Making Solar Cells a Reality in Every Home: Opportunities and Challenges for Photovoltaic Device Design

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***Abstract*—Globally, the cumulative installed photovoltaic (PV) capacity has topped the 100-gigawatt (GW) milestone and is expected to reach 200 GW by the year 2015. More than 90% of the installed PV capacity employs bulk-silicon solar cells. Engineering problems that include thermal and optical challenges have not permitted the large-scale commercialization of concentration PV systems, lack of functional reliability—and the concomitant lack of economic bankability—being a major barrier. For increasing the efficiency of single-junction cells beyond the Shockley–Queisser limit, several approaches based on concepts such as multiple exciton generation, carrier multiplication, hot-carrier extraction, etc., have been proposed; however, these do not seem to be commercially viable. Since both bulk-silicon and thin-film (amorphous silicon, cadmium telluride, and copper indium gallium selenide) solar cells remain as the only two commercially viable options for terrestrial PV applications, a multi-terminal multi-junction architecture appears promising for inexpensive PV electricity generation with efficiency exceeding the currently feasible 25%. The architecture exploits the present commercial silicon solar cells along with abundant and ultra-low-cost materials such as Cu_2O. With the availability of well-controlled manufacturing processes at the sub 2-nm length scale, it will become possible to manufacture ultra-high efficiency and ultra-low cost PV electricity generation modules based on silicon.**

***Index Terms*—Manufacturing, multi-terminal multi-junction architecture, nano-silicon, photovoltaics.**

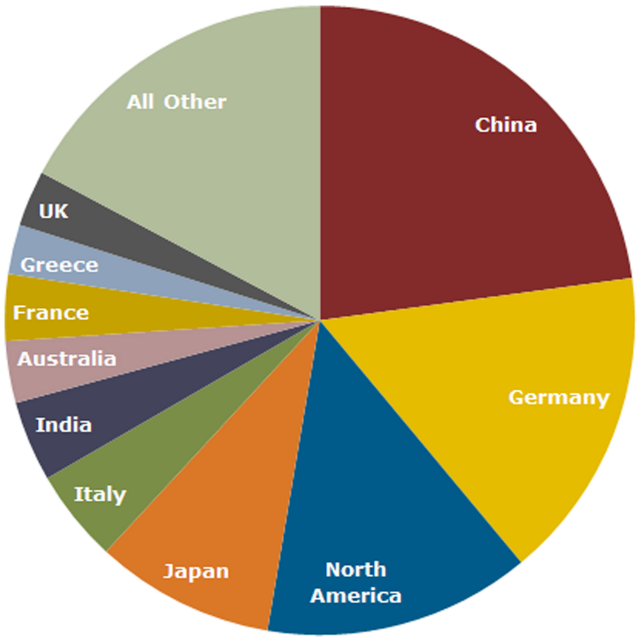

Fig. 1. Geographic breakdown of the PV electricity generation capacity expected to be added worldwide in 2013 [9]. ©NPD Solarbuzz.

I. Introduction

ALTHOUGH the earliest patents on silicon solar cells, granted during the 1940s [1], [2], indicated that the devices had very low efficiencies (<1%), hopes of higher efficiencies continued to fuel research. In 1954, Chapin and co-workers reported a 6%-efficient silicon solar cell [3]. Using the now obsolete International Electrochemical Commission (IEC) 60904-3: Ed 1 spectrum, Zhao and co-workers in 1999 [4] reported a silicon solar cell with 24.7% efficiency. Re-evaluating this same solar cell using the IEC 60904-3: Ed 2 spectrum, Green [5] in 2009 revised the efficiency to 25%.

The development of highly efficient silicon photovoltaic (PV) devices and related improvements in power electronics and module manufacturing led to predictions that PV electricity can be billed to consumers at the rate of $0.10/kWh [6]. That prediction has been recently vindicated [7]. Moreover, the cumulative installed solar PV electricity generation capacity worldwide has topped the 100-Gigawatt (GW) mark [8]. In 2013, the demand for new solar PV installations is expected to be 31 GW [9]. As shown in Fig. 1 [9], this PV demand is global, not being dominated in any particular region of the world.

For sustained global economic growth in this century, PV electricity generation is highly attractive because solar energy is essentially unlimited and PV systems provide electricity without any undesirable impact on the environment [10]. The cumulative installed solar PV electricity generation capacity

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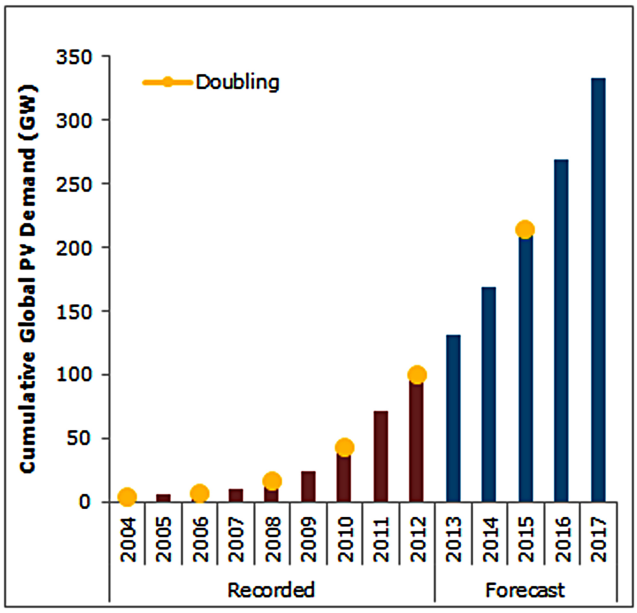


Fig. 2. Actual (2004–2012) and expected (2013–2017) growth in PV electricity generation capacity worldwide [11]. ©NPD Solarbuzz.

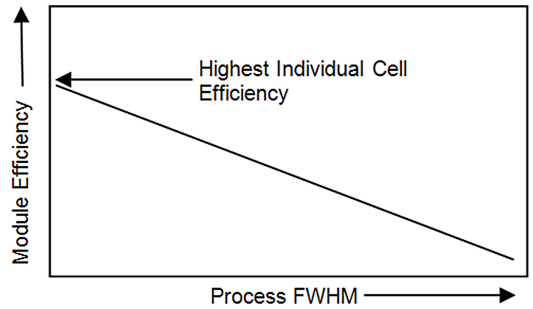


Fig. 3. Schematic of the relation between process FWHM and module efficiency [25]. Reprinted from G. F. Alapatt et al., "Fundamental issues in manufacturing photovoltaic modules beyond the current generation of materials," Adv. Optoelectron., vol. 2012, article no. 782150, 2012.

is expected to double from about 100 GW in 2012 to 200 GW in 2015, as shown in Fig. 2 [11]. The average selling price of PV panels has dropped to $0.65 per peak watt (Wp) [12]. Dominated by the second most terrestrially abundant element—namely, silicon [13]—PV energy generation is firmly moving to the terawatt scale [14].

The magnitude of the current globally installed solar PV capacity, the continually lowering cost of installed PV systems, and the continually lowering cost of PV generated electricity are the three factors that have established that PV technology is no longer only purely a research area, but it is a very important means to generate green electricity for meeting the needs of rich and poor all over the world [15]. Since huge investments have already been made in the processing of silicon and the functioning of the associated supply chain, only a truly disruptive technology can replace the well-established silicon-based PV technology. Indeed, although over 200 companies started in 2008 with the goals of inventing and commercializing disruptive PV technologies, most of these companies have either gone bankrupt or do not exist anymore. That outcome was to be expected [16]. A complete list of deceased companies is given in Ref. 17. Thus it is very important to understand the nature of innovations that will continue to reduce the cost of PV modules and other components of PV systems, similar to the cost-reduction history of silicon-based low-power electronics that has played and continues to play a vital role in enabling the information revolution.

