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Flexible Solar Cells

Mario Pagliaro,* Rosaria Ciriminna, and Giovanni Palmisano[a]

In memory of Angelo Patricolo

Thin-film flexible photovoltaics are paving the way to low-cost electricity. Organic, inorganic and organic–inorganic solar cells are deposited over flexible substrates by high-throughput (often roll-to-roll printing) technologies to afford lightweight, economic solar modules that can be integrated into, not installed on, various surfaces. Current conversion efficiencies under standard conditions are in the 3–15% range, but in real applications the overall productivity is high. These new photovoltaic technologies are ready to provide cheap, clean electricity to the 2 billion people who lack access to the grid as well as to energy-eager companies and families in the developed world facing the increasing costs of electricity generated using fossil fuel resources. This Review focuses on recent achievements in the area of flexible solar cells, highlights the principles behind the main technologies, and discusses future challenges in this area.

1. Introduction

The electron, it has been said, is the ultimate currency of modern society. Electricity indeed, being silent, clean, easily transported and converted into work, is the most widely used form of energy. Yet, besides a 16% share from nuclear fission,[1] we mainly produce electricity by burning hydrocarbons and, sadly enough, much cheaper coal. For example, still in 2006 nearly half (49%) of the 4.1 trillion kWh of electricity produced in the US used coal as its energy source.[2] Over the next decade, China alone will need to add some 25 GW of new capacity each year to meet demand, equivalent to one large coal power station every week. Unfortunately, coal contains mercury and along with the production of immense amounts of climate-altering CO_2, its combustion is causing pollution of the oceans and of the food chain. To abate emissions and stop climate change, the biggest challenge of our epoch is to get electricity directly from the sun.[3]

Concentrated solar power (CSP) has already been identified as the clean technology capable of satisfying the energy demands of our rapidly growing world.[4] Accordingly, investments are finally flowing and the first CSP plants are coming into operation, such as that in the city of Seville (Spain, Figure 1) which serves 6000 households. Direct conversion of solar radiation into electricity, namely photovoltaics (PVs), is being developed rapidly too: the average price for a PV module, excluding installation and other system costs, has dropped from almost USD 100 per watt in 1975 to about USD 4 per watt at the end of 2007 (Figure 2).

Figure 1. The Solucar 11 MW solar thermal plant outside Seville, Spain, produces enough electricity to power 6000 homes. Concentrated solar power is the large-scale technology capable to satisfy massive electricity demand (photo courtesy of the BBC).

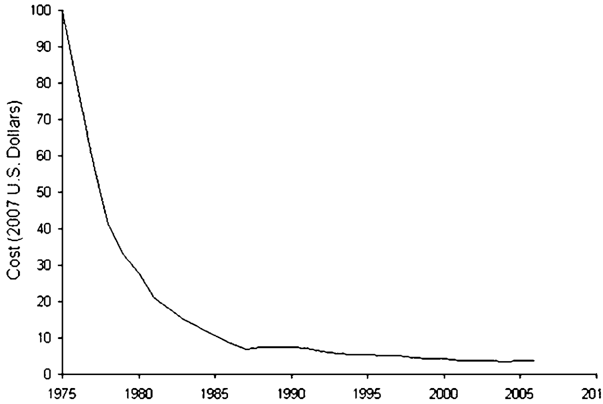

Figure 2. Variation in the average cost per watt of a PV module from 1975 to 2006 (source: Earth Policy Institute, 2007).

After forty years of losses and governmental subsidies, the USD 17.2 billion photovoltaics industry has turned into a profitable business, which has seen impressive annual growth rates over the last five years. World photovoltaic installations last year amounted to 2826 MW of electricity-generating capacity, up 62% as compared with 2006.[5] More than two-thirds of the installations were in Germany and Spain (and, beyond Japan, now in Italy and in California too), where direct financial incentives favour the installation of solar panels.

In this context, the installation of thin-film systems more than doubled last year and they now account for some 12% of solar installations around the world.[5] Thin-film (TF) photovoltaic modules are less expensive to manufacture than traditional polysilicon-based panels and have considerably lowered the barrier to entry into the photovoltaic energy business. The sector is thus rapidly switching from the heavy, fragile glass-coated silicon panels to thin-film technologies which use a number of different photovoltaic semiconductors,[6] and the revenue market share of TFPVs is expected to rise to 20% of the total PV market by 2010 (Figure 3).

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[a] *Dr. M. Pagliaro, Dr. R. Ciriminna, G. Palmisano*
Istituto per lo Studio dei Materiali Nanostrutturati, CNR
via U. La Malfa 153, 90146 Palermo (Italy)
Fax: (+39) 091-680-9247
E-mail: mario.pagliaro@ismn.cnr.it

Four years of high and increasing oil prices and the first ubiquitous signs of climate change have been enough to assist the market launch of a number of photovoltaic technologies based on thin films of photoactive materials that were left dormant (i.e., not further developed) in academic and industrial laboratories for years. For example, in 2004 a leading PV industry manager concluded that "*thin-film PV production costs are expected to reach $1 per watt in 2010, a cost that makes solar PV competitive with coal-fired electricity*".[8] Relevant to these arguments, however, the first thin-film solar modules that profitably generated electricity for 99 cents (US) per watt (i.e., the price of coal-fired electricity) were commercialized in late 2007 by the US company Nanosolar. These high-performance wafer-thin solar cells are mass-produced by printing an ink made of the inorganic semiconductor copper indium gallium diselenide (CIGS) on aluminum foil.

