

Photovoltaic technologies [☆]

Darren M. Bagnall ^{a,*}, Matt Boreland ^b

^a Electronics and Computer Science, University of Southampton, Southampton SO17 1BJ, UK

^b School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney NSW 2052, Australia

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ABSTRACT

Photovoltaics is already a billion dollar industry. It is experiencing rapid growth as concerns over fuel supplies and carbon emissions mean that governments and individuals are increasingly prepared to ignore its current high costs. It will become truly mainstream when its costs are comparable to other energy sources. At the moment, it is around four times too expensive for competitive commercial production. Three generations of photovoltaics have been envisaged that will take solar power into the mainstream. Currently, photovoltaic production is 90% first-generation and is based on silicon wafers. These devices are reliable and durable, but half of the cost is the silicon wafer and efficiencies are limited to around 20%. A second generation of solar cells would use cheap semiconductor thin films deposited on low-cost substrates to produce devices of slightly lower efficiency. A number of thin-film device technologies account for around 5–6% of the current market. As second-generation technology reduces the cost of active material, the substrate will eventually be the cost limit and higher efficiency will be needed to maintain the cost-reduction trend. Third-generation devices will use new technologies to produce high-efficiency devices. Advances in nanotechnology, photonics, optical metamaterials, plasmonics and semiconducting polymer sciences offer the prospect of cost-competitive photovoltaics. It is reasonable to expect that cost reductions, a move to second-generation technologies and the implementation of new technologies and third-generation concepts can lead to fully cost-competitive solar energy in 10–15 years.

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1. Introduction

Why photovoltaics? There was a time when this was a difficult question to answer. Fossil fuel was plentiful and apparently without end, and the Earth's environment appeared resilient. The photovoltaic (PV) industry was based on the niche applications of powering satellites and remote locations. However, the tide has changed dramatically, with growing recognition of the environmental impact of non-renewable energy sources and the economic volatility that comes from reliance on oil and gas.

Subsidy-based market strategies, particularly in Japan and Germany in the late 1990s, pump-primed a PV-industry that is increasing in economic importance and is now a billion dollar industry undergoing staggering growth (Fig. 1).

As well as providing an energy source that is acceptable to environmentalists, photovoltaics has the interest of a financial sector that now sees a business case for investment. It seems possible that it will be economic arguments rather than environmental arguments that will push PV energy into the mainstream.

Cost, in terms of \$/W, remains the greatest barrier to further expansion of PV-generated power and cost reduction is the prime goal of the PV sector.

2. Current status of photovoltaic technology

The current PV market consists of a range of technologies including wafer-based silicon and a variety of thin-film technologies. The range of current technologies and possible future options have been grouped from current *first-generation* to future *third-generation* technologies (Green, 2006).

2.1. First-generation PV

Current PV production is dominated by single-junction solar cells based on silicon wafers including single crystal (c-Si) and multi-crystalline silicon (mc-Si). These types of single-junction, silicon-wafer devices are now commonly referred to as the first-generation (1G) technology, the majority of which is based on a screen printing-based device similar to that shown in Fig. 2.

Originally built using single-crystal wafer silicon (c-Si) and processing technology from the integrated circuit (IC) industry, it is clear that 1G silicon PV benefited greatly from its symbiosis with the IC industry which provided the materials, processing

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* Corresponding author. Tel.: +44 0 23 8059 7609; fax: +44 0 23 8059 3029.
E-mail address: dmb@ecs.soton.ac.uk (D.M. Bagnall).

