be one of public perception. Cadmium is indeed a toxic element, but the risk of exposure once incorporated into PV modules is minimal. Testing of modules fate during fires, following standard protocols from the Underwriters Laboratory and the American Society of Testing Materials showed that Cd emissions during fires are negligible as Cd is encapsulated in the glass-glass structure of the modules.\textsuperscript{65} Also early testing of leaching of Cd from broken CdTe modules has shown concentrations of the element in water collected over the course of a year to be below drinking water threshold.\textsuperscript{66} More such testing may be needed as module designs have changed since the 90s. To their credit, all CdTe manufacturers are committed to 100% ownership of recycling, which in part is related to the issue of Te availability discussed later in this paper. One also notes that Cd will continue to be produced as a natural byproduct of Zn mining. Perhaps the best argument for CdTe PV is that it serves as a means to sequester this element in an environmentally beneficial manner. While scientific arguments can be
made that the toxicity of Cd is not a significant issue, governmental policy in individual
countries may dictate whether this issue impacts the deployment of CdTe solar cell.

C. Amorphous and Nanocrystalline Silicon (a/nc-Si)

Solar cells based on hydrogenated amorphous silicon (a-Si:H or a-Si) were first
reported in 1976. Silicon layers are deposited by plasma-enhanced chemical vapor
deposition (PECVD) using mixtures of H₂ and SiH₄. Hot-wire chemical vapor deposition
has been offered as an alternative, but has yet to be implemented in large scale
manufacturing. The addition of dopants to a-Si leads to the creation of additional
recombination centers that hinder performance. Because of this effect p-i-n device
structures are almost always used. Benefiting from synergies with the IC industry, a-Si
was rapidly commercialized and the first PV products appeared in the early 1980s. Early
devices rapidly surpassed 10% efficiency, but it was quickly recognized that these
devices suffered from light-induced degradation through the now well-known Staebler-
Wronski effect: light exposure leads to a reduction of the solar cell efficiency over
months which eventually stabilizes at efficiencies around 6-7%. Nevertheless, for
decades, a-Si was by far the most successful thin film technology, achieving market
shares approaching 10% early in the decade before falling and being surpassed by CdTe
a few years ago (Fig. 3).

Leading manufacturing and equipment supplier companies for a-Si include Sharp,
United Solar, and Oerlikon. One of the most attractive features of a-Si is that devices can
be deposited at low temperature (< 200 °C), enabling the fabrication of lightweight,
flexible laminates on temperature sensitive substrates. This is a unique trait that provides
a competitive advantage in markets such as consumer products and building integrated
photovoltaics (BIPV). Though discovered much earlier, another major change that has occurred over the past decade is the integration of micro (\(\mu\)-c-Si) or nanocrystalline (nc-Si) into device structures. The quality of PECVD deposited material is strongly influenced by the level of silane dilution in hydrogen, and high \(H_2\) dilution levels (>90%) lead to the formation of crystalline domains within the material. The primary advantage of nc-Si is that it is much less susceptible to Staebler-Wronski degradation. Another important feature is that a/nc-Si is the only thin film PV technology that has proven amenable to the formation of multi-junction devices. Most commercial devices are based on either tandem cells or even triple junction cells. A common configuration is the “micromorph” tandem, which pairs an a-Si top cell with a nc-Si bottom cell. Solar cells with record efficiencies are based on triple junctions that employ germanium alloys to further improve absorption in the red region of the solar spectrum. A related success story has been the introduction of the a-Si/c-Si heterojunction with intrinsic thin layer or HIT cell, which boasts 21% conversion efficiency. The intrinsic a-Si:H layers appear to be important for passivation of the underlying c-Si material.

Despite its distinguished history, the next decade will prove critical to amorphous silicon technology’s long-term viability. While necessary to improve stability, the transition from a-Si to nc-Si has come at an expense. Due to its relatively low absorption coefficient, nc-Si based devices need to be up to five times thicker than a-Si to collect sufficient light. This issue is exacerbated by the fact that the deposition rates for nc-Si are much lower than those for a-Si. Combined with the relatively low efficiencies, this has made manufacturing of a-Si/nc-Si based solar cells relatively expensive when compared to alternative technologies such as CdTe. Efforts to improve deposition rates include (1)
use of very high frequency (VHF: 25 – 100 MHz) plasma sources (2) operation at higher pressures and (3) development of linear plasma sources to maintain large area uniformity with VHF modulation.\textsuperscript{77-79} Another approach is to deposit nc-Si directly from silane without the need for excess H\textsubscript{2} dilution.\textsuperscript{80} The use of \textit{in situ} diagnostics such as optical emission spectroscopy our powerful tools to help advance these processes.

The other thrust to improve efficiency is focused on using advanced photon management techniques such as plasmonics, index matching, and improved antireflection coatings to reduce the silicon film thickness requirements. Despite these efforts, the relatively low champion cell efficiencies and lack of advancement over the past decade suggest that these efforts may not significantly reduce the cost/W\textsubscript{p}. These challenges may prove difficult to overcome in order to make a/nc-Si competitive in the utility grid sector. Barring a significant breakthrough, a/nc-Si may need to focus on market sectors that benefit from its low temperature, low weight capability. Another strategy might be to examine if a-Si could be used as a route to form ut-Si, perhaps by coupling with rapid thermal processing (RTP).