Rosaria Ciriminna graduated in chemistry at the University of Palermo (Italy) in 1995. She has worked at the Universities of Reading (UK) and Padova (Italy) and at ENS Chimie (Montpellier, France). She is currently a research chemist at the Institute of Nanostructured Materials (Palermo). Her research interests include sol-gel multifunctional materials for applications ranging from environmentally benign syntheses to sensing and photochemical processes.

Giovanni Palmisano is a PhD student in the chemical and materials engineering department at the University of Palermo. His studies have focused on the development of functional materials for electrochemical and photochemical oxidations and are now steered towards new-generation photovoltaics. He previously worked at the Csic Institute of Materials (Madrid, Spain) with Marisa Ferrer.

Mario Pagliaro is a research chemist and management thinker based at Palermo's CNR, where he also leads Sicily's Photovoltaics Research Pole and jointly directs the activities of the new Institute for Scientific Methodology. His research interests lie at the interface of materials science, chemistry, and biology. To date, he has co-authored six books, some 80 research papers, three patents, and several book chapters.

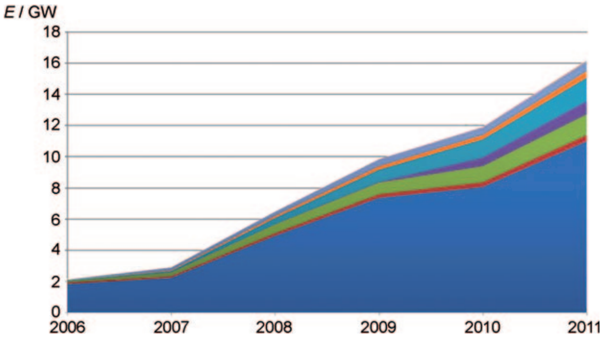

Figure 3. Forecast of the photovoltaic market with breakdown per technology, pointing to an annual growth rate of 70 % for thin-film photovoltaics from 2007 to 2010 (source: Yole).[7] Legend (from top to bottom): organic (pale green), DSSCs (brown), CdTe (pale blue), III V (orange), CIS/CIGS (mid-blue), a-Si/μ-SI (purple), a-Si (green), Si thin wafer (red), Si wafer based (dark blue).

From a scientific viewpoint, this and the other new solar cells are the result of advances in nanochemistry. Ironically, the inventor of the silicon solar cell already in 1954 clearly forecasted that thin-film technology would be the configuration of forthcoming industrial cells.[9] Indeed, it has been our ability to chemically manipulate matter on the nanoscale for industrial applications that has recently made possible the synthesis of the photoactive layers needed to carry out the photovoltaic conversion with the stability required for practical applications. In the last 20 years, the application of powerful synthetic methodology has allowed chemists to make materials where size and shape are as important as structure. In other words, we have learned how to make nanoscale building blocks of different sizes and shapes, compositions and surface structures,[10] such as in the case of the "nano ink" developed by Nanosolar (Figure 4) to make its CIGS panels. In this Review, we describe the main new commercial flexible solar modules, highlight the principles behind these devices, and present the new opportunities offered by these devices.[11]

Figure 4. Nano ink: The ink serves a useful purpose by effectively locking in a uniform distribution. The homogeneous mixture of nanoparticles in the ink in suitable overall amounts ensures that the atomic ratios of the four elements (copper, indium, gallium, selenium) are correct even across large areas of deposition (photo courtesy of Nanosolar).

2. Why Flexible PV Modules?

Like the internet was not invented by taxing the telegraph,[12] so cheap and abundant electricity from the sun will not be obtained by adding taxation on carbon dioxide emissions, but rather by inventing new, cheap solar modules capable of converting light into electrical power with more than 50% efficiency instead of the current 20% or so (Figure 5). These modules,

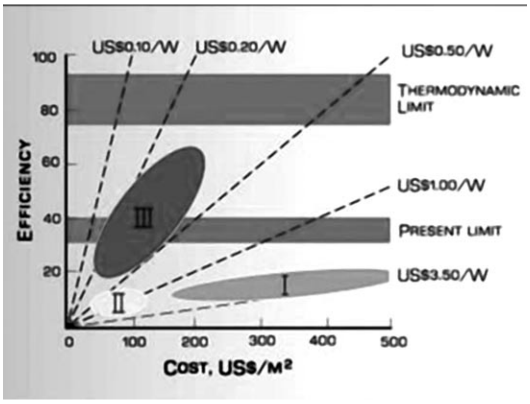

Figure 5. Efficiency and cost projections for first-, second-, and third-generation photovoltaic technology (wafers, thin films, and advanced thin films, respectively). (Reproduced from ref. [13], with permission.)

furthermore, will increasingly be flexible and lightweight to reliably produce electricity with little maintenance while being integrated into existing buildings, fabrics, tents, sails, glass, and all sort of surfaces. By doing so, the price of solar energy will be lowered to the level of coal-generated electricity so that people living in huge emerging countries will rapidly adopt solar energy for their economic development.

One piece of good news from this report is that the first such commercial modules are now ready and commercially available. Their efficiency of 3–15% under standard conditions is still low, yet the price of solar electricity generated through thin-film second-generation PV technologies is considerably lower than that of traditional silicon-based panels. In perspective, much higher conversion efficiencies may be achieved with the introduction of third-generation PV technologies[13] such as those that companies like QuantaSol[14] are about to launch on the market.

In general, the technology trend is that of the so-called plastic electronics, namely to print circuits and devices on flexible substrates at room temperature (low energy) and with roll-to-roll processes (high throughput). For example, flexible displays that use organic light-emitting diodes (OLEDs) applied in thin layers over plastic finally make electronic viewing more convenient than reading on paper (Figure 6). The thinness, lightness and robustness enabled by the flexibility of OLED-based displays creates digital reader products that are as comfortable and natural to read as paper.[15] In its turn, a flexible solar module (Figure 7) of the type described below might easily power the OLED device enabling unlimited access to thousands of pages.