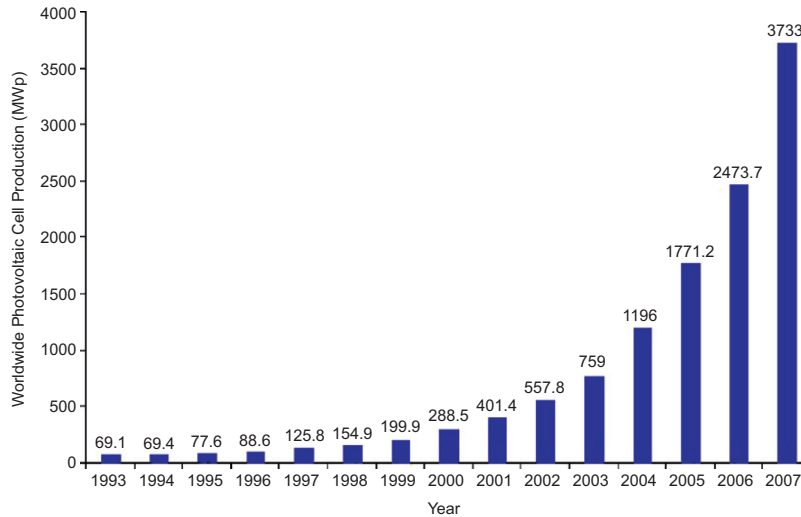


Fig. 1. Yearly worldwide production in photovoltaics in MWp (EurObserv'ER, 2008).

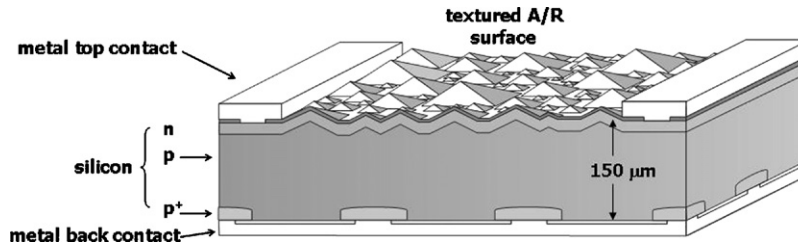


Fig. 2. Schematic of a single-crystal solar cell.

know-how, and manufacturing tools necessary to allow a rapid move to large-scale production.

New device technologies including BP Solar ('Saturn cells'; see, for example, Bruton et al., 2003), Sanyo ('HIT cells') and Sunpower are pushing commercial single-crystal wafer silicon efficiencies to the 18–21% range offering the potential for lower \$/W as a result of increased efficiencies (see company websites, e.g. Sharp; Q-Cells; Kyocera; Sanyo; Sunpower) for the most up-to-date information). However, multi-crystalline silicon (mc-Si) currently accounts for 63% of the world market, including manufacturers with cell efficiencies around 13–14% but at overall lower \$/W cost.

Half of the cost of first-generation photovoltaics is the cost of the 200–250- μm -thick silicon wafer—a cost incurred for largely mechanical reasons since the majority of solar absorption occurs in the top few tens of microns. So reduction of wafer thickness offers cost-reduction potential. Production costs will also be reduced over the next decade by the continued up-scaling of production, by increased production concentration, smarter processing and shorter manufacturing learning curves. Devices that use alternative silicon sources such as Scott's edge-defined film-fed growth (www.schott.com/photovoltaic/english/products/) and EverQ's string-ribbon technologies (www.sitrus.net/en/index.php); also Evergreen Solar: www.evergreensolar.com/app/en/home) are also offering cheaper wafer-like silicon grown directly from the silicon-melt, eliminating the wastage inherent in the traditional wafering of c-Si/mc-Si ingots.

In spite of much progress, 1G PV costs around US\$4/W, and this is still around four times too expensive for truly competitive commercial production. It is likely that the cost-reduction trend will reach its limit before 1G PV reaches full cost-competitiveness, though it should be noted that relative cost reductions (for both 1G and 2G) are resulting from spiralling energy costs.