For further cost reduction, design concepts for new manufacturable devices need to be developed beyond the current generation of bulk and thin-film solar cells. Several concepts—such as multiple exciton generation (MEG), carrier multiplication, hot-carrier extraction, intermediate-band solar cells, nanostructured solar cells, etc.—have been proposed to replace the extant solar cells. The purpose of this review is to critically examine published theoretical and experimental results relating to the proposed concepts and suggest directions for further research on the design of PV devices.

This review paper is organized as follows. In section II we describe the upper efficiency limit of PV devices. The current status of commercial PV devices is presented in Section III. Design guidelines for manufacturable PV devices are presented in Section IV. Research approaches currently being pursued for solar cells are examined in Section V. Section VI includes details on light management in PV cells. In Section VII, we propose multi-junction-multi-terminal silicon-based devices for highly efficient and inexpensive PV electricity-generation modules. We argue in Section VIII that such modules can become possible with the availability of well-controlled and low-cost manufacturing processes at the ∼2-nm length scale, thereby making solar cells a reality in every home. The paper concludes in Section IX.

II. Upper Efficency Limit of Photovoltaic Devices

On considering the sun as a black body of temperature T = 6000 K and assuming that a PV device (without any consideration of material-related issues) is operating at a temperature of T = 300 K, the upper thermodynamic efficiency limit of the PV device is given by -

$$\eta = \left(1 - \frac{300}{6000}\right).100\% = 95\%$$

Any PV device (including concentration solar cells) operating at a temperature of 300 K will always have efficiency lower than 95 %. After the discovery of the silicon solar cell in 1954 [3], several attempts were made to predict the efficiency of a silicon solar cell as well as the optimum bandgap for obtaining the highest efficiency [18]–[21]. In 1961, Shockley and Queisser published a fundamental paper on the efficiency of a single-junction solar cell [22] and predicted its upper limit. Popularly called the SQ limit, this is generally accepted as the theoretical upper limit because it is based on atomic processes described by the basic laws of physics.

The major factors accounted for in the calculation of the SQ limit are as follows: the bandgap of the semiconductor, the ratio of the temperature of the solar cell to the temperature of the sun, the probability that an incident photon with energy higher than the bandgap of the semiconductor

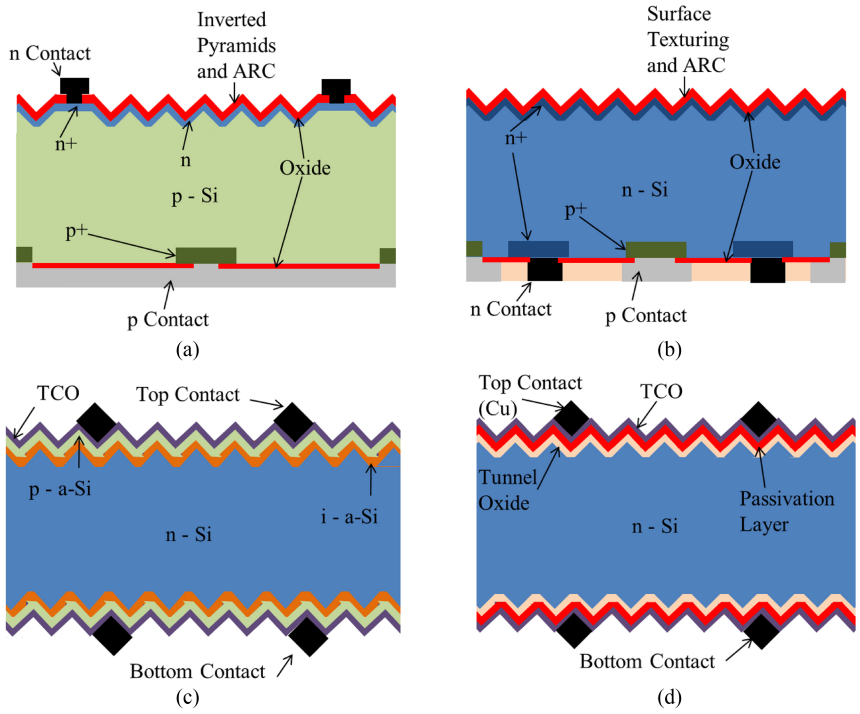


Fig. 4. Architectures of four highly efficient silicon solar cells: (a) passivated emitter with rear locally diffused (PERL) cell, (b) real contact cell (RCC), (c) heterojunction with intrinsic thin layer (HIT) cell, and (d) a hybrid solar cell with copper electrodes.

will produce an Electron Hole Pair (EHP) a factor that involves the transmission of radiative recombination from the solar cell, and the angle subtended by the sun. Although practical solar cells cannot achieve the limit proposed by Shockley and Queisser, it is possible to achieve efficiency quite close to this limit by using a semiconductor that has a very small defect density. For single-crystal silicon solar cells, a maximum efficiency of 25% has already been achieved, whereas the SQ limit is approximately 30%. Till date, no experimental results have indicated that the SQ limit can be breached.

The SQ limit of a single-junction solar cell can be extended to a multi-junction solar cell wherein a large number of solar cells are arranged in such a way that the topmost semiconductor has the highest bandgap and the bottommost cell has that lowest bandgap, to absorb the entire solar spectrum. The SQ limit of such a multi-junction solar cell is about 86.8 % [23].

III. Current Status of Commercial PV Devices

Silicon solar cells dominate the PV market. As an example, of the 22-GW capacity added worldwide to PV electric generation in 2011, silicon solar cells accounted for 89%, while CdTe and CuInSe/CuInGaSe solar cells together for the remaining 11% [24]. There is a direct relationship between the efficiency and the cost of a PV module, which translates into a direct relationship between the efficiency and the cost of an installed PV system. The efficiency of a PV module is lower than the efficiency of any individual small-area solar cell within the module, due to the series resistances of the interconnects and the variability in the efficiency of the individual solar cells [25].

The variability of any process has a Gaussian distribution and can therefore be characterized by the full-width-at-half-maximum (FWHM) of the distribution. Fig. 3 [25] is a schematic of the variation of the efficiency of a PV module with the FWHM of the overall processing variability that results in the variability of efficiency of individual solar cells. As the FWHM of a process parameter increases, the efficiency of the PV module drops. Current semiconductor manufacturing employs advanced process control (APC) [26]. The use of more APC equipment in the PV industry can reduce the FWHM of various processes and thereby increase the efficiency of the PV modules.

Tables I–III present the efficiencies of different types of PV cells and modules that are commercially available, but data on "champion PV modules" were discarded from consideration. Both organic and DSSC modules are marginally commercially available only for a few small consumer applications but not for bulk power generation. Silicon solar cells are twice as efficient as organic solar cells and DSSCs. The low efficiencies of organic modules and DSSC modules are, in part, also due to the low efficiencies of the individual solar cells inside these modules. More importantly, these tables demonstrate that solar cells made with well-controlled processes make up modules with high efficiency. Whereas silicon modules of large area (more than 10,000 cm^2) are available, the areas of organic and dye-sensitized solar-cell (DSSC) modules are very small. Especially, DSSC modules do not exceed 17 cm^2. It is difficult to make large-area modules with unreliable technology because of the loss of efficiency while interconnecting cells with diverse open-circuit voltages and short-circuit currents. The efficiency of an organic module is roughly half that of the individual cell, even when the module area

TABLE I
COMMERCIAL NON-CONCENTRATOR PV TECHNOLOGY:(ap) = APERTURE AREA; (da) = DESIGNATED ILLUMINATION AREA; (ta) = TOTAL AREA

Cell Type	Highest Cell Efficiency	Cell Area (cm^2)	Ref.	Highest Manufactured Module Efficiency	Module Area (cm^2)	Ref.
Si (mono crystalline)	25.0±0.5	4.00 (da)	27	21.5	16307 (ta)	28
Si (multi crystalline)	20.4±0.5	1.002 (ap)	27	15.3	16700 (ta)	29
CdTe thin film on Glass	18.3±0.5	1.066 (ap)	27	12.8	7200 (ta)	30
CIGS on glass	19.6±0.6	0.996 (ap)	27	14.5	10713 (ta)	31
a-Si (tandem)	13.4±0.4	1.050 (ap)	27	10.4±0.5	905 (ap)	26

is 300 cm^2. If the area of a DSSC module or an organic module is significantly enhanced, the module efficiency is expected to drop significantly as well. This problem is not expected to afflict a-Si, CIGS, and CdTe modules. Without any fundamental breakthrough in the material synthesis and performance of organic and DSSC solar cells, it is not possible that the PV modules based on these two types of solar cells will be ever used for bulk power generation.