\textbf{D. Copper Indium Gallium Chalcopyrites (CIGS)}

The first copper chalcopyrite PV devices were also introduced in 1976 in the form of copper indium diselendide (CuInSe\textsubscript{2} or CIS) by Kazmerski and co-workers.\textsuperscript{81} CIS has a band gap of 1 eV. However the band gap may be continuously engineered over a very broad range (1 – 2.5 eV) by substituting either Ga for In or S for Se. The abbreviation CIGS(S) is now used to describe this material, as current manifestations often involve either four or all five elements. Much like CdTe, the development CIGS followed a combination of starts and stops. The early 1990s brought a rapid succession of
improvements that elevated device efficiencies to over 16%.\textsuperscript{82,83} While most PV technologies have recorded little or no improvement in champion cell performance over the last decade, CIGS has continued a steady advance and recently crossed the 20% threshold, making it the clear efficiency leader among thin film technologies.\textsuperscript{13} Commercial production of CIGS began in earnest in 2007, and several companies are now operating facilities with 10-30 MW/year capacities. Substrates include soda lime glass, metal foils, or high temperature polyimide (PI). The latter has garnered substantial interest for applications such as BIPV and portable power. In the case of deposition on flexible substrates it is critical to match the coefficient of thermal expansion, with highest efficiencies obtained on titanium and stainless steel foils. The insulating nature of PI is advantageous for monolithic integration, but process temperatures are limited to <450 °C, which limits efficiency. Groups are also pursuing lift-off techniques,\textsuperscript{84} which would could decouple processing temperature from choice of substrate.

The basic structure of the CIGS device is quite similar across manufacturers. Fabrication begins with the deposition of a Mo back contact followed by the \textit{p}-type CIGSS absorber (1-3 µm), a thin buffer layer (50-100 nm), with doped ZnO serving as the transparent front contact. Here the similarities end. Scores of firms are working to commercialize this technology, and each appears to employ a somewhat unique strategy, particularly with respect to formation of the CIGSS absorber. A recent issue of Progress in Photovoltaics was completely dedicated to the topic of chalcopyrite thin films,\textsuperscript{85} and the reader is directed to the papers in that issue for a more comprehensive overview of these topics. At present, the performance of commercial modules is 60-70% of the efficiency of champion cells, with much of this difference attributed to the quality of the
The approaches to CIGS fabrication may be classified into three basic categories: co-evaporation, selenization/sulfurization of metal films, and non-vacuum techniques. Here we assess the major advantages and issues associated with each, and conclude this section by addressing the other major issues that impact CIGS manufacturing.

1. Coevaporation

Coevaporation is the process that has produced world-record cells, and typically employs some variant of the three stage process developed at NREL. This process alternates between copper-rich and copper-poor conditions to produce the large grains and graded Ga/In profiles characteristic of high efficiency material. Companies such as Q-Cells and Global Solar are pursuing in-line production using co-evaporation. There are a number of important practical challenges involved in the manufacturing of CIGS solar cells. Evaporation sources typically have a cosine flux distribution, and it is difficult to introduce sharp changes in composition or maintain uniformity over large areas under the diffuse conditions of high vacuum. In addition, sources must be mounted in a top-down configuration in order for large glass substrates to be supported and heated to 600 °C. In situ diagnostics such as thermometry and laser light scattering, which are critical for process control in the batch process, are being adapted for use in the manufacturing environment. Likewise, atomic absorption spectroscopy and X-ray fluorescence are employed for controlling element flux and in-line detection of film composition, respectively. Another challenge with co-evaporation is that the relatively unreactive Se must always be supplied in great excess, leading to practical concerns related to condensation and materials management. Despite these challenges Q-Cells has
announced 12-13% mass-produced modules and a 14.2% champion module with this process. Through systematic optimization and accompanying improvements in yield this may turn out to be a viable large-scale manufacturing strategy.

2. **Metal Selenization/Sulfurization**

Another method for synthesizing CIGS films is selenization or sulfidization of a stack or alloy of the constituent metal films predeposited on a substrate in a predetermined stoichiometry. There are many variations of this approach but essentially this is a two-step process where in the metals are sputtered onto the substrate and then converted to CIGS through annealing in a chalcogen-containing environment. Practitioners include Showa Shell Solar, Honda Soltec, Johanna Solar Technology, Avancis, and Sulfurcell. The chalcogen utilization can be improved by more than an order of magnitude as compared to chalcogen utilization during co-evaporation.

In general these two step approaches try to mimic the composition profiles of champion absorbers by functionally grading the composition of the initial Cu/In/Ga precursor and optimizing the annealing conditions. The latter process may employ either selenium or sulfur, and the most common approach employs both, in what has come to be known as sulfidization after selenization (SAS) schemes. The chalcogen source can be either elemental vapors or hydride gasses (H₂Se/H₂S). The latter have the advantage of being more reactive and easy to control, though they present safety concerns due to their toxicity. The presence of hydrogen does not appear to be detrimental and the gas sources seem to be the preferred choice. There are many pathways and intermediates involved in transforming the metal into the chalcopyrite, requiring careful optimization of the time-temperature-reactant profiles employed. The SAS scheme creates a CIGSS surface,
with may be advantageous for band gap profiling as well as improving the interface with the window layer, which are also sulfides (CdS, ZnS, In$_2$S$_3$). The best module efficiency obtained with this process have been as high as 15.7%.86

3. **Solution Processing**

The third general approach to CIGS manufacturing has been to eliminate vacuum processing. In general these are also two-step processes, application of a coating followed by a high temperature step for annealing or sintering. Ostensible advantages include reduced capital requirements, improved materials utilization, potentially lower energy requirements, and compatibility with roll to roll (R2R) processing.90 A general challenge with the non-vacuum based approaches is the potential of contamination introduced by either the compounds themselves or the solvents employed. As such, it has been much harder to produce dense, homogenous absorber layers. It is also more challenging to produce chemically-graded structures with this technique. Record cell efficiencies trail co-evaporation and metal selenization, but values up to 14% have been obtained by a number of techniques.