Flexible solar PV devices offer a convenient alternative energy source for indoor and outdoor applications. Besides being flexible and thus easily integrated with elements of various shapes and sizes for the design of innovative energy-generating products, these unbreakable flexible modules are lightweight and suitable for applications where weight is important, while they offer a much faster payback than products based on conventional PVs.[16] Typically, the photovoltaic material is printed on a roll of conductive substrate (which may be conductive plastic)[17] making highly efficient use of the photoactive material. As a result, this simple, highest-yield technique in air is capital-efficient and eliminates the need for costly vacuum-deposition techniques originally used to fabricate thin-film solar cells. The photovoltaic functionality gets integrated at low cost in existing structures, printing rolls of the PV material anywhere, from windows to roofs, through external and internal walls, replacing the traditional installation approach with an integration strategy (Figure 8).

Figure 6. Long-awaited flexible electronics are now a reality with OLED displays enabling ubiquitous, comfortable reading (photo courtesy of Plastic Logic).

Figure 7. Plastic solar cells, such as that on the left which is entirely organic (photo courtesy of Konarka) or that on the right which uses amorphous Si (photo courtesy of Flexcell), are lightweight (25–50 $g\,m^{-2}$) and ideally suited for customised integrated solutions.

3. Inorganic Thin Films: Flexible a-Si Modules

Following the introduction in 1997 of triple-junction modules, which provide relatively high levels of efficiency and stability (stabilized aperture area cell efficiency of 8.0–8.5%),[18] the most successful flexible PV modules developed thus far use amorphous silicon (a-Si) thin-film technology (Figure 9). In a triple-junction cell, cells of different band gaps are stacked together (Figure 10). The top cell, which captures the blue photons, uses an a-Si alloy with an optical gap of about 1.8 eV for the intrinsic (i) layer. The i layer for the middle cell is an amorphous silicon-germanium (a-SiGe) alloy that contains about 10–15% Ge and has an optical gap of about 1.6 eV, which is

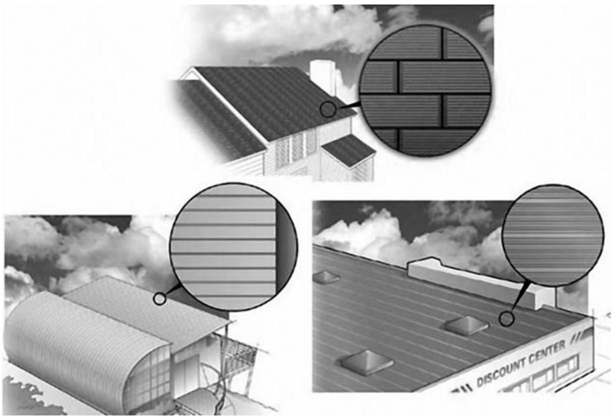

Figure 8. New flexible solar modules are integrated, rather than installed, into existing or new buildings (picture adapted from Konarka).

Figure 9. Thin-film PV modules laminated together with polyolefin membranes, which act as a waterproofing system. Roofing membranes are joined by means of hot air welding equipment normally used for the construction of flat roofs (reproduced from ref. [18], with permission).

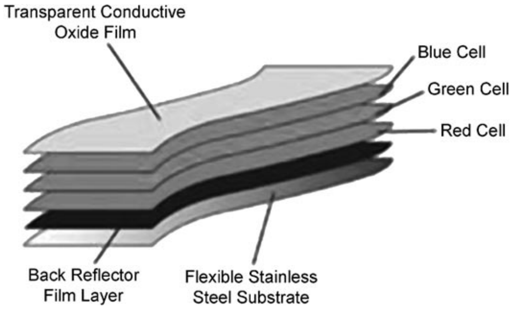

Figure 10. Schematic of a triple-junction structure containing amorphous silicon (reproduced from http://www.uni-solar.com, with permission).

ideally suited for absorbing green photons. The bottom cell captures the red and infrared photons and uses an i layer of a-SiGe alloy with an optical gap of about 1.4 eV. Light that is not absorbed in the cells gets reflected from the aluminum/zinc oxide (Al/ZnO) back reflector, which is textured to facilitate light trapping.

The resulting thin-film photovoltaic product has the ability to capture a greater percentage of the incident light energy, which is a key to a higher energy output at lower irradiation levels and under diffused light. As an example, the overall annual energy yield of the thermally insulated a-Si plant over the roof of a school in Switzerland (Figure 9) was almost comparable to that of a 20° tilted open-rack c-Si power plant, despite the lower irradiance and higher reflection losses associated with the latter.[19]

Usually, the cell is deposited using a vapour-deposition process at low temperatures; the energy payback time is therefore much shorter than that for conventional technology. The roll-to-roll process utilizes a flexible, stainless steel substrate (Figure 11). Once the solar cell material has been fitted with suitable electrodes, the cells are encapsulated in UV-stabilized, weather-resistant polymers. In a high-volume manufacturing plant operated by United Solar Ovonic (Michigan, USA), solar cells are deposited on rolls of stainless steel. Rolls of stainless steel (2500 m long, 36 cm wide, and 125 μm thick) move in a continuous manner in four machines to complete the fabrication of the solar cell. A wash machine washes the web one roll at a time; a back-reflector machine deposits the back reflector by sputtering Al and ZnO on the washed rolls; an amorphous silicon alloy processor deposits the layers of a-Si and a-SiGe alloy; and finally an anti-reflection coating machine deposits indium tin oxide (ITO) on top of the rolls. The coated web is next processed to make a variety of lightweight, flexible and robust products.