Current PV technology can be classified into the following three categories: (a) power generation without concentration (Table I), (b) power generation with concentration (Table II), and (c) throw-away device technology (Table III). Categories (a) and (b) represent mature technologies and cells with good long-term reliability. Category (c) represents cells of use mostly in products that have to be replaced every few years. These cells may be called throw-away cells. Reliability experiments indicate that the longest lifetime of organic PV (OPV) solar cells is only 3–4 years [33]. Although these experiments were not conducted consistently with industry standards [34], even so their results demonstrate the fundamental weakness of OPV technology. Other than for throw-away products and some niche applications, OPV cells and DSSCs are unsuitable for the large-scale PV generation of electricity.

Benign solar intensity (about 0.75–1.0 kW/m^2) does allow many types of PV systems to function reliably for over 25 years. Both III-V compound semiconductor solar cells and silicon solar cells are currently being used for concentration PV (CPV) application. Fundamentally, there is nothing wrong in assuming that CPV systems should provide electricity at lower cost compared to non-CPV systems. However, engineering problems that include thermal and optical challenges have not permitted the large-scale commercialization of CPV systems, lack of functional reliability—and therefore of economic bankability—being a major barrier [35]. Several companies are currently carrying out field trials of low-concentration MW-size PV systems, yet the cumulative installed solar CPV electricity generation capacity worldwide is only 130 MW as of March 2013 [36].

Due to many limitations on currently available materials, CPV systems have not provided a reliable and cost-effective solution for terrestrial applications. Silicon solar cells can be used at low concentration (∼1-5 suns), and the cost of silicon CPV systems remains high. At high concentration (>400 suns), III-V compound semiconductor solar cells are used. As these solar cells are used in space, the device-design concepts are already fairly advanced. Therefore, no major improvement in device design is expected that can cut down the cost of a III-V compound semiconductor CPV system for terrestrial applications.

Three proven device architectures are available for high-efficiency silicon PV modules: (a) passivated emitter with rear locally-diffused (PERL) architecture, (b) rear contact cell (RCC) architecture, and (c) heterojunction with intrinsic thin layer (HIT) architecture. All three device architectures are shown in [Fig. 4(a)]. A record efficiency of 25% was obtained for a PERL cell [Fig. 4(a)] by decreasing surface and bulk recombination as well as by improving contacts [5], [27]. In the RCC architecture [Fig. 4(b)], front contacts are moved to the rear of the cell, thereby increasing the area facing sunlight. Surface passivation and local contacts are employed to reduce recombination losses [37]. In laboratory tests, 24% efficiency has been achieved [37]. In an HIT cell [Fig. 4(c)], the surface of the crystalline silicon is properly passivated by coating it with amorphous silicon. This passivation along with better grid formation helps to increase the efficiency of HIT cells up to about 25% [38]. A hybrid solar cell with amorphous silicon for passivation has also been fabricated in which silver is replaced by copper to reduce the cost [Fig. 4(d)]; the efficiency of this cell is 22% [39].

Every record-setting single-junction silicon solar cell has an architecture that is either PERL or RCC or HIT. Only marginal improvements in efficiency can therefore be expected for single-junction solar cells.

TABLE II
COMMERCIAL CONCENTRATOR-BASED PV TECHNOLOGY; (ap) = APERTURE AREA; (da) = DESIGNATED ILLUMINATION AREA

Cell Type	Highest Cell Efficiency	Cell Area (cm^2)	Ref.	Concentration Factor
GaInP/GaAs/GaInNAs	44.4	0.3124 (ap)	32	947
Si	27.6±1.0	1.00 (da)	27	92

TABLE III
THROW-AWAY PV TECHNOLOGY. ALL AREAS ARE THOSE OF AN APERTURE

Cell Type	Highest Cell Efficiency	Cell Area (cm^2)	Ref.	Highest Sub module Efficiency	Sub module Area (cm^2)	Ref.
Organic	10.7±0.3	1.021	27	6.8±0.2	294.5	27
DSSC	11.9±0.4	1.007	27	9.9±0.4	17.11	27

IV. MANUFACTURING DESIGN GUIDELINES

For large-scale terrestrial applications, the following guidelines must be followed in the design of devices, systems, and processes: (a) The supply of raw materials must not be constrained. (b) The variability of every key process and process-induced defects must be kept as low as possible. (c) The unit production cost must be kept as low as possible. (d) There should be prospects for cost reduction in the future. (e) Manufacturing must follow green manufacturing principles to avoid environmental, health, and safety problems. (f) The PV systems must have long-term reliability.

Adherence to these guidelines would make the business enterprise economically bankable. Decision-makers at all levels—and, especially, device designers—must keep these guidelines in view, when considering any new material or device architecture.

A. Unconstrained Supply of Materials

To long-term researchers, the current interest in PV devices and other clean technologies appears pretty much at the same intensity as in the mid-1970s and early 1980s. During that period, several materials were proposed as candidates for solar cells. In 1980, one of us [40] co-authored a paper on the economic requirements for new materials for solar cells and predicted—based on the abundance of raw materials—that silicon was the best candidate. It is worth mentioning here that currently there is oversupply of polysilicon and underutilization of polysilicon manufacturing plants [41]. In future, the bulk-silicon PV module manufacturers might migrate a higher proportion of their production to monocrystalline and n-type wafers in search of higher conversion efficiencies and thinner wafers ($\leq$ 140-μm thin) [42]. Increased demand for highly pure polysilicon by semiconductor and PV industries is likely to increase the price of that material. However, as explained in Ref. 43, such price increases are short lived. The abundant occurrence of silicon on earth will stabilize the price of polysilicon.

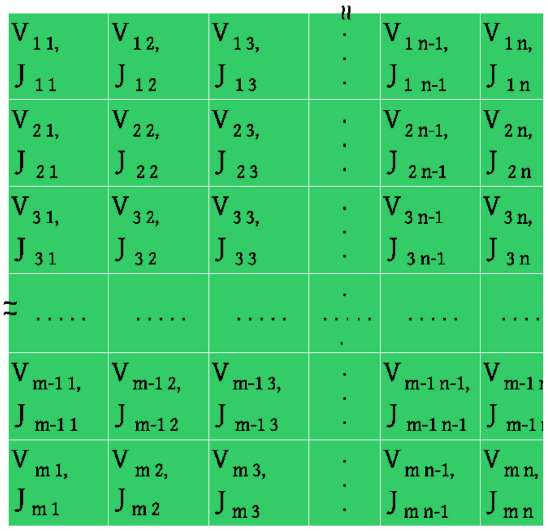
Over the last 33 years this prediction has been correct, and it is expected to remain true in the future [10], [13]. Indeed, the supply chains of indium, gallium, and tellurium for manufacturing CIGS and CdTe solar cells are not robust [43]–[45]. The limitations of CIGS and CdTe solar cells being known, thin-film solar cells based on copper, zinc, tin and sulfur (CZTS) are being explored [46]. The CZTS solar cells are at an early stage of development and have the potential to replace CIGS and CdTe solar cells.