2.2. Second-generation PV

The obvious next step in the evolution of PV and reduced \$/W is to remove the unnecessary material from the cost equation by using thin-film devices. Second-generation (2G) technologies are single-junction devices that aim to use less material while maintaining the efficiencies of 1G PV. 2G solar cells use amorphous-Si (a-Si), CuIn(Ga)Se_2 (CIGS), CdTe/CdS (CdTe) or polycrystalline-Si (p-Si) deposited on low-cost substrates such as glass (Fig. 3). These technologies work because CdTe, CIGS and a-Si absorb the solar spectrum much more efficiently than c-Si or mc-Si and use only 1–10 μm of active material. Meanwhile, in very promising work of the last few years, p-Si has been demonstrated to produce ~10% efficient devices using light-trapping schemes to increase the effective thickness of the silicon layer (Fig. 4) (Green et al., 2004; Yamamoto, 1999).

2G PV offers the potential to slash costs and financial pay-back and energy pay-back times compared to 1G, just as long as efficiency and fabrication costs per unit area remain comparable to 1G technology. Research results from leading laboratories have provided ample evidence of the potential of thin-film PV, 16.5% (CdTe), 18.4% (CIGS) (Green et al., 2006). However, PV based on CdTe and CIGS has been slow to scale up. This is partly due to the gap between lab efficiencies (above) and the best module efficiencies of 10.7% for CdTe (Green et al., 2006) and 13.4% for CIGS (Green et al., 2004) that are low as a result of unresolved issues relating to poor material reproducibility and uniformity over large areas (see, for example, Compaan et al., 1999; Noufi and Zweibel, 2006). Though perhaps the fundamental issue for both CdTe and CIGS technologies is the historical absence of symbiosis with a highly profitable IC industry. In comparison with silicon-wafer processes, thin-film process tools and production lines are

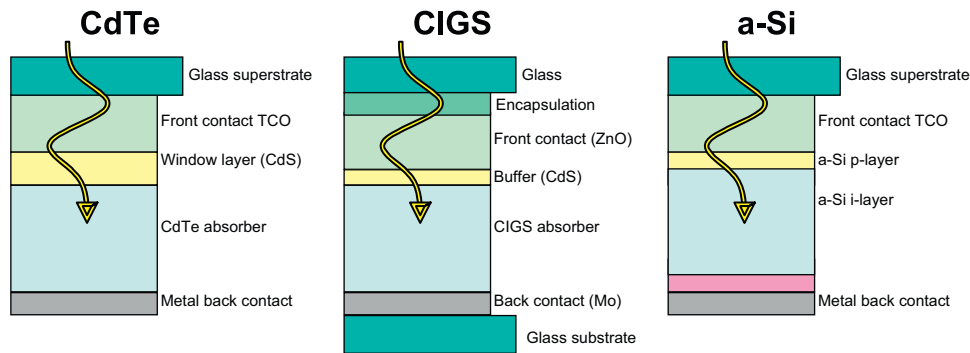


Fig. 3. Schematic diagrams of thin-film CdTe, CIGS and a-Si thin-film PV devices.

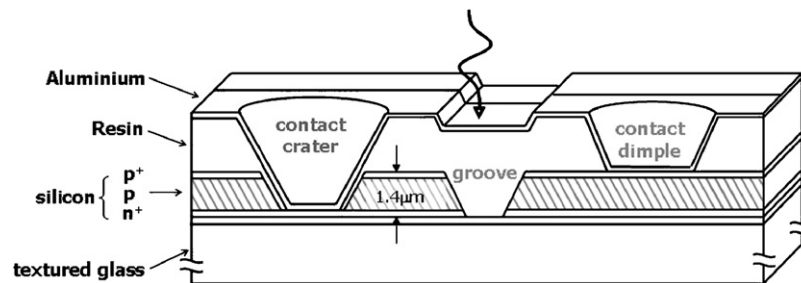


Fig. 4. Key features of the crystalline silicon on glass (CSG) technology (Green et al., 2004).

almost exclusively bespoke tools based on in-house and proprietary know-how, with correspondingly steep and expensive manufacturing learning curves. To some extent, this is changing for a-Si and p-Si technologies as there is now a cross-over from the flat-panel displays sector.