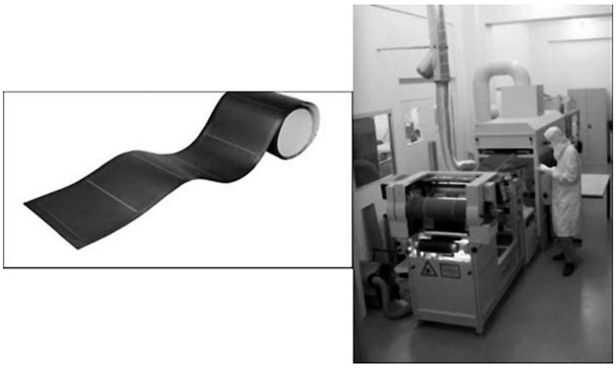

Figure 11. United Solar Ovonic flexible PV laminate is made of a-Si triple-deposited over steel (left), while thin films of Flexcell are deposited roll-to-roll over plastic substrates (right). (Reproduced from http://www.uni-solar.com and http://www.flexcell.ch, with permission.)

Flexcell (Switzerland) uses a four-step roll-to-roll manufacturing process in which metal coating of a plastic roll (thickness 50 μm) is followed by (chemical vapour) deposition of a-Si layers and the transparent conducting oxide (TCO) through layer structuring and module encapsulation with plastic foils.

In contrast to the higher thermal coefficient for crystalline Si photovoltaic cells (−0.5%/°C), the thermal coefficient for triple-junction photovoltaic cells is −0.21%/°C. This means that at a normal cell temperature of 60°C, the relative power output of a crystalline module would be reduced by about 17% from the standard test conditions rating, while the output of the triple-junction module would be reduced by about 4–6%. The effect of this characteristic is a higher level of energy output at normal to high cell temperatures. For example, comparison of amorphous, mono- and polycrystalline silicon-based PV modules connected to the residential grid in Japan clearly showed that the amorphous modules outperformed the crystalline module by about 15% in terms of annual energy yield (Figure 12).

Triple-junction PV modules, furthermore, perform more than 40% better under low light conditions (50–100 $W\,m^{-2}$) than most present crystalline technologies. In Northern and Central European climates, where low-light conditions and diffuse light prevails, this enhanced sensitivity under low light also results in a higher yearly energy output when normalised to W_p purchased power. The world's leading companies in a-Si TFPV manufacturing are undergoing rapid expansion from an annual production capacity of about 30 MW to 300 MW by 2010, to apply this technology as widely as possible and drive the expansion of its market share by applying its products to free-land applications and building-integrated photovoltaics (BIPVs).

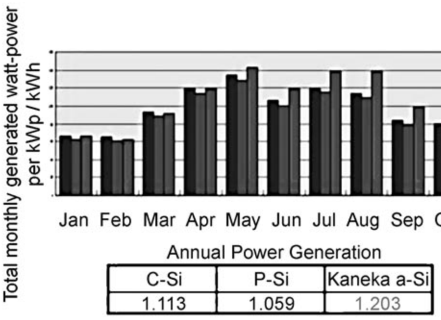

Figure 12. The trend in the monthly final yield over 1 year for a-Si and c-Si modules in Japan clearly shows that a-Si modules consistently yield more energy (reproduced from http://www.kaneka.com, with permission).

4. Inorganic Thin Films: Flexible CIGS Modules

CIGS cells exhibit the highest efficiencies among all thin-film PV devices. Copper indium diselenide ($CuInSe_2$) has an extremely high absorption that allows 99% of the available light to be absorbed in the first micrometer of the material. This makes it an optimal PV material for thin films. Adding small amounts of gallium to $CuInSe_2$ boosts its light-absorbing band gap, which makes it more closely match the solar spectrum thereby improving the voltage and the efficiency of the PV cell. In early 2008, with the aim of improving the quality of the material applied (by chemical vapour deposition), researchers at the US National Renewable Energy Lab developed a thin-film CIGS solar cell with an efficiency of 19.9%, setting a new record for TFPV cells and approaching the 20.3% efficiency of silicon-based rigid cells.[20] Remarkably, the conversion efficiency of CIGS is also very stable over time as these cells are truly self-repairing: some of the chemical bonds break easily, freeing copper atoms to wander through the crystals where a natural tendency to distribute themselves evenly means that they spread into damaged spots in the crystal, where their presence fixes the problem.[21]

Global Solar Energy (Arizona, USA) is currently the leading manufacturer of flexible CIGS thin-film solar modules. Its manufacturing process involves deposition of CIGS materials onto a thin, pliable and unbreakable substrate. The CIGS material is made by coating rolls of stainless steel about the thickness of aluminum foil with molybdenum, CIGS, cadmium sulfide and a TCO. Continuous roll-to-roll coating of thin-film PV layers on flexible substrates for CIGS makes use of vacuum deposition methods and exploits the fact that already the front and back contacts, namely two out of the three thin-film layers required in any of the thin-film approaches, are deposited with vacuum-based methods regardless of the specific absorber or semiconductor. The company sold 4.2 MW worth of CIGS material in 2007 and plans to manufacture 75 MW of its 10% efficient solar modules by the end of 2009 and 175 MW by the end of 2010. Indeed, it opened a new facility in Tucson and is completing construction of a new plant in Berlin (Germany) where it will produce 35 MW starting in late 2008, mostly as the lightweight, conformable modules called PowerFlex Solar Strings (Figure 13), which offer the CIGS solar material in a form ready to use in BIPV applications such as shingles, rolled roofing materials, and exterior wall coverings.