B. Low Variability of Key Processes

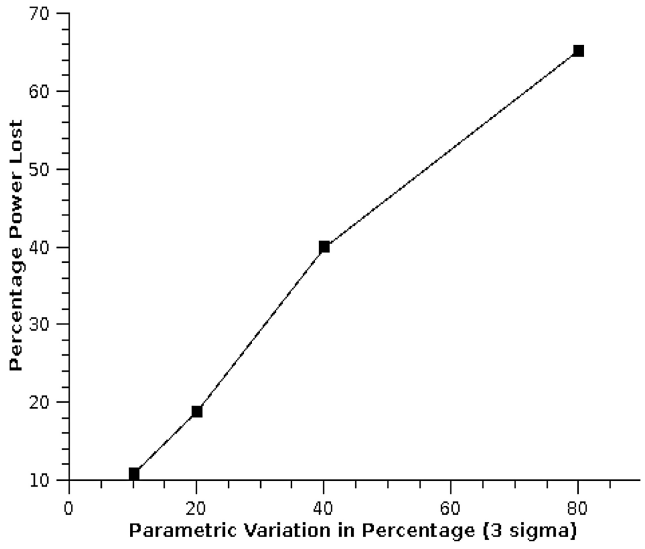
The cost of ownership [13] of a device is the ratio of (i) the sum of fixed costs, temporally variable costs, and the cost due to yield loss to (ii) the product of the throughput, the composite yield, and the utilization factor. As the cost of ownership decreases when the yield improves, key processes must have as little variability as possible. Furthermore, every process must induce as few defects as possible. In the present context, the power output of each solar cell in a PV module and the power output of each PV module in a PV system must lie within very narrow bands of acceptability. This is because in a series/parallel connection of multiple solar cells to get the desired voltage/current, the component with the minimum voltage/current will dictate the power output of the PV module. Likewise, performance variations of PV modules in a system will dictate the power output of the system.

Fig. 5(a) is a schematic of a PV module with m $\times$ n solar cells connected in series and parallel, and Fig. 5(b) is a plot of the power lost with variation in solar-cell performance [25]. The loss in output power increases from 10% to 65% as the variability in the performance of the components increases from 10% to 80%. Therefore, any manufacturing variability that affects the performances of solar cells will result in lower yields of modules, and is one of the main technical reasons for the failures of several thin-film solar-cell companies [25].

Fig. 6 schematically depicts the relationship between defect density and process complexity. As a process becomes more complex, the variability of its output decreases. Usually, more complex processes such as lithography result in microstructures with both low variability and low defect density. Simple processing techniques—such as non-vacuum roll-to-roll processing and spin coating—yield microstructures with both high variability and high defect density. Bottom-up techniques, claimed to be very simple processing techniques, lead to poor industrial scenarios [47]. Although simple processing techniques might look inexpensive at first glance, metrics such



(a)



(b)

Fig. 5. (a) Panel with m × n cells. (b) Power lost as function of process variation [25]. Reprinted from G. F. Alapatt et al., "Fundamental issues in manufacturing photovoltaic modules beyond the current generation of materials," Adv. Optoelectron., vol. 2012, article no. 782150, 2012.

as defect density, yield, and throughput decide the ultimate cost of ownership.

C. Low Production Cost

For reducing the production cost of PV modules, it is necessary to use larger substrates rather than smaller ones—which is also the experience derived from integrated circuitry (IC) and display industries [43]. Other than the efficiency of PV modules, the energy consumed in the manufacturing processes, the cost of raw materials, the cost of automation, throughput, and yield are important factors in the overall production cost. Of course, factors such as labor cost and the cost of water and electricity also affect the cost of PV modules, along with waste disposal costs, environmental remediation costs and the costs of complying with legislated mandates. The appropriate production capacity of a

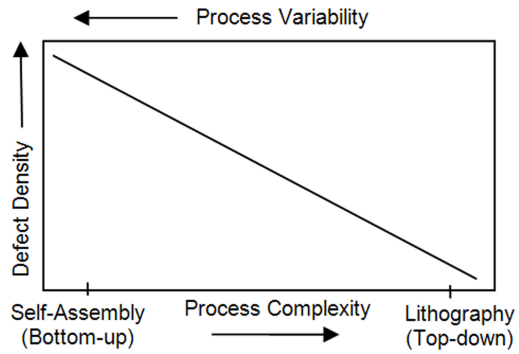


Fig. 6. Relationship of process variability to process complexity and defect density.

manufacturing unit must be determined after considering all of these factors.

D. Prospects for Further Cost Reduction

Other than increasing the efficiency of PV modules, any manufacturing process chosen should be capable of further cost reduction. Scenario planning is likely to be an effective tool for future planning [48]. Alignment with the IC and display industries on the sizes of wafers and substrates appears highly desirable for the PV electricity generation industry. Real or virtual vertical integration of the supply chain and distribution networks over time will further drive down the cost of PV modules, as also will co-location with manufacturing units for glass [6], [10], [15].

E. Environmental, Safety, and Health Issues

The techniques used for PV manufacturing are quite similar to manufacturing techniques for the $350-billion semiconductor industry. Similar to semiconductor industry, some potentially hazardous materials are utilized in the life cycle of PV systems, none of which present a risk different or greater than the risks found routinely in modern society [49]. As part of green manufacturing, recycling and conservation efforts are continuously considered and adopted by the manufacturers of solar panels [50].

The only material that poses additional concern in the current generation of PV devices is cadmium in CdTe solar cells [43]. In addition to the concern about the health of the workers, public health may be compromised by chronic exposure to cadmium compounds released into the environment as by-products of different manufacturing steps. The same issues will arise from the uncontrolled disposal of spent PV modules containing CdTe solar cells. All of these issues may be accentuated if the hazardous elements and compounds are released as nanomaterials. Scenario planning appears necessary both for green manufacturing and risk management [51].

F. Reliability

The cost of electricity generated from a solar panel is calculated after assuming a certain lifetime performance for the PV modules. For solar panels, a long lifetime is particularly required since the lifetime directly influences the cost per watt

TABLE IV
KEY APPROACHES FOR HIGH-EFFICIENCY SOLAR CELLS; (ap) = APERTURE AREA

Approach	Year Proposed	Semiconductor	Cell Efficiency	Cell Area (cm^2)	Ref.
Multi-junction	1958 [56]	InGaP/GaAs/InGaAs	37.8 (Apr 2013)	1 (ap)	57
Intermediate-band	1955 [58]	InAs/GaAsSb	8 (Jun 2012)	Not published	59
Multi-exciton generation	1993 [60,61]	PbSe	4.5 (Dec 2011)	Not published	62
Down-conversion	2002 [63]	Eu, Y, etc.	17.2 (May 2012)	4	64
Plasmonics-based	1982 [65]	Ag, Au, etc.	6.6 (Jan 2012)	0.13	66

of power output. In addition, solar panels can be used as long as they are functioning satisfactorily and are not subject to the same technology trends as other consumer electronic products are. Therefore, long-term reliability is a key issue.

Over the last 60 years, the reliability of semiconductor products has continually improved [52]. The same is true for PV solar cells. Solar cells of any type that cannot operate reliably for 25–30 years will not contribute to large-scale adoption of PV electricity generation technology. Silicon solar modules are now marketed with a guarantee that the output power will stay within 15% of the originally rated value during their 25-year lifetime [53].

As an evidence of the high inherent reliability of silicon-based electronics, silicon solar panels installed 20 years ago are still performing with minimal degradation (8.3% decrease in nominal power output) [54]. In contrast, CdTe modules manufactured by First Solar experienced premature power loss associated with degradation at high temperatures [55]. The manufacturer posted a fourth-quarter loss as a major write-down, to account for costs associated with replacing defective solar panels [55]. Due to the weak nature of the bonds in organic materials, serious material degradation happens over just a few years, which renders organic solar cells and DSSCs economically unviable [31] except in niche applications.