The non-vacuum strategies may be further divided into electrodeposition, particulate deposition, and solution processes. Electrodeposition has been around for decades91 and achieved cell efficiencies as high as 13.8%,92 but concerns about up scaling appear to have limited commercial interest. The particulate route is currently the most actively pursued, with variations employing particles composed of CIGS, metal, metal oxides, and/or metal selenides. In all of these methods a coating of particles is first formed on the substrate surface and reacted and/or sintered at high temperature to form the final film. It was found that CIGS particles required excessive temperature for
Likewise, problems with handling and premature oxidation have limited the utility of metal particles. The best results have come using slurries containing mixtures of metal oxide or selenide powders. This approach was pioneered by Kapur and co-workers at ISET, and more recently championed by Nanosolar. The latter has reported 14% efficient cells, and has stated that 10-11% modules will be available by Fall 2011. Solution approaches have employed the use of soluble metal salts, organometallics, and hydrazine-based compounds. Best results have been obtained with the latter, however the highly reactive and toxic nature of hydrazine poses additional complications for manufacturing.

4. Materials Chemistry

With five elements and numerous binary and ternary phases, the CIGSSS system presents much greater complexity than the PV technologies described previously. Extensive theoretical work has made great advances in understanding the electronic structure and role of defects in this system. These studies have been aided by improvements in advanced characterization techniques. Raman and time resolved photoluminescence are becoming useful for identifying the presence of secondary phases and certain defects. It is well-known that sodium plays a critical role in the morphology and electronic properties of CIGS. When soda lime glass substrates are used, sodium diffuses into the CIGS layer from the glass. Once the importance of Na was realized, more controlled and systematic approaches that employ sputtered layers of Na-containing material have been developed to gain control over Na introduction into the CIGS. There is also significant attention being paid to the window layers deposited on the CIGS absorber. While CdS remains the leading choice, both indium and zinc sulfides are being
pursued and in some cases commercialized. Part of the interest is due to the desire to remove Cd, but a second motivation is improving the blue response of these devices. There are strong interactions between the buffer and the underlying absorber, and simultaneous optimization of these layers is required for best performance. Some concerns remain about the use of ZnO as the front TCO, and its potential impact on long-term device stability. Moisture exposure is particularly detrimental, both to the TCO and the heterojunction itself. Encapsulation in glass partially alleviates this effect, but further development of transparent ultrabarriers is required to improve the long term stability of flexible CIGS solar cells.\textsuperscript{101}

A longer-term concern is the availability and price of In. Recycling of indium will alleviate constraints on CIGS long-term production, but research is needed to develop technologies for efficient and low cost recycling of all the elements from the CIGS modules. The possibility of substituting indium/gallium with earth abundant alternatives such as zinc/tin is discussed below.

**IV. Materials Availability at TW/year Manufacturing**

Manufacturing solar cells at a rate of 1 TW/year will be a colossal undertaking, and a basic question to be asked is “are sufficient material resources available?” The two elements of concern most often discussed are tellurium and indium.\textsuperscript{102, 103} The former is a byproduct of copper mining, while indium is a byproduct of zinc extraction. Tellurium is one of the least abundant elements in the earth’s crust, comparable to the platinum group metals. However, there is great debate and uncertainty in the assessments of Te resources, with the level of concern ranging from critical\textsuperscript{104} to manageable\textsuperscript{105} to non-
existent. Protagonists point to recycling programs and the recent development of mining Te directly as opposed to depending on byproduct streams. Antagonists point to even most optimistic estimates that project a production rate at around 200 GW/year. Pessimistic estimates put this number at ~ 20 GW/year. With a lifetime of 30 years this rate can only supply 0.6-6 TW of the world demand. The upper end of this estimate is a significant amount but still represents only about ~20% of the projected 30 TW demand later in the century.

Indium is also scarce, and there are concerns about its price and preferred use in higher value products such as flat panel displays. One concern is that rising demand will increase prices of indium and tellurium by several factors so that the absorber material will become more expensive and larger fraction of the materials cost. Such a rise can quickly erode the cost advantages of CdTe and CIGS thin film technologies.