Figure 13. The new PowerFlex Solar Strings thin-film flexible photovoltaic material by Global Solar Energy Inc. (photo courtesy of Global Solar Energy Inc.).

5. Plastic Solar Cells

Once fully developed, efficient and stable polymeric solar cells will rapidly find widespread application.[22] Indeed, as compared to Si-based solar cells, efficient solar cells employing organic semiconductors will be less expensive and more easily manufactured while, being lightweight and flexible, they will be rapidly integrated into existing estates.

Molecular bulk heterojunction cells can be efficiently printed using inkjet printing technology, opening the route to the large-scale production of organic solar cells. As recently as March 2008, Konarka Technologies (USA) successfully demonstrated the manufacture of solar cells by highly efficient inkjet printing,[23] with little or no loss compared to clean-room semiconductor technologies such as spin coating (Figure 14).

Figure 14. These rolls are commercial-grade solar photovolatics printed by inkjet printer (image courtesy of Konarka Technologies, Inc.).

Developed in the early 1990s, the bulk heterojunction (BHJ) solar cell concept accounts for the short exciton diffusion length in disordered organic semiconductors as well as the required thickness for sufficient light absorption.[24] This approach (Figure 15) features a distributed junction between donor and acceptor material: both components, which are blends of polymer donors and highly soluble fullerene derivative acceptors, interpenetrate one another. Bulk heterojunctions have the advantage of being able to dissociate excitons very efficiently over the whole extent of the solar cell, and thus generating polaron pairs anywhere in the film. This gives rise to short circuit currents that are higher by orders of magnitude than the previously described devices and with the highest power conversion efficiencies. As an example to illustrate the potential of the technology, Konarka Technologies reported an efficiency of 5.21% for plastic solar cells with an active area of 1.024 cm^2.[25]

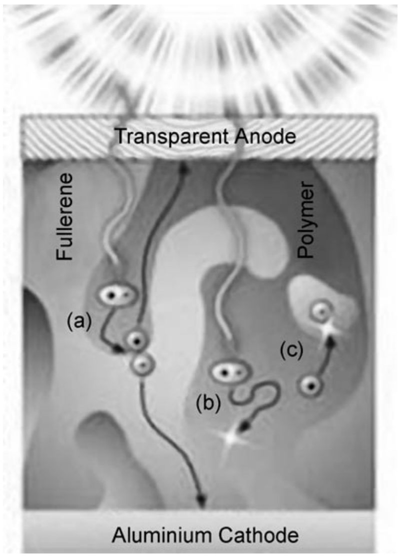

Figure 15. Processes of generation and recombination in disordered organic solar cells (image courtesy of Dr. C. Deibel: http://blog.disorderedmatter.eu). Following light absorption by the donor-conjugated polymer, excitons are photogenerated that diffuse to the donor–acceptor junction and dissociate to polaron pairs where they either a) give rise to a photocurrent with the help of an external electric field, b) recombine radiatively or c) recombine with other mobile or trapped charges.

In a classical inorganic solar cell, weakly Coulomb-bound pairs of charge carriers (an electron and a hole) are generated by the absorbed sunlight. In organic semiconductors, the screening of opposite charges is much weaker as the dielectric constant is lower. This leads to a much stronger interaction of the photogenerated positive and negative charges. Another significant difference between organic and inorganic solar cells is that organic semiconductors are amorphous and thus charge transport is more difficult than in crystals. However, an advantage is the ability to synthesise tailor-made organic substances, which allow fine-tuning of the absorption range, the charge-transport properties, and self-assembly through nanochemistry techniques. Moreover, very thin (100 nm) organic films can absorb almost all the light shone on them (within their absorption range),[26] which should be compared to an absorption length of around 300 μm for thick standard crystalline silicon wafers and of 1 μm for thin films of polycrystalline $CuInSe_2$.

Konarka Technologies is pursuing large-scale commercialization and in collaboration with German firm Leonhard Kurz they are trying to devise a high-speed press capable of producing Power Plastic cells. The semiconducting conjugated polymers are dissolved in standard industrial solvents to create an ink which is then applied through standard inkjet printing. The roll-to-roll line contains five stands (Figure 16). Each stand corresponds to a layer of the solar cell. The first substrate to be

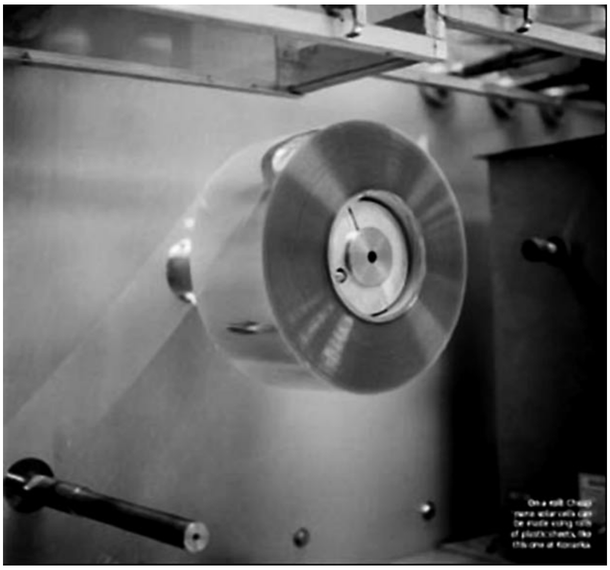

Figure 16. A plastic solar cell production line, where solar cells are printed roll-to-roll as newspapers are (photo courtesy of Konarka).

applied is a semitransparent electrode, typically a TCO layer. Next comes a patterning step that separates the cells from each other so they can later connect in series. Deposition of active layers is then followed by the introduction of a top electrode to complete the active stack. The completed cells are cut apart and laminated to produce voltage outputs as requested by customers.