V. CURRENT RESEARCH APPROACHES

Both bulk and thin-film semiconductors are currently being explored to function as absorber layers in solar cells. The theoretically highest possible efficiency of a single-junction PV solar cell is the SQ limit [22]. The derivation of the SQ limit is based on the assumption that only radiative recombination takes place in the semiconductor. Several approaches have been proposed to boost the efficiency of the single-junction solar cell beyond the SQ limit. Most of these approaches rely on either capturing the generated EHP before it thermalizes, or on generating more than one EHP per incident photon, or on altering the solar spectrum available for energy conversion. Key approaches are listed in Tables IV and V.

A. Two-Terminal Multi-junction Solar Cells

The upper bound on the efficiency of a single-junction solar cell has been known from the early days of PV development for terrestrial applications [71], [72]. In a multi-junction cell, materials with different bandgaps are optically and electrically connected in series, each material absorbing a certain band of the solar spectrum. The thermodynamic limit on the efficiency of a solar module consisting of an infinite number of solar cells connected in series and operating at room temperature (300 K) is 86.8% [72].

Highly efficient current-matched multi-junction solar cells are often fabricated of III-V compound semiconductors [73]. Two-terminal multi-junction III-V compound semiconductor solar cells are the building blocks of PV modules for space applications. Commercial amorphous-silicon tandem solar cells [27] are also multi-junction devices. However, these thin-film amorphous silicon solar cells have a much lower efficiency ($\sim$12%) [27] in comparison to the III-V multi-junction solar cells ($\sim$38%). III-V multi-junction CPV cells have achieved about 44% efficiency [32].

In multi-junction solar cells, current matching is a design imperative, because a departure leads to significant reduction in overall efficiency. Therefore, the thickness and the bandgap of each junction material are carefully selected. In addition, since the solar cells are electrically connected in series, tunnel junctions are created between each junction to allow the flow of charge carriers. Moreover, for some III-V multi-junction solar cells, the selected materials must be lattice matched to deliver optimal performance. Such matching constraints tend to complicate the processing of materials, and the resulting enhancement makes these solar cells economically uncompetitive for large-scale terrestrial applications.

B. Down-Conversion Solar Cells

In down conversion, an incoming photon with energy higher than twice the bandgap is converted into two or more photons for subsequent absorption [74]. A layer of material with down-conversion capability is deposited on the front face of the solar cell to alter the spectrum available to the solar cell. Till date, there has been no improvement in the efficiency of any solar cell above the SQ limit [22]. Most down-conversion layers act as anti-reflective coatings (ARCs) and offer minor improvements in the efficiency.

C. Up-Conversion Solar Cells

In up conversion, several photons of energy lower than the bandgap of the absorber layer in the semiconductor are converted into a photon of energy higher than that bandgap [74]. The up-converting material is deposited on the back of the solar cell. Low-energy photons that have passed through the solar cell are absorbed by this material, and the up-converted photon is sent back into the cell for absorption. To

TABLE V
KEY APPROACHES FOR HIGH-EFFICIENCY SOLAR CELLS, WITH NO EXPERIMENTAL ESTIMATE OF EFFICIENCY REPORTED

Approach	Year Proposed	Reference
Up-conversion	2002	63
Hot-carrier	1982	67
Time-asymmetry	2012	68
Strain-engineered artificial atom	2012	69
Magneto-electric power generation	2011	70

date, no improvement in the efficiency above the SQ limit has been reported [75].

D. MEG-Based Solar Cells

MEG is a process whereby high-energy photons create multiple charge carriers [76], and is quite similar to impact ionization [61]. One may be able to obtain several electrons and holes at the cost of a single photon, thus making good use of the high-energy photons in the solar spectrum. Some researchers argue that MEG can be observed in bulk semiconductors [77] while others argue that one can observe MEG only in nanostructures [78].

The chief evidence for the efficacy of MEG to break the SQ limit for single-junction solar cells has been provided by Semonin et al. [62]; this group fabricated and tested PbSe quantum-dot solar cells. However, the presented evidence is flawed. The open-circuit voltages reported in Ref. 62 for gaps of 0.72 eV and 0.98 eV are 0.18 V and 0.34 V, respectively, while the respective short-circuit current densities are reported as 38.67 mA/cm^2 and 33.34 mA/cm^2. According to the theory of the SQ limit, the AM1.5 G values of the open-circuit voltage should be 0.34 V and 0.59 V, respectively, and the corresponding values of the short-circuit current density should be 58.50 mA/cm^2 and 48.59 mA/cm^2.

Although the authors of Ref. 62 did not mention explicitly that they have surpassed the SQ limit, they did state: "Our findings are a first step toward breaking the single junction Shockley-Queisser limit ... of present-day first and second generation solar cells, thus moving photovoltaic cells toward the third-generation regime." The MEG has been claimed as a method to possibly break the SQ limit without showing any evidence to back up that statement. Thus, contrary to that claim in Ref. 62, current evidence does not indicate that the SQ limit has been exceeded.

Several reasons can be ascribed for the anomalous results reported in Ref. 62. First, the very low values of the open-circuit voltage clearly indicate the poor quality of the junction barrier. The fabricated solar cells must have had high defect densities. Second, the solar cells had small areas, thereby facilitating peripheral collection of light—which leads to a falsely high value of the efficiency. Third, the reference cell and the test solar cells were not fabricated from the same material. Other sources of error include the consequences of chopped light beams, the uncertainty of the calibration source, and wrong assumptions regarding the spectral width of the monochromatic beam [79]. It would have been prudent to let the US National Renewable Energy Laboratory certify the efficiency [80].

Whereas the concept of generation of multiple charge carriers is physically well established [81], no experiment has shown that these charge carriers can be extracted for current generation. Indeed, it follows from experimental data presented in Fig. 2 of Ref. 81 that the charge carriers generated through MEG decay so quickly that it is impossible to extract those carriers to sustain a photo-generated electric current.

E. Intermediate-Band Solar Cells

In 1960 Wolf [21] discussed the role of intermediate-energy gap states in controlling the efficiency of solar cells. In an intermediate-band solar cell, an intermediate level within the bandgap is created and conditions are made such that this new intermediate level does not act as a recombination center [82]. With such a level within the bandgap, electrons are able to be excited from the valence band to the conduction band in a two-step process. First, an electron jumps from the valence band to the intermediate level, and then it further gets excited into the conduction band. In the normal excitation process, in contrast, the electron jumps from the valence band directly into the conduction band. The highest efficiency obtained is about 8%, which is far below than SQ limit [59], [83].

F. Hot-Carrier Solar Cells

The goal in a hot-carrier solar cell is to extract an EHP before it can thermalize. Thus, photo-generated hot electrons/holes can be transported across the bandgap to the conduction/valence band without losing excess energy. If such a scheme can be implemented, it will allow for better utilization of high-energy photons in the solar spectrum. Under AM1.5 illumination at 300 K, the maximum efficiency has been predicted to be 66% for ideal hot-carrier devices [84].

The practical realization of actual hot-carrier solar cells has never been successful. Thermalization in the absorber layer leading to insufficient collection of hot carriers at electrical contacts [84,85], emission from the absorber layer, and radiation into the environment pose fundamental changes and seriously reduce the efficiency [86].

G. Nanopillar Solar Cells

Instead of planar layers of semiconductors, one could use an array of upright semiconductor nanopillars [87]. Each nanopillar would be an autonomous solar cell, the p-i-n structure being either longitudinal (i.e., along the length of the nanopillar) [88] or radial (i.e., in the transverse plane) [89]. The fabrication of nanopillar arrays is accomplished by a variety of processes including templating, etching, and ion-beam milling.