One issue that is often overlooked in these discussions is that if materials availability becomes the determining factor, the standard for comparison reverts back to c-Si. Wadia et al. argued that many other compounds would be preferable to silicon based on the energy involved in its extraction and purification. However with energy payback times at 1-2 years and continuously decreasing, that becomes less of a concern. Their analysis focused on the absorber materials, which is a small fraction of the overall contribution to the material costs involved in thin film PV. Glass and other materials used in module construction are the largest factor in the total cost, and they are universal to all technologies. In addition to silicon, PV technologies without significant material constraints include dye-sensitized solar cells (DSC), organic photovoltaics (OPV), as well as earth abundant inorganics, and each are reviewed briefly below.
A. **Dye-sensitized solar cells**

Dye-sensitized solar cells are based on the photoelectrochemical effect discovered by Bequerel in 1839. A relatively new concept, DSC was introduced by Grätzel and co-workers in 1991.\textsuperscript{108} A comprehensive review on the complex chemistry and processes involved in this system was recently published by Hagfelt and co-workers.\textsuperscript{109} This hybrid material is typically composed of organometallic dye molecules adsorbed to a mesoporous titania nanoparticle film, with the pore space filled by an electrolyte. In this structure light is absorbed by the dyes, which then inject an electron into the conduction band of a wide band gap semiconductor like TiO\textsubscript{2}. The electron is transported by hopping through the nanoparticle network to the front contact where it exits and performs useful work before returning to the platinized back contact. Here the electron reduces a redox couple, which in turn diffuses through the electrolyte and regenerates a dye molecule to complete the cycle. Dye sensitization of oxides was well-known at the time, and Grätzel’s key innovations were in creating a nanoparticle film with high surface area to improve light harvesting and in choosing components with appropriate kinetics for fast charge transfer and slow recombination. Grätzel’s group rapidly optimized the device to over 10% within a few years of its introduction.\textsuperscript{110} This brought the attention of industry and today a number of small companies including G24i, Solarprint and Dyesol are engaged. Most current products are directed at the consumer market; for example, DSC on flexible substrates that replace rechargeable batteries for portable electronics. A beneficial feature of DSC is that their performance improves under diffuse and low light conditions,\textsuperscript{111} enabling their use indoors and without direct solar exposure. Devices can be fabricated in a number of colors and levels of transparency, which is an attractive
feature for architectural and BIPV applications. Manufacturing can also be done at low temperature using flexible substrates.

Unfortunately, champion cell efficiency has been stagnant at ~11% for the past 15 years (Figure 5). The three main components in a DSC, the Ru-based dye, the photoanode, and the iodine-based redox couple, have also remained largely unchanged. Further optimization of any one of these components individually is not likely to yield significant improvements in efficiency. The recent review by Hamann and co-workers\textsuperscript{112} provides an excellent overview of the complexity of the issues involved. First, the leading dye does not capture much light past 750 nm, and harvesting the red and near-infrared portion of the spectrum is needed to increase current densities. In addition, replacing Ru is an important long-term concern with respect to materials availability. Second, the $\text{I}_3$/I\textsuperscript{-} redox couple is positioned with a 550 mV overpotential relative to dye regeneration. An alternative redox couple could potentially allow the $V_{oc}$ to be improved by up to 300 mV, but recombination rates are typically much faster with non-iodine redox couples. A combination of these two changes could elevate device performance to $>16\%$. However as cautioned by Hamann and colleagues,\textsuperscript{112} this will most likely require simultaneous optimization of both dye and electrolyte and perhaps the development of new photoanodes with faster charge transport as well. While there are photoanode designs based on wide band gap semiconductor nanowires that attempt to improve efficiencies, six years after their first introduction, the efficiencies remain low.

With respect to manufacturing numerous module fabrication strategies are being pursued, which in general can be divided into monolithic or sandwich constructions. The former offers advantages with respect to materials cost, while the latter may be more
amenable to R2R processing. Substrates include glass, metal, and polymer foils, with best performance being obtained on glass. Critical issues include stability and the production of large area modules. At present mini-modules with areas < 100 cm² are used, with resistance losses being one of the major challenges. The stability of a DSC module is strongly related to the device encapsulation. Standard practices for lifetime and stability testing, such as IEC61646 for thin film PV, do not exist for DSC. However, long-term light soaking at 55-60 °C under resistive load has shown that efficiencies remain above 80% of their initial value for over 25,000 hours.¹¹³ These Dyesol data on a ~1 cm² cell indicate that carefully encapsulated glass-based DSC can last for over 20 years in a typical Middle European climate. The longest outdoor test of DSC modules (110 cm²) by Toyota and Asin was 2.5 years, showing efficiency losses of 6% (relative) per year.¹¹⁴ Faster degradation could be attributed to differences related to sealing methods, cell/module area, or environment. Hermetically sealing flexible DSC is more challenging, and current products using DSC on plastic substrates have lifetimes of only a few years. For outdoor applications, the sealing material must, for example, be mechanically and thermally stable, stable under UV exposure, and chemically inert to the electrolyte. Moreover, it should prevent mass transport between adjacent cells. The issue is so important that Hagfelt et al. ¹⁰⁹ suggested that the leading manufacturing approach for DSC may be the one that provides the most functional encapsulation method. Replacing the liquid electrolyte with a gel or solid would greatly reduce encapsulation requirements, but these changes have resulted in decreased efficiency. Elimination of glass, implementation of R2R manufacturing methods, and increased lifetimes will be critical to economics, particularly if device efficiency remains below 12%.
B. Organic PV (OPV)