All of these layers are remarkably thin. The base TCO layer, for example, is about 100 nm thick. Some of the active layers of semiconducting polymers are only tens of nanometers deep. Such shallow layers dry quickly and thus promote the use of fast web speeds. Another strategic step in fabrication consists of heating, which creates islands of crystals within otherwise amorphous polymer. This annealing process of poly(3-hexylthiophene):methanofullerene [6,6]-phenylbutyric acid methyl ester, better known as P3HT:PCBM, to get the correct nanostructure occurs at about 110 °C and takes just a few seconds of heating.[23] Cleanliness during deposition is important, however, rather than encasing the whole production line in a clean room to keep out dust, only the coating stations are sealed off. This setup lets the entire line reside in an ordinary factory environment. The cells manufactured by Konarka's roll-to-roll production line today should reach 3 % efficiency, which will come down a bit on the module scale.

High efficiency is not paramount in many of the applications envisioned for plastic cells. Customers care about total power (and lower cost), so if one needs more power from a plastic PV device, it is enough to use larger extensions of the cheap polymeric module. In early 2006, portable battery chargers and square-meter tent materials of Power Plastic (a trademark of Konarka Technologies) were delivered to the US Army. One crucial feature of plastic solar cells is that they can be obtained with printed patterns and colours, which as crucial aesthetic attributes considerably add value to Power Plastic. Indeed, rather than bringing end products to the market itself, the company is partnering with companies and allowing these partners to integrate solar cells into their products in compelling ways, instead of trying to compete with solar panel makers on the cost per watt. For example, the company has a partnership with Air Products to make windows that generate electricity using Konarka's solar films, and another collaboration with Sky Shades to commercialize power-generating shades (Figure 17). Furthermore, the lightweight and flexible nature of Power Plastic enables development of the product design from tethered to, to designed in and around (Figure 18).

Figure 17. By integrating Power Plastic into fabrics, shades that generate electricity will be commercialized by the end of 2008 (image courtesy of Sky Shades).

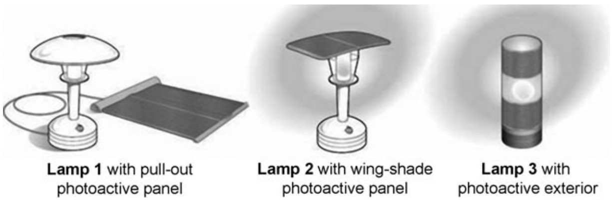

Figure 18. Design evolution with Power Plastic (image courtesy of Konarka).

Among the first organic PV products, there will probably be a solar-powered camping lantern, followed by tents that generate their own electricity, and trickle chargers (which charge the battery at the same rate that it is discharging) for portable devices such as mobile phones and MP3 music players, awnings and canopies, and powered smart cards.[27] Another related application will be solar sails. Such sails are being already explored worldwide and represent a potentially huge market. Once integrated in the fabric of the sail, the organic photovoltaic material is stabilized towards the harsh conditions of navigation in the open sea and will provide boats with increasing levels of energy, well beyond the amount needed to power the navigation electronic devices. For example, the boat shown in Figure 19 currently navigates Italy's sea using a hybrid motor (diesel–electric) with solar electricity produced by both amorphous Si and organic (polymer with carbon nanotubes and carbon nanofibers) photovoltaic thin films.[28] In the latter case, the cell is deposited over a flexible polyethylene terephthalate substrate and its efficiency is lower as compared to the cells in a-Si. However, the production price of the polymer/carbon nanotube cell would be considerably lower while the range of potential applications is far wider, and researchers are currently working on its improvement using data fed back from ongoing experiments at sea.

Figure 19. This ship currently navigates into Italy's sea using a hybrid motor (diesel + electric), with solar electricity being produced by either Si or organic (polymer with carbon nanotubes) photovoltaic thin films (photo courtesy of Michelangelo Calamai & Figli).

Most recently, researchers at the Fraunhofer Institute for Solar Energy (Germany) developed a flexible solar module that is as small as the page of a book whose front electrode instead of being made of expensive ITO is made of a poorly conductive transparent polymer electrode interconnected with a highly conductive metal layer on the rear side of the solar cell. The connection is made through numerous tiny holes in the solar cell and offers the advantage that a low-priced material can be used.[29]

6. Organic–Inorganic Thin Films: Flexible DSSCs

Invented in the early 1990s, dye-sensitized solar cells (DSSCs or DSCs) were first commercially used in 2003 and the initial modules based on this versatile hybrid (organic–inorganic) technology were used to build one wall at CSIRO's Institute (Australia). Like plastic solar cells, DSSCs share low weight and a low cost of production. However, their typical efficiency of 7% in commercial modules is about twice that of polymeric modules; whereas their good performance under diffuse light conditions is a feature they have in common with inorganic thin-film solar modules. DSSCs work well over a wide range of lighting conditions and orientation, as they are less sensitive to partial shadowing and low-level illumination, making DSSC-based modules particularly well suited for architectonic applications.[30]

Attempts to create photoelectrochemical solar cells by mimicking photosynthesis started in the 1970s, with early attempts to cover crystals of semiconductor titanium dioxide with a layer of chlorophyll. However, the electrons were reluctant to move through the layer of pigment, so the efficiency of the first solar cells sensitized in this way was about 0.01%. Then, in the late 1980s, scientists discovered that the problem could be overcome by using nanotechnology.[31] Instead of using a single large crystal of titania semiconductor, they worked with a sponge of small particles, each about 20 nm in diameter, coated with an extremely thin layer of pigment. This method increased the effective surface area available for the absorption of light by a factor of 1000—now the sunlight was very efficiently converted into an electric current. The first system used a 10 μm thick, optically transparent film of TiO_2 particles of tens of nanometers in size with a photosensitizer dye chemically linked (usually, by -COOH, $-PO_3H_2$, or $-B(OH)_2$ functional groups) to the surface of the semiconductor, a solution containing a redox mediator, and a metallic counter electrode. Remarkably, even this first cell displayed an efficiency of 7.1% and a photocurrent density up to 12 $mA\,cm^{-2}$.