However, the maximum efficiency experimentally realized is under 7% with arrays of gallium-arsenide nanopillars [89] and under 14% with arrays of indium-phosphide nanopillars [88]. These efficiencies are considerably lower than those of the commercially sold single-junction silicon solar cells (25% efficiency), gallium-arsenide solar cells (29% efficiency), and indium-phosphide solar cells (22% efficiency) [27].

H. Thermophotovoltaic Cells

Thermophotovoltaic (TPV) systems convert heat into electricity by thermally radiating photons which are source of optical energy for a low-bandgap PV device [90]. A TPV system is a remarkable example of how a PV system can be integrated with existing energy-generation systems. In comparison to the solar spectrum, the radiant light from a thermal source is concentrated mostly in the infrared and visible regimes. Hence, a semiconductor with a small bandgap must be used for enhanced conversion efficiency. Appropriate semiconductors include Ge, GaSb, InGaAs, and InAsSbP. The economics of TPV systems will ultimately decide the feasibility of large-scale implementation. TPV systems have been built along with large furnaces and have also been integrated on to 1 cm^2 chips [91]. The achieved efficiency of such systems is generally low at present, with champion devices possessing efficiencies slightly above 10%. The use of expensive and less abundant materials in the fabrication of TPV device is a fundamental roadblock in commercialization.

I. Parametric Oscillators

Several theories have been put forth to use optical energy to produce electrical energy without using the PV effect. One of them is the parametric mechanism proposed in 1986 [92], whereby photons are used to periodically vary an energy-defining parameter of a system, the parameter itself being oscillatory. Although theoretical descriptions exist, experimental verification has never occurred—despite parametric oscillators being common in electronic circuits. The major bottleneck in developing a photoparametric energy converter is the absence of materials that are optimized for this process.

VI. Light-Management Designs

Light management in a solar cell requires maximal entry of light into the solar cell followed by efficient absorption in the absorber layer(s). As light management paves the way toward the use of thinner semiconductors, module costs reduce due to higher efficiency of material utilization.

One way of enhancing the entry of light into the solar cell is the reduction of mismatch between the optical impedance of the semiconductor and the intrinsic impedance of vacuum (i.e., air). Accomplished by an ARC on the front face of the solar cell [93], [94], this is a cost-effective way to increase the efficiency because coating techniques are highly developed in the optics industry [95]. Multilayered ARCs are being designed and tested towards broadband, polarization-insensitive, and omnidirectional reduction of reflection [96]–[98].

A recent experimental result [99] confirmed theoretical predictions [100], [101] that a biomimetic coating can reduce reflection over a broad spectral regime and over a large range of incidence angles. The efficiency was found to have multiplied by a factor of 1.05 when an array of nanonipples made of acrylic resin was manually glued to the top of a crystalline-silicon PV module [99]. Such nanonipple arrays are said to replicate superhydrophobic cilia present on the eyelets of dipterans such as moths, house flies, and butterflies [102] and have long been known to reduce reflectance [103]. For acceptance of biomimetic coatings by the PV-module industry, long-term reliability and economics require serious investigation.

Another way to trap incident light and reduce the reflection is to texture the front face of the semiconductor at transverse length scales greatly larger than optical wavelengths in the solar spectrum [104]. Etching with an acid, KOH, or plasma is the commonest way to texture the front face into a random array of pyramids. U-shaped and V-shaped grooves are also popular textures [105]–[107]. Bioinspired textures are being theoretically considered as well [108]. However, the downside of surface texturing is a larger surface area; thus, surface states and defects will increase the surface recombination rate unless special passivation is done.

The metallic back reflector of a solar cell can also be textured at transverse length scales greatly larger than a thousand nanometers, but planar backing appears to perform better [109]. In contrast, periodic texturing of the metallic back reflector was indicated in the early 1980s to help trap light better, if the period were a few hundred nanometers [110]. In other words, the use of a metallic diffraction grating as the back reflector may result in higher efficiency, thereby promising highly efficient thin-film silicon solar cells [111].

The realization that the periodically corrugated metal/semiconductor interface could guide surface-plasmon-polariton (SPP) waves [112] has led to much recent research. The reason is the existence of an electric field of large magnitude within a $\sim$200-nm-thick region close to the interface inside the semiconductor when an SPP wave is excited, the high electric field being favorable to more EHP generation. If the semiconductor is periodically nonhomogeneous in the direction normal to the interface, multiple SPP waves can be excited in some wavelength range within the solar spectrum, leading to even better conditions for the generation of more EHPs [113]. Thereby, very thin films of solar-grade semiconductors will be needed, leading to reduction of manufacturing costs.

Plasmonics has had another impact on research on light management in a solar cell. Provided certain conditions are met, the polarizability tensor of a metallic nanoparticle embedded in a dielectric material (or even a semiconductor such as silicon) can have components of very large magnitude. Accordingly, very high electric fields can exist in the vicinity of a nanoparticle [114], leading to enhanced EHP generation. This phenomenon is being explored to enhance the absorptance of light in the 700–1100-nm wavelength regime in silicon thin films with embedded metal nanoparticles [115], [116]. When the metal nanoparticles are positioned on an air/semiconductor interface, the enhancement of the electric field is much more in the semiconductor than in air [117]. This enhancement can lead to better trapping of light in a solar cell [118], so long as the surface density of the metal nanoparticles is not so high as to significantly block incoming light.

All of the current research focus seems to be on the enhancement of the electric field in the absorber layer(s) and on the enhancement of the short-circuit current density, but not on the open-circuit voltage. Although there is some evidence that plasmonics can improve the short-circuit current density, not

a single carefully designed experiment with statistical analysis of the results has been reported as yet. Nevertheless, plasmonic strategies can be incorporated in solar cells, regardless of the semiconductor being used for PV electricity generation.

There is a recent proposal to deploy a time-asymmetric magneto-optical structure over a solar cell [68]. Functioning as a one-way shutter, the structure will stream light towards the solar cell but not allow light traveling in the opposite direction to escape. Both practical realization and cost effectiveness are questionable.

The use of ARCs and planar metallic back reflectors, as well as front-surface texturing at multi-wavelength length scales, have been effective and commercially deployed strategies for improving the efficiency of silicon solar cells. The most efficient PERL cell uses double ARC, inverted pyramid surface texturing and a planar aluminum reflector [5]. The incorporation of plasmonics is hoped to provide a further boost to the efficiency. The discussed light-management strategies could be useful for a wide variety of PV solar cells.

VII. Manufacturable, Ultra-High Efficiency, Low-Cost PV Solar Cells

Any new solar PV electricity generation system avoiding the existing state-of-the art silicon solar cell is undesirable, since the silicon solar cell has already been successfully commercialized and monopolizes the PV electricity generation market. The huge investment made in silicon technology for five decades and the low cost of polycrystalline silicon are two major factors that will not allow the large-scale commercialization of competing devices based on other materials. In addition, if a competing device's efficiency does not exceed 25%, it will not have an adequate opportunity for commercialization. Indeed, history offers a lesson: Even though ICs based on indium phosphide or gallium arsenide have better switching speeds than silicon ICs, the latter command more than 90% of the $1.5-trillion electronics market.

From a consideration of the current research approaches presented in Section V, it is evident that several will fail to deliver cost-effective and highly efficient PV solar cells. Multi-terminal-multi-junction solar cells offer the unique advantage that the current-matching requirement is unnecessary, as discussed in Section V A. Junctions in such a solar cell are not electrically connected within the solar cell; instead, the solar cell has multiple terminals. In the simplest case of a solar cell of this type with two junctions, there are four terminals. As each junction electrically operates independently of all others, junctions with different electrical properties can be used in a single solar cell. This is a great advantage since we can build up a complete multi-junction solar cell on top of an existing optimized single-junction solar cell. This concept has not been commercialized, although it was proposed as early as 2005 [119]–[123].