Carbon is abundant, and the potential for high volume manufacturing of flexible photovoltaics has spurred extensive efforts to develop solar cells using organic semiconductors. Brabec and colleagues\textsuperscript{115} recently provided a comprehensive review of the developments in OPV over the past decade and the challenges that lie ahead. Figure 5 charts the progress of champion cell efficiencies for the past 15 years. While most technologies have been relatively stagnant in their champion efficiency, organic PV has made great strides in the past decade, with Heliatek and Konarka being the current champions, each with devices certified at 8.3\%.\textsuperscript{116, 117} Many leading developments have occurred in the private sector, with other companies such as Solamer and Plextronics having held the efficiency record in recent years. OPV devices are comprised of a heterojunction between an electron donor molecule (e.g., P3HT, poly(3-hexylthiophene) or CuPC, copper phthalocyanine) and an electron acceptor molecule (e.g., C$_6$0 or its derivatives such as PCBM, phenyl-C$_{61}$-butyric acid methyl ester).\textsuperscript{118} The essentially limitless varieties of candidate organic semiconductor materials may be categorized as either solution-processable (polymers, dendrimers, oligomers, or small molecules) or vacuum deposited (small molecules or oligomers). Although superficially similar to inorganic $p$-$n$ junctions, the OPV junction is fundamentally different. Instead of directly creating an $e^-/h^+$ pair, photon absorption produces an exciton, an uncharged excited state that must diffuse to a donor/acceptor interface in order to dissociate into a free $e^-/h^+$ pair. In organic materials the exciton can typically only diffuse 5-10 nm before decaying to the ground state, a problem that limits performance and is typically referred to as the exciton bottleneck. There are two ways to deal with this. One can make a multilayer device that
uses very thin donor/acceptor layers such that a majority of excitons can diffuse to a heterojunction interface. This approach is commonly used in vacuum deposited devices. Or one can reduce the distance the exciton has to diffuse before reaching the heterojunction by mixing the donor and acceptor materials on a nanometer length scales to form a single-layer interpenetrating bicontinuous network called a bulk heterojunction. This approach is commonly used in solution-processable materials.

In the OPV device structure, the heterojunction active layer(s) is(are) sandwiched between a set of contact electrodes, with buffer layers likely to be present. In the bulk heterojunction approach an asymmetry in the device must be imposed by either using electrodes of different work function (typically a front TCO contact modified with a conducting polymer PEDOT-PSS, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) and a back contact metal of Ca or Al) or by inserting a buffer layer that blocks carriers from leaving one side of the device. An oxide buffer layer is commonly inserted to block holes from leaving the device through the front TCO contact, which inverts the direction of operation of the device and allows the use of a high workfunction Ag back contact. In the vacuum deposited multilayer approach, co-doping of buffer layers has been used to great effect to produce a true p-i-n structure that obviates the need for a mismatch in the contact work-functions.

There are several challenges to improve the efficiency of organic solar cells. These are being addressed through the development of novel donor and acceptor materials, new buffer layer and electrode geometries, innovative processing, and through the use of tandem architectures. A key issue is to significantly raise the short circuit currents ($J_{sc}$) to above 20 mA/cm$^2$. Present values are typically 10-12 mA/cm$^2$ with
champion values approaching 17 mA/cm². The main problem is that leading
photoactive layers do not efficiently harness photons in the red and infrared region of the
solar spectrum. Significant efforts have been directed at developing improved low band
gap polymers. Advanced photon management strategies are also being pursued to
increase optical density. A second challenge is to increase the open circuit voltage.
Key to this is achieving optimal band alignment of the device structure and minimizing
the band offset between donor and acceptor molecules while maintaining efficient charge
transfer. It is predicted that the maximal $V_{oc}$ in a standard donor-acceptor device is
0.6 V less than the bandgap energy/$e$. Thus the goal is for a $V_{oc}$ of 0.8 – 0.9 V for low
band gap absorbers with band gaps ~1.4 – 1.5 eV. $V_{oc}$’s above 1 V have been achieved,
but only with high band gap materials. Third, the fill factors (FF) have to be increased
beyond 0.7, which has been achieve in only a few champion devices. Organic solar
cells typically have poor FF relative to conventional $p$-$n$ junctions. This is due to high
series resistance and/or carrier recombination as the carrier mobilities in organic thin
films are lower than their inorganic counterparts.

Simultaneous achievement of $J_{sc} = 20$ mA/cm², $V_{oc} = 0.8$ V, and FF = 0.7, leading
to an efficiency of 11% has not been achieved yet. Doing this in a single junction device
will require simultaneous optimization of all the materials and interfaces. A possibly
faster route to this goal will involve the use of tandem configurations. These have been
demonstrated using the bulk heterojunction approach and are being used to effectively
boost efficiency in the evaporated small molecule approach as implemented for instance
by Heliatek. Passing the psychological milestone of 10% efficiency could bring organic
solar cells within striking distance of the existing thin film technologies, particularly
because manufacturing costs are expected to be low. With existing materials and devices, the energy payback time for OPV has been estimated to be between 0.3 - 3 years. This relatively high level of uncertainty reflects the range of assumptions used for this still developing technology. However, an efficiency of closer to 15% may be needed to achieve a true grid parity LCOE of ~$0.07/kWh. Much work still needs to be done to demonstrate acceptable performance in large area modules. At present OPV submodule (200 cm²) efficiencies from leading companies are approaching 4%. This value lags substantially behind the 9.9% efficiency in comparable sized DSC modules. Also, published champion OPV devices are fabricated on glass. To be economical, the substrate will likely need to be a low cost flexible material that is suitable for R2R processing.