While 2G expansion is slower than expected, its potential remains to bring significant \$/W cost reduction to PV in large-scale production via reduced materials usage. Given the impressive progress by thin-film silicon over the last few years, it seems that the full potential of 2G is most likely to be realised by silicon-based thin-film devices.

2.3. Third-generation PV

As 2G technology progressively reduces the active material cost with thinner films, eventually even the low-cost substrate will become the cost limit and higher efficiency will be needed to maintain the \$/W cost-reduction trend. The possible future is for third-generation (3G) devices, which exceed the limits of single-junction devices and lead to ultra-high efficiency for the same production costs of 1G/2G PV, driving down the \$/W (Green, 2006). 3G concepts can be applied to thin films on low-cost substrates to retain material cost savings, but there is also benefit in applying 3G concepts using thin films on c-Si as *active substrates*. This is an attractive proposition as this may allow current 1G PV manufacturing plants to access the step-change efficiencies of 3G without necessarily undertaking a step-change in retooling and thereby minimising the type of uptake barrier to investment that is seen for 2G PV.

The emergence of 3G approaches are already showing up commercially in 32% efficient, thin-film GaInP/GaAs/Ge triple-junction space-PV for satellites (Karam et al., 1999), these are too expensive for terrestrial applications, but nevertheless demonstrate the viability of the 3G approach. Lower-cost 3G PV is also appearing, such as Kaneka's 11.7% micromorph a-Si/ μ c-Si heterostructures

(Yoshimi et al., 2003), and 10.4% triple-junction a-Si/a-SiGe devices (Yang et al., 1994).

3. Future advances to 2050 and beyond

As we have discussed, progress in PV technology should be measured in \$/W, and many scientific advances, as fascinating though they may be, will only be relevant to the industry if they can be implemented at affordable costs. In this sense, we can envisage two routes to cheaper photovoltaic energy that will be brought about by new science and 3G concepts. The first is based on the pragmatic use of new technology to improve the performance or decrease the cost of current devices. The second, more revolutionary, possibility might involve new whole-device concepts. Indeed, in recent years we have seen the emergence of dye-sensitised (Gratzel, 2001) and polymer-based solar cells (including organic/inorganic hybrids) (see Brabec and Sariciftci, 2001; Kanicki, 1986) as fundamentally new types of device, and although none of these have come close to outperforming wafer-based silicon devices in cost or efficiency, there is every chance that these devices could demonstrate step-change improvements or that new types of device may yet emerge.

3.1. New science for enhanced efficiency (or reduced cost)

Solar cells lose energy in a number of ways. Optical losses include reflection from interfaces at the surface of a module and carrier losses include recombination losses as a result of poor interface or material quality. By far the biggest losses are due to the nature of the photovoltaic effect itself. Significant optical power is lost because of the large volume of infra-red light that has insufficient energy to raise an electron into the conduction band (sub-bandgap losses) and because high-energy photons can only raise one electron to the conduction band and wasting excess

energy by heating the solar cell (hot-electron or thermalisation losses). These fundamental losses directly lead to an efficiency limit of ~40% for all commonly used semiconductors and 43.9% for single-junction silicon solar cells (Shockley and Queisser, 1961). 3G concepts aim to harness some of this wasted energy (Green, 2006).

Some of the most interesting 3G concepts discussed over the last 30 years include multi-junction systems such as tandem cells (Henry, 1980), the use of quantum wells and quantum dots to enhance absorption (Barnham and Duggan, 1990), the use of fluorescent collectors (Goetzberger and Greubel, 1977; Weber and Lambe, 1976), impact ionisation to utilise the kinetic energy of carriers (Kolodinski et al., 1993; Landsberg et al., 1993), the use of impurity levels (Corkish and Green, 1993) and hot-electron effects (Ross and Nozik, 1982). While many of these exciting ideas have fired the imagination and provided interesting debate, most have proven very difficult to demonstrate in principle and have often only ever served to manage to decrease the overall efficiencies of devices they hoped to improve.