We present a strategy for a commercially promising multi-junction multi-terminal PV solar cell that is built on the robust foundations of currently established silicon solar-cell technology. At its simplest, this novel electricity-generating device can be made by integrating a large-bandgap cell on top of an existing silicon solar cell. Commercial thin-film deposition techniques can be used to integrate multi-junction multi-terminal solar cell. The design of the large-bandgap cell must satisfy the manufacturability guidelines discussed in Section IV, thereby enabling the technology to be ready for large-scale adoption without any manufacturing barriers. The cost of adding another cell on top of a silicon cell as well as the interconnection cost will be far less than the cost reduction offered by the higher efficiency of proposed solar cell

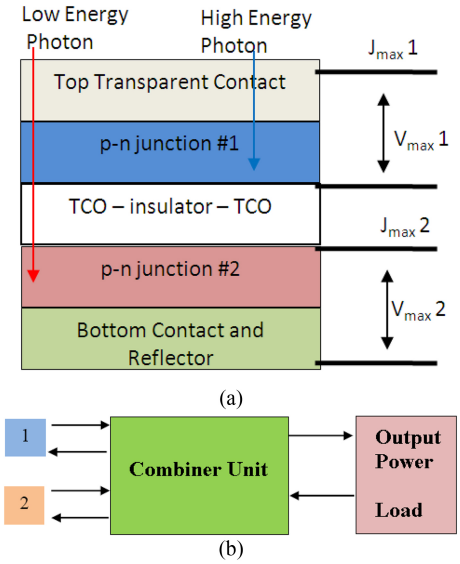


Fig. 7. (a) Schematic of the proposed two-junction four-terminal solar cell. (b) External electric circuitry to combine the electricity generated separately by the two junctions.

The schematic of this two-junction-four-terminal solar cell is shown in Fig. 7. It is worth mentioning here that we are not proposing a mechanically stacked 4 terminal cells with silicon as the bottom cell. A transparent conducting oxide (TCO) is used for the electrodes and an optically transparent insulating layer is deposited between the upper and lower cells to keep them electrically separate. As mentioned earlier in this section, the multi-terminal nature of this device removes the current-matching requirement in the multi-junction architecture by using an external circuit such as a highly efficient dc-dc converter. In addition, the transparent insulating layer removes the need for lattice matching between the bulk and thin-film materials, thereby simplifying the manufacturing of the solar cell. It is worth mentioning here that the use of multi-junction multi-terminal PV solar cells for local dc-power generation coupled with the delivery and the utilization of dc power will provide a solar PV electricity generation system with the highest energy efficiency [124].

Fig. 8 shows the variation in the simulated efficiency of a two-junction four-terminal solar cell with respect to the bandgap in the material of the upper cell, when the bottom cell is assumed to be made of silicon. This variation was calculated based on the standard solar-cell equations. After assuming the SQ limit, the maximum efficiency of 44% is obtained when the upper material's bandgap is about 1.8 eV. Based on material availability and the possible conversion efficiency of such a multi-terminal multi-junction cell using silicon as the base

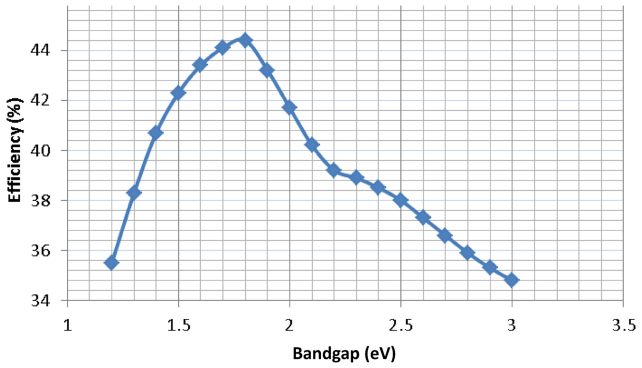


Fig. 8. Variation of the efficiency of a two-junction four-terminal solar cell with the optical band gap of the material in the upper cell, when the lower cell is assumed to be a silicon solar cell.

material (for the lower cell), we have identified copper (I) oxide, Cu_2O, as a candidate. This stable oxide of copper is a p-type semiconductor with a bandgap between 1.7 and 2.6 eV, depending on the conditions prevalent during its fabrication [125]–[127], and is an inexpensive material. Several research groups have already identified it as a PV material [128], [129]. However, the maximum AM 1.5G efficiency of Cu_2O cell is about 2 %. [130]. Preliminary experimental results have shown that high-quality Cu_2O films can be grown using photo-assisted chemical vapor deposition [130]. As shown in Fig. 9 [130], the dark current density-voltage (J-V) characteristics of Cu_2O diodes is much better than the data reported in the literature and indicates lower defects density in Cu_2O deposited by the photo-assisted CVD technique.

Cu_2O solar cells have been investigated in the past as standalone PV devices. Due to low efficiency, researchers became discouraged and progress has been very slow. In our proposed architecture, an ultra-thin film of Cu_2O with ultra-low defect density is supposed to provide highly efficient Cu_2O/Si solar cells. The defect density in a thin film of an electronic material in general, and of Cu_2O in particular, depends on the method of deposition of the thin film and the purity of the precursor material. The monolayer rapid photothermal-assisted chemical vapor deposition technique [133] using ultrapure precursors (at least five nines purity) is capable of providing ultra-high-performance semiconductor devices. In Fig. 9 we have used only 99% pure precursors and the results are better than the published results. Further understanding of the defect chemistry of Cu_2O and the use of a 99.999% pure precursor in the monolayer rapid photothermal-assisted chemical vapor deposition technique can potentially yield highly efficient Cu_2O/Si solar cells.

Other existing materials in consonance with the manufacturability guidelines of Section IV can be identified, and perhaps entirely new ones could be synthesized. Light-management strategies can be adapted to further boost efficiency—for instance, by texturing the front surface of the upper cell at the multi-wavelength scale and periodically texturing the metallic back reflector at the bottom of the lower cell at the sub wavelength scale.

After successful commercialization of the two-junction-four-terminal solar cell, the number of junctions (and terminals) could be increased. The proposed strategy is reminiscent of the development of silicon CMOS-based ICs from single-core microprocessors to dual-core and now multi-core microprocessors.

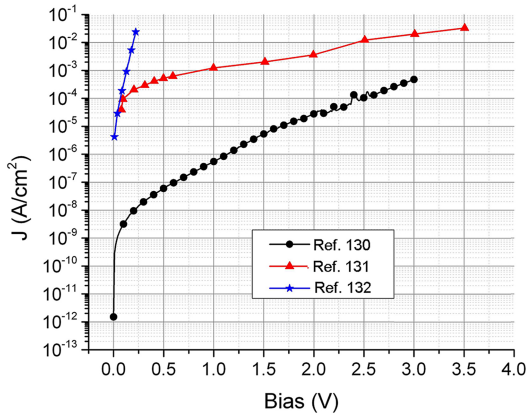


Fig. 9. Comparison of dark J–V characteristics of p-Cu_2O/n-Si diodes reported in the literature and present work [130]. Reprinted from N. Gupta et al., "Deposition and characterization of nanostructured Cu_2O thin-film for potential photovoltaic applications," J. Mater. Res, vol. 28, pp. 1740–1746, 2013.

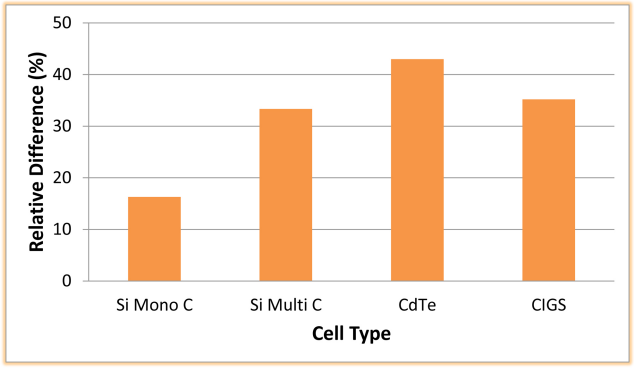


Fig. 10. Relative difference between the efficiency of a small-area solar cell and the efficiency of a PV module comprising a multitude of solar cells of a specific type.