Another important issue that has to be resolved is the stability of organic solar cells. The chemical, physical and mechanical degradation that are predominant in OPV materials and devices have been well discussed. The list of failure mechanisms of OPV cells is long and certainly as extensive as for any other photovoltaic technology. Major issues include photodegradation and the sensitivity of OPV components to oxygen, requiring the use of ultrabarriers for encapsulation. The current goal is to increase lifetimes from 3 to 5 years, which is expected to be sufficient for consumer applications. Due to the flexibility of organic synthesis, it can be estimated that there are on the order of 10¹³ different material combinations that could be employed. Whether the right combination of properties (e.g., band gap, charge mobility, exciton diffusion length, etc.) exists and how to identify them remain open questions. Optimizing the photoactive organic layer may be best addressed using a combinatorial approach. On the
other hand, candidate structures and trends may be identified using a rational method that combines computational methods with targeted synthesis.

C. Inorganic Thin Films from Earth Abundant Elements

This final class of materials includes metal oxides and sulfides that have band gaps in the range of 1 – 2 eV. Notable examples include cuprous oxide\textsuperscript{135} and fool’s gold (pyrite),\textsuperscript{136} but the most successful system to date has been copper-zinc-tin-sulfide (selenide), or CZTS.\textsuperscript{137} Pioneered by Katagiri,\textsuperscript{137} in the past decade champion CZTS devices have gone from less than 3\% to approaching 10\% efficiency (Fig. 5). These results have come with only a handful of publications. CZTS shares great similarities with CIGS, including similar device structures and fabrication techniques for the formation of the absorber layer. Initial studies focused on sulfidization of metal layers,\textsuperscript{138} but more recently co-evaporation\textsuperscript{139} and non-vacuum techniques\textsuperscript{140-142} have garnered significant attention. The current efficiency champion includes Se and was derived from hydrazine precursors.\textsuperscript{142} The similarities to CIGS may have accelerated CZTS solar cells’ initial success, but these same similarities may become limitations in the long run. Nevertheless the great success observed to date based on rather little investigation argues that these materials are deserving of further investment.

V. FUTURE OUTLOOK AND RECOMMENDATIONS

A. Redefining the boundaries of PV technologies

Photovoltaic technologies’ are often classified as being either 1\textsuperscript{st} generation (c-Si), 2\textsuperscript{nd} generation (thin film), or 3\textsuperscript{rd} generation concepts that have the potential to overcome the S-Q limit such as devices that employ multi-junctions, extract hot carriers,
or involve multiple electron/exciton generation. In 2001, Green formally classified the potential of 1st, 2nd and 3rd generation technology with respect to both power conversion efficiency and manufacturing costs, and his diagram is reproduced in Figure 6. The quotient of these two variables is proportional to the cost/W, which is reflected by the dashed lines in Fig. 6. The shaded ovals represent the original assessment of the three generations provided by Green. Advocates of DSC and OPV often describe these platforms as 3rd generation concepts. However it should be noted that Green did not make that distinction, limiting his definition to those concepts that can exceed the S-Q limit. In practical terms DSC and OPV should be considered thin film technologies, ideally competing for the low cost region of oval II in Fig. 6.

One of the key points that came out of the workshop discussions was the idea that these accepted boundaries have become outdated. In particular, it has become clear that CdTe and c-Si are not bound by the limits imposed by Green’s original figure. The current status and projected future of these two technologies have been added to Fig. 6. The point for CdTe reflects the present status of First Solar’s technology, which is based on 11.2% modules and self-reported production costs of $0.77/Wp, putting it on the fringe of the 2nd generation domain. The arrow indicates the expected potential of this technology based on the discussions above. Through improvements in efficiency and further integration of manufacturing it is not unreasonable to expect CdTe manufacturing costs to drop below $0.5/Wp within the next decade.

The diversity of products makes the situation for c-Si more complex to analyze, but the revised oval for c-Si also sits on the edge of the initial bounds proposed by Green. Module efficiencies range from 15–22%, with leading production costs as low as
$1.10/W_p$ reported by Trina Solar in the second quarter of 2010. Again, the arrow leaving the oval represents the future potential of this technology as discussed above. Here the largest gains are related to further reduction in the productions costs through reduction in Si requirements, as well as boosting module efficiency closer to 25%. This combination provides a pathway that approaches $0.5/W_p$. Some may find this projection overly optimistic. However, one of the enlightening consequences of First Solar’s emergence has been the ability of the x-Si industry to rapidly respond and reduce its costs. It is also important to note that silicon does not have to move as far as CdTe. As module costs drop below $1/W_p$ they become increasingly less important, as balance of systems issues including inverters, racks, installation, and space become important cost drivers. These costs drop with module efficiency, and thus silicon can afford to remain competitive despite higher manufacturing costs than CdTe. It is too early to project what may happen to CIGS, though it is plausible to expect that it might end up in a similar region, most likely somewhere between CdTe and c-Si.