In a similar way, dye-sensitised cells (Gratzel, 2001) still face difficult issues related to poor charge mobility and device stability and we cannot confidently predict that these devices will have a significant impact on large-scale energy generation. In the remainder of this paper we focus on new concepts that we believe can have significant practical impact.

3.2. Materials developments

Photovoltaic performance is heavily dependent on the properties of materials. In particular, the active layers of solar cells require long carrier diffusion lengths and bulk material must be defect-free, surfaces and grain boundaries must be passivated. Fundamental materials research, of materials, grain boundaries, surfaces and passivating materials can always be justified in this context. Although it seems unlikely that any future developments of known materials can produce a step-change in headline efficiencies, improvements in production yield or stability can be expected and research emphasis needs to be on materials produced by large-volume tools.

An exceptional case for materials developments can be made for semiconducting polymers, where the vast parameter space and inherent simplicity of device fabrication allows for considerable optimisation and optimism (McConnell and Matson, 2004). More complex 'materials' developments might also include the development of optical metamaterials, plasmonic materials, quantum dots and bandgap-engineering materials. These are all considered in context below.

3.3. Optical metamaterials

Photovoltaic arrays can either track the sun as it moves across the sky (at some expense) or remain fixed and have to accept a loss of efficiency as increasingly acute angles of incidence reduce the area of the device and significantly increase reflection. For fixed systems, around 20% of available photons are lost over a day as a result of reflection (Boden and Bagnall, 2006), now, the emergence of nanotechnologies and optical metamaterials are beginning to offer solutions to this issue. Currently, some commercial manufacturers use self-organised nanostructured glass surfaces to improve system efficiencies by around 10% (Wohlgemuth et al., 2005). More carefully constructed silicon nanostructures (Boden and Bagnall, 2006) that mimic the eyes of species of moth (Vukusic and Sambles, 2003) promise further improvements but are currently too expensive to implement. However, nano-embossing and nano-imprinting technologies are

rapidly developing and it is now possible to envisage regular commercial use of nanostructured broad-band antireflective surfaces within the near future, enhancing system efficiencies by more than 10% (Fig. 5).

Over the next 10 years, similar optical technologies might also allow for improved light-trapping in thin-film solar cells and concentrator cells (see below). As we have seen, thin-film silicon devices in particular require multiple reflections within the silicon layer to ensure the absorption of photons. Optical constructs are required to ensure that light is coupled into a waveguiding mode of the thin film (Heine et al., 1996). At present, thin-film silicon devices rely on diffuse reflectors produced by relatively simple etching regimes that are cheap to realise over large areas (for example, Chuangsuwanich et al., 2004; Yamamoto, 1999). Designed nanostructured surfaces are likely to offer routes that are optically more efficient and which might also be applicable to ultra-thin CdTe and CIGS-based thin-film devices. Increases in efficiency here are less important than the reduction in the thickness of absorbing material that is required and the commensurate reduction in cost.

A final prospect for enhanced light collection has recently arisen as plasmonics has emerged as a significant technology (Bohren and Huffman, 1983; Maier and Atwater, 2005; Mulvaney, 2001). Metal surface structures can support the formation of resonant charge oscillations (plasmons) with finite lifetimes and diffusion lengths that can be considered as a quasi-particle. Plasmonics can enhance absorption as a result of the prolonged photon interaction at a device surface or may be used to enhance scattering and direct photons into thin absorbing layers. By tuning the size of metallic nanostructures, it is possible to modify the wavelength response to cover a broad spectral range (Mulvaney, 2001). Meanwhile, the non-locality of photons allows only a relatively sparse density of features and therefore the possibility of inhomogeneous broadening. It seems likely that surface plasmonics might offer 5–10% improvements in system efficiencies (though probably as an alternative to the nanostructured surface approach outlined above). Implications for material or process reduction are just as important. This type of plasmonics application for solar cells might reach maturity over the next 10–15 years, with chemical self-organising mechanisms providing a route to cheap implementation. More complex plasmonic possibilities that will take tens of years to implement might involve the use of coupled plasmonic structures that might guide photons to specific absorption sites within complex devices.

