

slow turnover time for current power generation infrastructure, mean that the energy sector's extremely low R&D intensity is a cause for concern not only today, but also for decades to come (12).

Responding to Energy and Environmental Needs

The energy technology and policy options of industrial and developing nations are closely linked together in a global energy economy. During the past 50 years the progression to cleaner fuels and more efficient use of fossil fuels has resulted in an annual decrease in the emission of carbon to the atmosphere of about 0.08 g of carbon per megajoule of energy produced (13). This rate of "decarbonization" is not sufficient even to meet the modest Kyoto Protocol target of a 5% decrease in greenhouse gas (GHG) emissions from industrial nations by 2010. Many scientists have instead argued that emissions reductions of 70% or more are necessary to stabilize the atmospheric GHG concentrations at 550 or 450 parts per million (5). Achieving these levels would require a doubling or tripling, respectively, of the current rate of decarbonization. Without a sustained and diverse program of energy R&D and implementation, we are crippling our ability to make the necessary improvements in the global energy economy.

Declining investments in an area at the heart of the environment-economy nexus is detrimental for both long-term U.S. energy security and for global environmental sustainability. First, it is necessary to understand and evaluate the impacts of current energy R&D efforts. Second, meeting the emerging global challenges will require increasing both U.S. and international energy R&D. Finally,

a broader collaborative environment is needed to support diverse energy research and implementation options and policies that work within and between highly industrialized and developing nations.

References and Notes

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8. Dollar values (unless otherwise noted) have been converted from current to constant 1996 dollars by using the gross domestic product chain-type price index (available at www.bea.doc.gov/bea/dn/0898nip3/table3.htm).
9. A linear regression with R&D as the independent variable and patents as the dependent variable yields an R^2 of 0.72 and a t statistic of 7.0 (significant at the 1% level).
10. A linear regression with energy R&D as the independent variable and energy-related patents as the dependent variable yields an R^2 of 0.84 and a t statistic of 10.0 (significant at the 1% level).
11. The investment-patent record for fossil-fuel, renewable, and nuclear energy has been studied separately (R. M. Margolis and D. M. Kammen, *Energy Policy*, in press).
12. Energy products are generally sold at very small margins (fractions of a cent per kilowatt-hour) so that alternate measures, such as the price/earnings ratio for energy companies, also warrant study.
13. N. Nakicenovic *et al.*, *Energy* **18**, 401 (1993).
14. The U.S. Patent and Trademark Office's "Patent Bibliographic Database" is available at www.uspto.gov/web/offices/ac/ido/oep/patbib/index.html.
15. "National Patterns of Research and Development Resources" (National Science Foundation, Washington, DC, published annually). The most recent volume of this NSF publication (and many others) is available at www.nsf.gov/sbe/srs/pubdata.htm.
16. See "Federal R&D Funding by Budget Function" (National Science Foundation, Washington, DC, published annually), Table 12. We define U.S. Department of Energy (DOE) Energy Technology R&D as the sum of expenditures for fossil-fuel energy, nuclear energy, magnetic fusion, solar and renewable energy, and energy conservation.
17. Data on R&D are included in "Research and Development in Industry" (National Science Foundation, Washington, DC, published annually).
18. "Annual Report" (Electric Power Research Institute, Palo Alto, CA, published annually).
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20. We thank S. DeCanio, S. Devotta, J. Holdren, H. Dowlatabadi, R. May, A. Rosenfeld, and V. Ruttan for comments and advice. Supported by the Summit Foundation and the Class of 1934 Preceptorship at Princeton University, both awarded to D.M.K.

REVIEW

Photovoltaic Technology: The Case for Thin-Film Solar Cells

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The advantages and limitations of photovoltaic solar modules for energy generation are reviewed with their operation principles and physical efficiency limits. Although the main materials currently used or investigated and the associated fabrication technologies are individually described, emphasis is on silicon-based solar cells. Wafer-based crystalline silicon solar modules dominate in terms of production, but amorphous silicon solar cells have the potential to undercut costs owing, for example, to the roll-to-roll production possibilities for modules. Recent developments suggest that thin-film crystalline silicon (especially microcrystalline silicon) is becoming a prime candidate for future photovoltaics.

The photovoltaic (PV) effect was discovered in 1839 by Edmond Becquerel. For a long time it remained a scientific phenomenon with few device applications. After the intro-

duction of silicon as the prime semiconductor material in the late 1950s, silicon PV diodes became available. They were soon indispensable for supplying electrical power to tele-

communications equipment in remote locations and to satellites. Then, in the 1970s, a major reorientation took place in the general perception of the energy supply problem: The oil crisis of 1973 led to a general public awareness of the limitation of fossil fuels; many governments (including those of the United States, Japan, and several European

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countries) started, a few years later, ambitious programs in the search for alternative energy sources, including PV solar energy. This trend was reinforced by public controversy over nuclear fission reactors and by a series of accidents in nuclear power stations, especially those of Three Mile Island (in 1979) and Chernobyl (in 1986).