The discussion above on Green’s chart and PV classification is pertinent because it has been highly influential on the overall landscape of research activity supported by agencies such as NSF, the Department of Energy, and similar agencies around the world. This can be quantified by examining the publication trends. In the past decade, extensive resources have been invested in pursuing 3rd generation concepts, DSC, and OPV. These investments are reflected by the number of publications in each subject. Figure 7 displays on a semi-logarithmic scale the number of papers returned by Web of Science each year in the past decade in response to a keyword search of “solar” + a selected adjective. Any such study is imperfect, though alternative keywords
(photovoltaics, solar cells, etc.) yielded very similar results. The numbers reported here are also in quite good agreement with those cited in reviews of individual technologies.\textsuperscript{109, 128} The leading PV manufacturing technologies (c-Si, CdTe, CIGS) each return only 60-100 pubs/year, and those numbers have remained essentially unchanged over the past decade. In contrast, the interest in each of the next generation technologies (DSC, OPV, nano*) has grown exponentially, expanding by an order of magnitude over the past decade and currently averaging \~\textasciitilde1500 pubs/year in each topic. This asymmetry raises a red flag that many fundamental aspects of conventional technologies may not be adequately investigated. This point was made salient at the workshop, where representatives from thin film PV manufacturing companies lamented the dearth of graduates ready for employment who are skilled in areas relevant to their needs. The situation is not as bad in c-Si, which has benefited from crossover and displacement from the IC industry.

There have been numerous scientific breakthroughs in the area of 3\textsuperscript{rd} generation PV,\textsuperscript{144-147} but practical devices are far from the point of commercialization.\textsuperscript{148, 149} In general 3\textsuperscript{rd} generation PV rely on the use of nanostructures such as quantum dots and nanowires to generate the desired effects. A critical yet unresolved problem with devices that employ such structures is that they will be dominated by interfaces. Interfaces are integral to PV (the $p$-$n$ junction), but their density should be minimized. Interfaces typically serve as either recombination centers or barriers to charge transport, and the demonstrated pathway to high efficiency has been through their elimination. Record heteroepitaxial multi-junction cells are produced by molecular beam epitaxy.\textsuperscript{150} The detrimental impact of interfaces is quite plainly seen by comparing the performance
within the silicon system (c-Si > mc-Si > nc-Si > a-Si). Likewise, record CdTe and CIGS thin film devices are characterized by their large grain size.\textsuperscript{151}

\section*{B. Cross-cutting areas for investment}

Five challenges and topics that cut across the boundaries between the PV technologies discussed above are discussed as areas that warrant additional research investment.

1. \textit{Development of National User Facilities for Photovoltaic Manufacturing Research}

All PV technologies discussed here have matured to a point that future advances will require simultaneous optimization of the many components that constitute a complete solar cell. An innovative process or new material may have tremendous intrinsic properties, but its value cannot be accurately assessed or fully exploited until integrated into a complete device structure. This poses a major barrier for both small business and university researchers alike, who most often cannot maintain the infrastructure of a full solar line. User facilities that would provide robust process lines on which researchers could test and develop their innovations is a critical link in the technology development chain that is currently missing in the United States.

An excellent model that one might follow is the National Nanotechnology Initiative (NNI), which involves multiple government agencies and has invested $14 billion USD over the past decade into building infrastructure to promote and facilitate research, development, and technology transfer related to nanotechnology.\textsuperscript{152} Within the NNI framework is an integrated partnership of fourteen user facilities, supported by NSF,
providing unparalleled opportunities for nanoscience and nanotechnology research. We advocate that a similar investment be made in photovoltaic manufacturing science, perhaps organized with facilities focused on individual process technologies. Such facilities would dramatically accelerate the rate at which innovation can be harnessed to meet the terawatt challenge. Such an investment would require a substantial commitment, but it is fully justified in light of both the importance of sustainable energy to humanity and the clear economic opportunities afforded by PV manufacturing.

2. **Advanced photon management**

The importance of this topic is self-evident as this phrase was used in conjunction with the discussion of nearly every technology. Typically, advances and improvements in efficiency involve materials that are applied externally to the cell, allowing them to be developed independently without impacting cell designs that are highly optimized. This decoupling is important because strategies and materials can be used in different technologies. Specific topics within this area, in order of increasing complexity are as follows.

1) **Antireflection Coatings.** Multi-layer or nanostructured antireflection coatings can extend photon collection both across the spectrum and at diffuse angles beyond normal incidence.\(^{153}\)

2) **Increasing the Path Length through the Absorber.** Texturing, microstructures, or nanostructure-based on plasmonics divert photons coming normal to the surface to more oblique angles, increasing the path lengths of these photons through the absorber and, thus, the probability of absorption.\(^{39}\)
3) **Optical field enhancement.** Plasmonic enhancement of the optical field in the vicinity of a metal nanoparticle is used to increase optical absorption and hence carrier generation.\(^{154-156}\)

4) **Downshifting.** This is the process of converting high-energy UV and blue photons, and downconverting their energy to the middle of the visible spectrum where quantum efficiency values typically approach 100\%.\(^{157}\)

5) **Downconversion.** Often called photon splitting, this is the process of transforming one high energy photon into two photons that still have sufficient energy to create electron-hole pairs.\(^{158}\)

6) **Upconversion.** This is the reverse process whereby two low energy photons are combined to produce one high energy photon that is capable of generating an electron-hole pair.\(^{159, 160}\)

These last two processes are a very long way from being practical, but provide perhaps the best opportunity to truly surpass the S-Q limit by altering the solar spectrum to produce a photon distribution that is more aligned with the requirements of a single junction device.\(^{157}\)

3. **Can glass be replaced?**

This is a simple but critical question. A detailed analysis of thin film manufacturing suggested that under optimal conditions manufacturing costs could be reduced to about $40 -50/m\(^2\) through economies of scale.\(^{107}\) It is not realistic to expect costs to be any lower for any technology that requires the use of glass and a transparent conducting oxide. A low cost, light-weight alternative that provides the same level of
transparency, protection, and thermal stability would be nothing short of revolutionary. A positive answer to this question is essential if technologies such as OPV and DSC are to become cost-competitive for principal power generation.