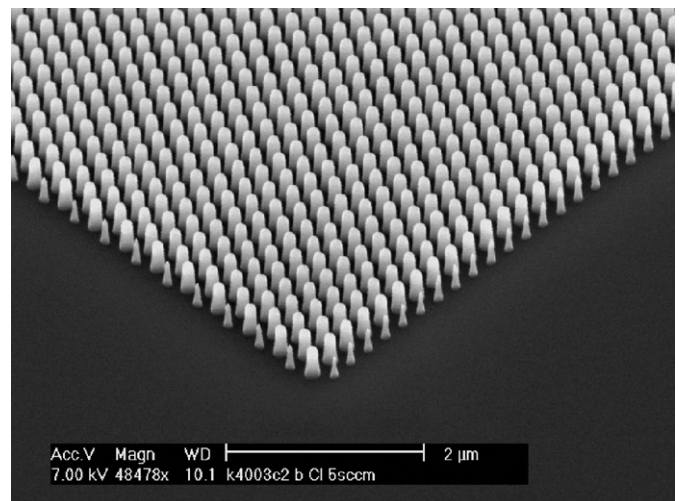


Fig. 5. SEM micrograph of a silicon 'moth-eye' antireflective surface (Boden and Bagnall, 2006).

3.4. Multi-junction devices

The only proven 3G technology is that based on the use of multiple junctions (Green, 2006; Yang et al., 1994; Yoshimi et al., 2003). Single-junction devices perform optimally at the wavelength equal to the bandgap, inherently losing efficiency at all other wavelengths across the solar spectrum. Multi-junction devices stack different solar cells with multiple bandgaps tuned to utilise the entire spectrum. Light is first incident on a wide bandgap device that can produce a relatively high voltage and thereby make better use of high-energy photons, then lower-energy photons pass through to narrow bandgap sub-devices that can absorb the transmitted IR-photons. Maximum efficiencies of 55.9%, 63.8% and 68.8% are predicted for two- (tandem), three- and four-junction devices (Green, 2006). However, costs escalate as fabrication becomes increasingly problematic with the increasing number of interfaces and cells. Material systems based on GaAs, InP or GaN can use different compositions of aluminium or indium alloys to modify bandgaps while maintaining lattice constants (bandgap engineering) and can produce monolithic multi-junction devices in a single growth run (with tunnel junctions between each device). In more pragmatic devices, multi-junction cells are mechanically stacked, with devices bonded together at the end of the process.

Tandem devices are naturally the most advanced multi-junction technology and there are many examples of combinations of 1G and 2G devices to produce 3G devices. The highest-performing devices are, however, expensive devices that can only be reasonably contemplated for concentrator or space applications (Karam et al., 1999). More cost-effective terrestrial multi-junction devices combine the polysilicon and amorphous thin-film silicon technologies (Yang et al., 1994; Yoshimi et al., 2003). These devices are relatively inexpensive for their efficiency but do not realise the full potential of multi-junction efficiency improvements (Fig. 6).

Multi-junction cells no longer require proof of principle, but they do require technological advances aimed at cost reduction. These cost reductions can come about by the capacity to produce much cheaper devices or by using concentrator systems. A key issue with concentrator systems is the need for mechanical tracking and associated higher costs and maintenance costs. At the device level, key requirements are in material growth, bonding and insulation, and the application of nanotechnology and the principles of self-alignment and self-organisation may well help solve some of these difficulties over the next 20 years. We are

confident that some large-volume high-efficiency multi-junction devices will be well positioned in the terrestrial market place within 20 years.