The Australian company Dyesol has pioneered the commercialization of DSSCs after obtaining a license from the inventors and has developed the technology in practically every aspect.[32] The company recently introduced a flexible, foldable, lightweight and camouflaged solar panel for military applications which has been found to be superior to other PV technologies in maintaining voltage under a very wide range of light conditions, even in the dappled light under trees (Figure 20).

Figure 20. The flexible DSSC-based solar module developed by Dyesol for the Australian Army camouflages itself in trees where it provides constant voltage under a wide range of illumination levels (photo courtesy of Dyesol).

In general, DSSCs are very tolerant to the effects of impurities because both light absorption and charge separation occur near the interface between two materials which allows for roll-to-roll production, such as in the case of the G24i manufacturing process that transforms a roll of metal foil into a 45 kg, half-mile long dye-sensitized thin film in less than 3 h (Figure 21).[4] This material is robust, flexible, lightweight and generates electricity even indoors and under low-light conditions. In 2007, the US company G24 Innovations started production in a factory based in the UK.[33] Its modules are less than 1 mm thick, and scale-up of the original production capacity of 25 MW in 2007 to 200 MW is planned in a few years, following market response to initial commercialization. The first product is a solar charger series, which works indoors and outdoors and is compatible with mobile phones, laptops, audio players and digital cameras (Figure 22).

Figure 21. Roll-to-roll production of the first PV modules results in a flexible, lightweight PV material that suits different applications (photo courtesy of G24 Innovations).

In Israel, OrionSolar (now Solar 3G) has developed inexpensive modules comprised of 15 cm × 15 cm dye cells, based on a low-cost method of depositing TiO_2 in a sponge-like array on flexible plastic sheets (Figure 23).[34] The company has developed a manufacturing line that costs 40% less than the cost of a silicon line per megawatt output operating efficiently in the 8 MW domain. This means that manufacturing can be put in place at 15% of the capital cost of a typical silicon photovoltaic line.

Typically, nanocrystals of mesostructured TiO_2 in the anatase phase are prepared by sol–gel hydrothermal processing of a

Figure 22. The G10 charger commercialised as G24i (photo courtesy of G24 Innovations).

Figure 23. OrionSolar dye cells have an additional advantage: they are particularly suited to warmer climates (photo courtesy of OrionSolar).

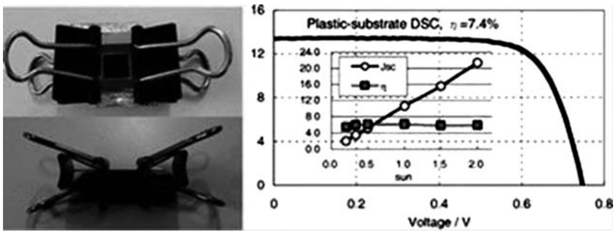

Figure 24. A 7.4% efficient flexible DSSC can be easily obtained by simple pressing (reproduced from ref. [37], with permission).

suitable titania precursor in the presence of a template such as Pluronic P123. The xerogel is isolated as a thin film supported over a glass that is further covered by another conductive glass.[35] However, by a lift-off technique, pre-sintered porous, composite layers comprising nanoparticles of TiO_2 up to tens of micrometers thick are easily transferred to a second flexible substrate, and the original electrical properties of the transferred porous layers are maintained.[36] This avoids the need to use process temperatures of up to 500°C as commonly used for sintering the TiO_2 nanoparticles together and has opened the route to mass production of plastic solar cells based on the DSSC technology.

A plastic substrate can also be used to afford flexible solar cells, whose efficiency is much improved by a method consisting of mechanical compression of a water-based TiO_2 paste to coat the film and prepare the TiO_2 photoelectrode without any heat treatment.[37] The resulting device (Figure 24) shows the highest light-to-electrical energy conversion efficiency based on plastic-substrate dye-sensitized solar cells: 7.4% under 100 $mW\,cm^{-2}$ (1 sun) AM1.5 illumination. Beyond its low cost (titania is widely used in toothpastes, sunscreen, and white paint) and ease of production, the unique advantages of titania-coated solar cells over Si-based cells lie in their transparency (for power windows), easy bifacial configuration (advantage for diffuse light) and versatility (the colour can be varied by selection of the dye, including invisible PV cells based on near-IR sensitizers). By 2015, it is expected that companies will attain 10% efficient modules that approach the criteria for solar module certification.

7. Personalizing Solar Power

Compared to traditional Si-based photovoltaics, flexible PV technologies offer a unique versatility that architects and engineers will harness to renew the facades of existing buildings, as well as in the construction of new buildings and in the development of power-generating products. In other words, these new technologies enable a true personalization of solar power. Flexible solar cells provide building component manufacturers with thin and lightweight PV foils that allows a seamless integration with building materials of various architectural shapes, thus combining PVs and architecture, and also cost-effective PV integration.