4. **The science of manufacturing**

With champion efficiencies nominally plateauing (Fig. 5), the continued reductions in cost/W<sub>hp</sub> observed during the past decade has been due almost exclusively to advances in manufacturing technology. Manufacturing and process development is often overlooked as empirical knob turning, but there are many fundamental issues that have not been addressed. Development of competitive manufacturing techniques requires sophisticated modeling to understand how to maintain uniformity with respect to both space and time. Accompanying this goal is the development of in-line diagnostics for real time process control. The previous two topics presume a fundamental understanding of how process conditions relate to materials chemistry and device performance, which simply does not exist at a satisfactory level for the thin film technologies. Developments in intelligent and potentially self-correcting control of process flow would help enable and accelerate throughput volume.

5. **Reliability science**

An overlooked issue is that the economics of PV are predicated on sufficient lifetimes, with targets traditionally of 20-30 years. Changes that improve efficiency are only beneficial if they last. There are limited tools beyond standard lifetime testing that can be used with any confidence to predict reliability. In part, this reflects the limited knowledge with respect to the underlying mechanisms that are responsible for both cell
and module degradation. Improved understanding of these mechanisms and the thermodynamics of their temporal evolution is necessary for all technologies and is especially critical for the emerging approaches. New advances in diagnostic tools to characterize structural and electronic changes as a device/module ages as well as models that accurately describe and predict behavior would accelerate progress in these areas.

VI. SUMMARY AND CONCLUSIONS

Photovoltaics manufacturing has surpassed the 10 GW/yr production threshold and is poised to accelerate as electricity production by PV reaches parity with conventional electric power generation technologies later this decade. It is expected that various forms of crystalline silicon will dominate the market for the foreseeable future. Significant opportunities remain to improve 1st generation solar cells, mainly through continued reduction of material requirements as well as additional improvements in module efficiency. Thin film CdTe has established itself as a major player in the global marketplace. Pending further improvements in efficiency, CdTe’s market share could evolve to anywhere between 5 – 25%. After decades of being the leading thin film technology, the prospects of amorphous silicon making a major contribution to the utility sector appear constrained by high manufacturing costs and low efficiency. CIGS has gained a foothold in PV manufacturing at ~100 MW/year, and the demonstrated potential in efficiency provides reason for guarded optimism. The next five years will be critical for CIGS to demonstrate robust manufacturing to allow it to break out and join CdTe as a major player in the global PV market. Although encouraging progress has been made, DSC and OPV are still limited at present by low efficiency and stability. Unless glass can be replaced, costs will remain critically high, leaving them to compete with a-Si and
CIGS in niche applications requiring flexibility and/or low temperature processing. If materials availability becomes a constraint at TW/year manufacturing levels it will likely favor silicon-based technologies, though understudied systems like CZTS deserve attention as their potential remains unknown. Fundamental challenges remain in 1st and 2nd generation PV technology, and additional investments in these areas are expected to have the most immediate impact in meeting the challenge of sustainable electricity production.

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Table 1. Top 10 crystalline silicon manufacturers in 2009. (Source Greentech Media, May 2010).

<table>
<thead>
<tr>
<th>Rank</th>
<th>Company</th>
<th>2009 Module Production (MW-dc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Suntech Power</td>
<td>704</td>
</tr>
<tr>
<td>2</td>
<td>Sharp</td>
<td>595</td>
</tr>
<tr>
<td>3</td>
<td>Yingli Green Energy</td>
<td>525</td>
</tr>
<tr>
<td>4</td>
<td>Kyocera</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>Trina Solar</td>
<td>399</td>
</tr>
<tr>
<td>6</td>
<td>Sunpower</td>
<td>398</td>
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<tr>
<td>7</td>
<td>Canadian Solar</td>
<td>326</td>
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<tr>
<td>8</td>
<td>Solarfun</td>
<td>313</td>
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<tr>
<td>9</td>
<td>SolarWorld</td>
<td>288</td>
</tr>
<tr>
<td>10</td>
<td>Sanyo</td>
<td>260</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. (Color online) Projected convergence of the cost of electricity produced by PV and the conventional grid prices.

Figure 2. (Color online) Workshop demographics.

Figure 3. (Color online) Market size and the share held by relevant technologies in 2008 and 2009.

Figure 4. (Color online) Champion efficiencies reported for cells and commercial modules for the established PV manufacturing technologies.

Figure 5. (Color online) The evolution of champion cell efficiencies since 1995 for various PV technologies.

Figure 6. (Color online) Green’s 2001 classification of PV technologies superimposed with the current status (solid) and projected evolution (arrows) of c-Si and CdTe technologies.

Figure 7. (Color online) The number of papers returned on Web of Science each year in response to a search of “solar” + the individual keywords listed in the figure legend (c-Si = "crystalline silicon").
Academia 43%, Industry 36%, Government 21%
2008 Total = 5491.8 MW

2009 Total = 7861.3 MW