VIII. Discussion

To cover all terrestrial applications, PV modules employing bulk silicon as well as PV modules employing thin films are needed. For instance, building-integrated photovoltaics (BIPV) requires thin-film PV modules for semi-transparency. However, their lower efficiency makes them unattractive for rooftop electricity generation because the available area is limited. Therefore, in order to cater to customers of rooftop applications, First Solar, a manufacturer of CdTe thin-film PV modules, acquired TerraSun, a manufacturer of bulk-silicon PV modules [134].

Using the data presented in Table I, we have analyzed the relative difference in the efficiency of an individual solar cell and the efficiency of a PV module comprising solar cells of the same type. As shown in Fig. 10, monocrystalline-silicon solar cells exhibit the smallest relative difference. Multicrystalline-silicon solar cells also attractive, going by the chosen metric. Better understanding of electron-hole

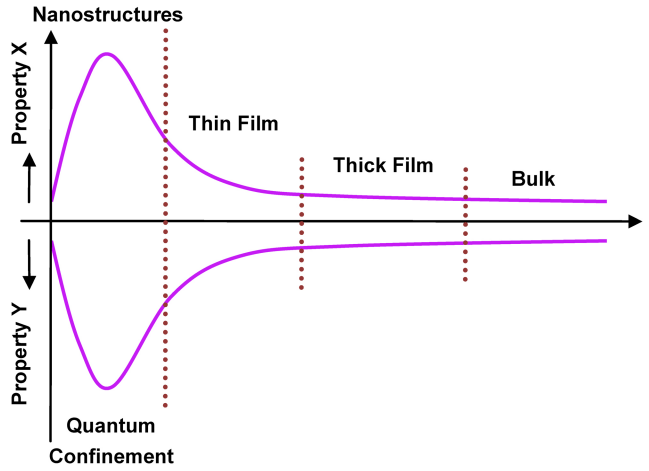


Fig. 11. Schematic of the size dependences of the properties of any material. Reprinted from R. Singh et al. "Semiconductor manufacturing in the nano world of the 21st century", Proc. 25th International Conference on Microelectronics (MIEL 2006), Vol. 1, pp. 3–9, 2006.

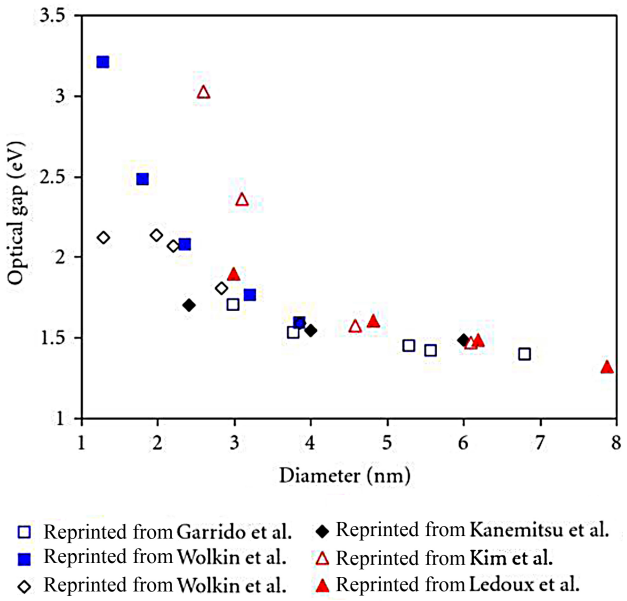


Fig. 12. Experimental results on the variation of optical bandgap of nanostructured silicon with diameter of silicon nanograins [139]. Reprinted from V. A. Belyakov et al., "Silicon nanocrystals: fundamental theory and implications for stimulated emission," Adv. Opt. Technol., vol. 2008, article no. 279502, 2008.

recombination at surfaces and interfaces in both bulk-silicon and thin-film solar cells will reduce the relative difference in efficiency. In addition, more use of advanced process-control equipment in the processing of thin-film solar cells can reduce the parametric variation of efficiency of solar cells in thin-film PV modules. The multi-junction multi-terminal architecture presented in Section VII will be the ideal choice for manufacturing the next generation of solar cells.

Several of the fabrication techniques mentioned in Section V involve self-assembly. Due to fundamental problem of process variability, self-assembly is not suitable for large-scale manufacturing of semiconductor products [15], [25], [47]. Even after many years of research, there is still no commercial future for PV solar cells fabricated by self-assembly.

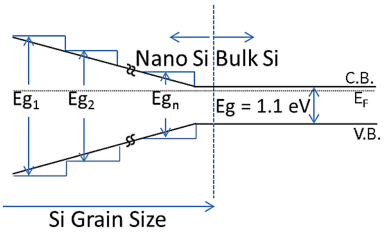


Fig. 13. Thermal equilibrium energy band diagram of hetero-face silicon cells utilizing quantum-confinement effects.

As schematized in Fig. 11 [135], the properties of nanomaterials differ vastly from their bulk counterparts, due to the large ratio of volume to surface area and the phenomenon of quantum confinement [136], [137]. Although several properties of nanomaterials have been known for a few centuries, scientific explanations began to emerge only during the last fifty years.

The use of a specific property of a nanomaterial is very different from building an entire technology to exploit that property. Clever design concepts are necessary to exploit quantum confinement in nanostructured solar cells [138]. One enticing possibility is to use the dependence of the bandgap on the size of nanograins in nanostructured silicon. As shown in Fig. 12 [139], the direct bandgap of nanostructured silicon increases with the reduction of nanograin diameter below about 8 nm. If a new process can be invented that meets all the manufacturability guidelines discussed in Section IV, the device designer will have the freedom to design many types of ultrahigh-efficiency silicon solar cells that exploit the effects of quantum confinement. As shown in Fig. 13, starting with bulk silicon as the substrate, hetero-face solar cells [140] with very low front-surface recombination can be designed. It should be similarly possible to design single-junction and multi-junction multi-terminal solar cells of nanostructured silicon.

Since 2011, silicon ICs with identical features of 22 nm have been in production [141], with the gate length around 25 nm in a CMOS device. Very soon, 14-nm silicon ICs will be manufactured [142]; already, 5-nm silicon ICs can be fabricated for research and development [143]. Therefore, a nanostructured-silicon multi-junction PV solar cell can be made with adequate process control. This can be expected to become possible sooner rather than later, because not only the PV solar-cell industry but also the IC industry will benefit from the improvements in process control. Better process control that will work at dimensions of the order of 2 nm has the potential to create several useful and inexpensive devices based on actual nanotechnology, with silicon still the material of choice because of its abundance and low cost. The commercialization of solar cells based on the use of nanostructured silicon has the potential of providing ultralow-cost and ultrahigh-efficiency solar PV dc electricity generation systems.

IX. Concluding Remarks

In conclusion, many new materials and device designs for photovoltaic electricity generation are being proposed and researched in academic laboratories and by start-up companies. However, only those approaches will be commercially

successful that will use very well-controlled and well-understood manufacturing processes as well as materials that are easily available and can be easily processed.

Researchers should be able to develop proof-of-concept devices with measurable electrical properties. Once a proof-of-concept PV device with efficiency considerably in excess of 25% has been fabricated and tested in a certifying laboratory, investors and decision makers can judge its merits and sponsor research on manufacturing it. This will lead to a tremendous growth in the generation of electricity from solar energy. Local dc-power generation by solar PV systems coupled with the delivery and the use of dc power will making energy available for rich and poor alike.

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