Since the beginning of the 1990s, ecological considerations linked with the CO₂/global warming problem have taken over as a main driving force in promoting alternative energy sources, in particular, PV solar energy. The past two decades have seen constant and substantial progress in the field of PV modules: commercial prices of modules (when purchased in large quantities) have shown a sustained average reduction of 7.5% per year; during the same time, the worldwide production of modules has increased on average by 18% per year (Fig. 1). Although these two trends can be expected to continue in the near future, it will take many decades before PV modules can substantially contribute to electricity generation. The reduction in PV module cost progresses with the increase of production, but we are rapidly reaching a stage where a further decrease in cost is conditional on the global availability of raw materials. Thus, PV technologies that involve the use of lesser quantities of cheaper and less refined input materials are favored.

The present cost of electricity from PV installations is generally (except in remote areas) about an order of magnitude higher than the current commercial prices of electricity generated by hydraulic power and nuclear and fossil fuels. Because of physical reasons, it appears at present to be very difficult to substantially increase the energy conversion efficiency of low-cost PV modules over 15%. Thus, it becomes necessary to reserve large surfaces for the PV generation of electricity, which also means that the costs of substrates, encapsulation, wiring, and supporting structures are decisive factors in

the cost breakup of PV solar installations. This requires a full integration of PV installations into the existing environment and habitat.

Although solar cells and PV installations do not generate any CO₂ during their operation, they do, however, consume considerable amounts of energy and cause the generation of CO₂ and certain pollutants during their manufacture. The energy payback time and the ecological balance sheet of solar modules and PV installations are, therefore, important issues to be considered when choosing a future technology.

Principle of Operation of PV Solar Cells

Photogeneration. A PV solar cell is basically a semiconductor diode. The semiconductor material absorbs the incoming photons and converts them into electron-hole pairs. In this photogeneration step, the decisive parameter is the bandgap energy E_{gap} of the semiconductor. In an ideal case, no photons with an energy $h\nu < E_{\text{gap}}$ will contribute to photogeneration, whereas all photons with an energy $h\nu > E_{\text{gap}}$ will each contribute the energy E_{gap} to the photogenerated electron-hole pair, with the excess energy $(h\nu - E_{\text{gap}})$ being very rapidly lost because of thermalization.

The maximum limit for the photogenerated electric current density J_{ph} is therefore given by the flux of photons with an energy $h\nu > E_{\text{gap}}$. Thus, J_{ph} decreases with increasing bandgap E_{gap} . At the same time, the net energy transferred to each electron-hole pair increases, as it is equal to E_{gap} . There exists an "optimum" for E_{gap} (~ 1.1 eV) for which a maximum of energy can be transferred from the incident sunlight to the totality of photogenerated electron-hole pairs. At this bandgap, roughly half of the incident solar energy is transferred.

This limit will only be approached if optical losses due to reflections, shading by grid patterns, and so forth are minimized and if the

semiconductor is thick enough to absorb all useful incident photons. The latter condition is particularly difficult to fulfill in semiconductors with an indirect bandgap (such as crystalline silicon), because of their low values of absorption coefficients, but is more favorable in amorphous semiconductors or in semiconductors with a direct bandgap. Therefore, crystalline silicon can only be used for solar cells if it is either relatively thick (~ 100 μm) or if sophisticated light-scattering (light-trapping) schemes are employed; this is one of the reasons why research into thin-film crystalline silicon solar cells has only recently begun on a wide scale.

Charge separation. In the second step of the energy conversion process, the photogenerated electron-hole pairs are separated, with electrons drifting to one of the electrodes and holes drifting to the other electrode, because of the internal electric field created by the diode structure of the solar cell. The dark (nonilluminated) characteristics of the diode and the photogenerated current can, in principle, be linearly superimposed (1, 2); this results in the solar cell equivalent circuit shown in Fig. 2A and the current-voltage (I - V) curve at the output of a solar cell, shown in Fig. 2B. Maximum power can be retrieved from the solar cell at the maximum power point MPP, which is equiv-

Fig. 1. Price evolution (from factories) (blue) for PV modules and total yearly world production (red) of PV solar cells (logarithmic scale); the prices are in current dollars per 1-W peak power rating (\$/Wp) (blue). If corrected for inflation, the price decrease between 1975 and 1985 is much steeper; the projection after 1998 is based on maintaining the same cost reduction rate of 7.5% as well as the same growth rate of 18% as in the period from 1993 to 1997 (58–60). The replacement of a single large-scale 1-GW nuclear power station by PV electricity generation would require (depending on location and climate) between 5000 MW_p and 10,000 MW_p of PV modules.