Perhaps the most promising futuristic prospect for multi-junction approaches will be based on polymer semiconductors, or combinations of polymer semiconductors with crystalline semiconductors. The intrinsic ability to tune polymer bandgaps and the forgiving low-cost, low-temperature, versatile deposition capability make polymers a natural choice, although the contacting issues generic to multi-junction cells and the long-term stability issues that affect polymer solar cells will remain problematic. By 2050, it is possible to imagine that self-organised semiconducting polymer structures in multi-junction arrangements could be the mainstream 50%-efficient photovoltaic technology.

3.5. Spectral conversion

A number of 3G concepts would make use of surface layers and structures to convert the solar spectrum to a spectral distribution that is more useful to the underlying device. Classically, one would like to use non-linear optics (NLO) concepts to produce bandgap energy photons from low-energy photons (up conversion). The reverse of this type of process could produce bandgap photons of short-wavelength, high-energy photons (down conversion). These schemes have been explored theoretically and predicted to produce device efficiencies of 63% for up conversion and 40% for down conversion (Trupke et al., 2002). NLO crystals are routinely used to efficiently perform these types of conversion. However, even the most efficient NLO materials can only operate at specific wavelengths and angles of incidence, and with relatively high and often coherent optical densities. At the moment, NLO materials seem unlikely to be able to help mainstream photovoltaics.

More likely systems for spectral conversion are based around quantum dots (van Sark et al., 2004), rare-earth doping (Matsura, 2002) and luminescent dyes (Richards and McIntosh, 2006). In each case, an 'optical' layer above a device is designed to absorb one set of photons and then emit a set of more appropriate photons. The generic difficulties associated with these processes are associated with the need for broad-band absorption across the wavelength ranges of interest (most of these systems have very sharp spectral features) and the need for 100% efficiency (or transparency) in spectral regions close to the band edge.

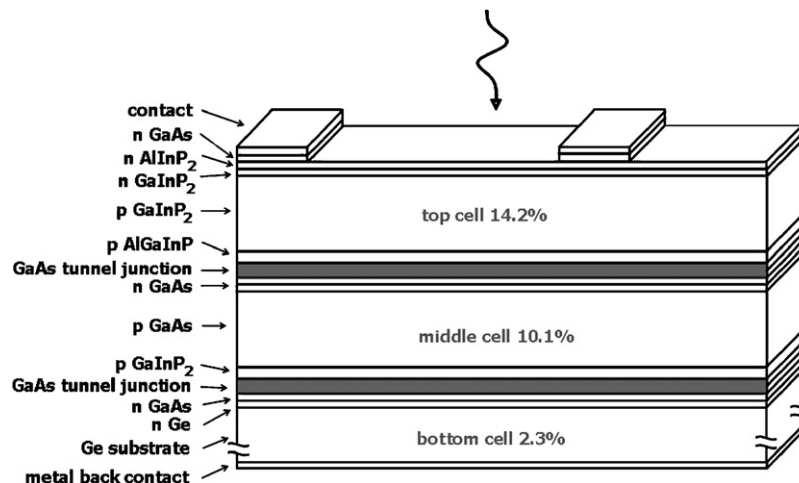


Fig. 6. Schematic cross-section of the Spectrolab triple-junction cell (Karam et al., 1999).

Broad-band absorption can be achieved by the use of inhomogeneous broadening mechanisms. In the case of quantum dots, this would be readily achieved by changing the size distribution of the dots. For rare-earth doping systems, broadening requires variation in the material supporting the atoms and this is more problematic. Meanwhile, mixtures of dyes are needed to broaden absorption. In each case, broadening the absorption leads to broadening of the emission and this will normally decrease the optical conversion efficiency.