In wealthy countries, the building industry has become entirely customer driven. Customers needs are identified locally and then met by tailoring design and architecture on demand. Flexible, coloured solar modules offer a solution to the low versatility and poor aesthetics of traditional solar panels, enabling the production of semi-finished products that can be adapted to individual building situations.[38] In general, as Hagemann[38] put it, we are evolving from the old, serial PV product development scheme to one in which basic and applied research are carried out together using information fed back from manufacturing, marketing and social evaluation of technology (Figure 25). Therefore, the value-added chain becomes one for which design and marketing enter such a chain from the very beginning of the product development, thus enriching the value of the product with unique features such as decorative elements.

Flexible photovoltaic materials actually change the way buildings receive and distribute energy. In the Soft House (Figure 26) designed by Kennedy & Violich Architecture, for example, all surfaces that define space can also be producers of energy.[39] The boundaries between traditional walls and utilities shift: curtains are transformed into mobile, flexible energy-harvesting surfaces with integrated solid-state lighting. In other words, many of the hard wall surfaces of a standard prefabricated house are replaced with movable curtains that contain embedded thin-film plastic solar cells (Figure 26). By integrating specific household electronics (laptop computers, LED lighting, TVs, stereos, and some heating and cooling systems) with this DC power source, more than half the daily power needs of an average American household are fully met, as curtains move to follow the sun, generating up to 16 000 Wh of electricity. Prospective homeowners will thus have an extremely energy-efficient house that still offers the benefits of prefabricated construction, such as speedy construction and cost savings.

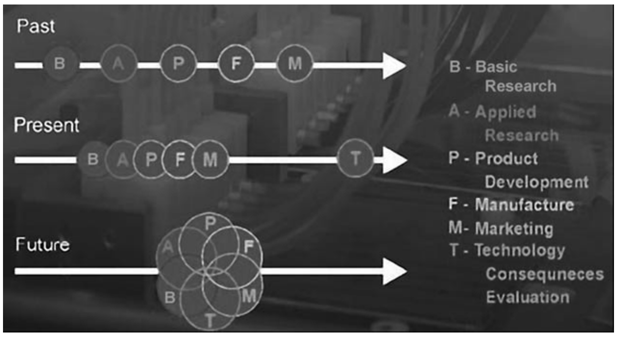

Figure 25. The old PV product development scheme is being replaced by one in which basic and applied research are carried out together using information fed back from manufacturing, marketing and social evaluation of technology (photo courtesy of Dyesol).

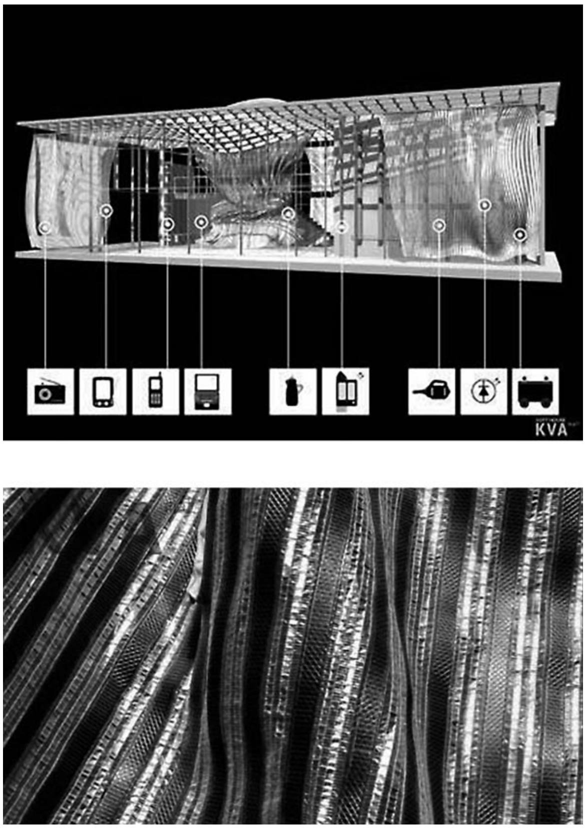

Figure 26. Top: A 3D rendering of "Soft House", which uses household curtains to collect solar energy and provide lighting. Bottom: The flexible array of semitransparent organic photovoltaic curtains used in the Soft House; the PV cells are woven into a malleable fabric (photos courtesy of KVA MAT X).

8. Outlook and Conclusions

With a focus on several practical aspects and with reference to up-to-date industrial information, this Review has highlighted the advancements that have been made and are in progress in the field of flexible solar cells, aimed at facilitating diffusion of these technologies.[11] We need to curb CO_2 emissions soon and we need to reduce our dependence on increasingly expensive hydrocarbons; thus, we need to use renewable materials and solar energy on a massive scale. Accordingly, along with the interest of citizens, companies and governments, private and public investment in solar energy is eventually booming. Numerous start-up PV companies are attracting financial investment from the world's leading venture capitalists, including oil companies. Google, for example, largely funded Nanosolar in the US, whereas investors in Konarka (Japan), a manufacturer of plastic solar cells, include some of the world's largest oil companies. Similarly, we believe that the increasing wealth in Islamic states will play a crucial role in making cheap solar electricity a reality for mankind, both because it is an intrinsically ethical field of investment highly recommended by the Sharia code[40] and also because the huge profits raised from high oil process in recent years need to be reinvested in preparing for the day when oil and gas reserves will be over. State-owned funds such as Abu Dhabi's Masdar, for example, already massively invest in solar energy.[41] Two billion people who lack access to the electric grid will greatly benefit from the advances that are being made, and so will companies and citizens in the developed world where the electricity bill has become an earnest economic problem. Flexible photovoltaic modules will be among the main tools used to get rid of this dependency.

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Keywords: photovoltaics · solar energy conversion · sustainable energy · thin films

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