It is therefore likely that spectral conversion will always be a difficult issue, and it seems unlikely that very-high-efficiency devices could be created. We can, however, anticipate two promising avenues for exploitation that might have an impact on commercial production. First, it seems highly probable that quantum dots embedded in dielectric layers directly above traditional devices might readily add 3–5% to device efficiency with little extra cost (van Sark et al., 2004). Second, spectral conversion could be applied within fluorescent collectors (Goetzberger and Greubel, 1977; Weber and Lambe, 1976), where large-area waveguiding layers containing dye molecules, quantum dots or nanocrystals could be used to concentrate light into the sides of small-area pn junctions. Here the benefit is not high-efficiency devices, instead it is in semiconductor volume reduction; two orders of magnitude less silicon might be needed to produce 20% devices (Markvart, 2006).

3.6. Self-organised quantum devices and nanostructures

In addition to the possible use of quantum dots as spectral converters, the use of quantum wells and quantum dots has also been proposed to extend the bandgap (Barnham and Duggan, 1990) and as a means to provide multiple electrons from a single photon through impact ionisation (Kolodinski et al., 1993; Ross and Nozik, 1982).

Quantum wells, wires or dots can be used to engineer the bandgap of materials. An example would be the growth of SiGe quantum wells or Ge quantum dots by chemical vapour deposition on a silicon wafer. The SiGe would provide regions of narrowed bandgap, allowing increased absorption in the infra-red. Invariably, such enhancements might result in increased absorption, but the quantum features also introduce carrier traps and more defective crystal growth, and this in turn leads to increased carrier recombination. To overcome this, quantum dots could exist in a layer separated by a thin insulator, which should in principle reduce the loss mechanisms, but will also reduce carrier transfer from dot to bulk semiconductor.

Impact ionisation is a process in which absorbed photons in semiconductors of at least twice the bandgap can produce multiple electron–hole pairs. Kolodinski et al. (1995) proposed the use of Ge superlattices for this purpose. Alternatively, Si/Ge or Si/SiO₂ superlattices could be used (Green, 2006), or certain quantum dots (Ellinson et al., 2005) that can generate two or three excitons (electron–hole pairs) per photon, which could tunnel or transfer (via polariton modes) from surface layers into the conduction band of 1G or 2G devices and thereby increase the efficiency. The prospects for impact ionisation will be limited by the finite flux of high-energy photons and the need for effects over a broad spectral range. As with some of the other concepts already discussed, the most likely practical implementation would be in the simple addition of a cheap layer of self-organised structures that might add 2% or 3% to device efficiency.

A truly futuristic and nanotechnological approach to photovoltaics might involve the use of self-organised structures. Most of mainstream PV to date has been based on layered, large-area devices. An alternative would be the use of arrays of high densities

of self-forming nanodevices. Many semiconductors have been grown in nanowire or nanorod form (Kayes et al., 2005) via vapour–liquid–solid (VLS) techniques. It is also possible to imagine other seeded or selective growth techniques to provide small high-quality crystallites that could also form the basis of nanodevices. Advantages of such approaches would include the reduction of material volume, uniformity of device behaviour, good crystalline growth on amorphous substrates and prospects for multi-junctions.

4. Conclusions

Over the next 20 years, we can foresee only small improvements in the production efficiencies of 1G silicon technologies. However, we can expect fabrication, installation and operational cost reductions (up to 30%) that will continue to provide reduced \$/W and increasing completion. In the same period, we will witness a change from predominantly 1G production to an era of 2G devices probably based on thin-film silicon (up to 30% cost reduction). While these two mainstreams will dominate the commercial PV sector, we expect that we will see increasing use of new and 3G technologies that will enhance the performance (or reduce the cost) of 1G and 2G solar cells. These technologies are very likely to include some multi-junction concepts and constructs based on the emerging fields of optical metamaterials, plasmonics, quantum technology, nanotechnology and polymer semiconductor science.

By 2020 and possibly much sooner, we fully expect photovoltaics to have become a truly cost-competitive energy supply, though the timing of this will depend on levels of research investment, the levels of national, international and multinational co-operation and the rate of increase in the cost of non-renewable energy supplies.

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