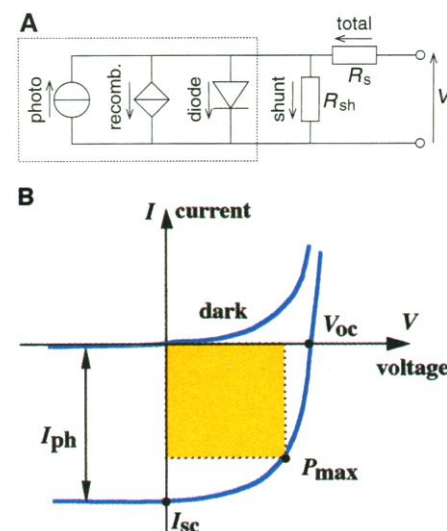
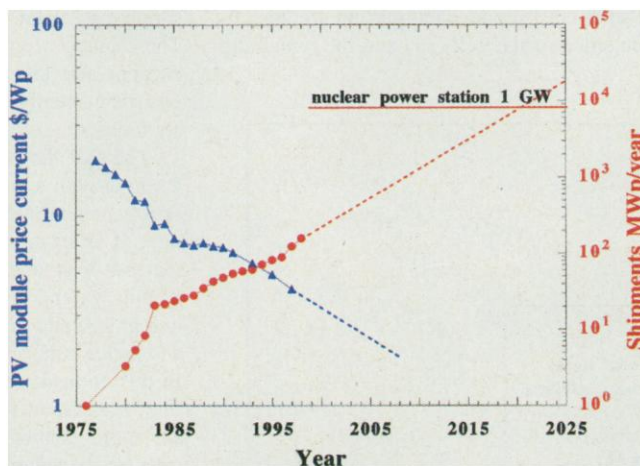


Fig. 2. (A) Electrical equivalent circuit of a PV solar cell (67). The diode is a dark (nonilluminated) p-n or p-i-n diode. Additional recombination (particularly in the i-type layer of p-i-n diodes) is represented by the current source, which counteracts the photogenerated current. R_s and R_{sh} are resistors that represent electrical losses (for example, R_s losses due to contact resistance and R_{sh} losses due to pinholes through the solar cell). (B) Typical I - V characteristics of a solar cell, with the three characteristic parameters: short-circuit current I_{sc} , open-circuit voltage V_{oc} , and fill factor $FF = P_{\text{max}}/(V_{oc} \times I_{sc})$; P_{max} is the electrical power delivered by the cell at the maximum power point MPP.

alent to the product of the open-circuit voltage V_{oc} times the short-circuit current density J_{sc} times the fill factor FF (FF expresses the form of the I - V curve). J_{sc} , V_{oc} , and FF are the three key parameters characterizing solar cell performance. The maximum limit for J_{sc} is given by the photogenerated current density J_{ph} .

V_{oc} , on the other hand, cannot exceed E_{gap}/q (q is the charge of an electron) and is, in general, quite a bit lower owing to recombination. At open-circuit conditions, all photogenerated carriers recombine within the solar cell diode. Thus, if recombination can be minimized, V_{oc} can more closely approach the limit (E_{gap}/q). However, from thermodynamic considerations of the balance between radiation and generation, one finds that recombination cannot be reduced below its radiative component, yielding a lower basic limit for V_{oc} (3).

Considering FF, Green (1) has calculated it as a function of V_{oc} by assuming that the I - V characteristics of a diode are, in an ideal case, an exponential function. The calculations show that the limit for FF increases with E_{gap} .

The optimum value of E_{gap} for the total energy conversion efficiency (including charge separation) is ~ 1.5 eV, with a "limit" efficiency approaching 30% (4). Gallium arsenide (GaAs), indium phosphide (InP), and cadmium telluride (CdTe) are semiconductor materials that have bandgap energies very near to the optimum value. However, the first two are too costly for large-scale terrestrial applications, and CdTe has toxicity problems. With crystalline silicon, laboratory cells have been produced that are near the corresponding efficiency "limit" of 25% (4). However, such record cells are based on sophisticated designs and are not suited for large-scale commercial utilization. As we go from small-size, expensive laboratory cells to large-area, low-cost commercial modules, various additional losses must be allowed for, and compromises between performance and cost must be found; therefore, one often ends up with

module efficiencies that are, in the best case, $\sim 15\%$.

A way to increase efficiency over the above limits would be to use multijunction cells (tandems and triple junctions) by optically cascading two or more solar cells with different bandgaps. This concept has led to interesting laboratory experiments, in which very high efficiencies [up to 32.6%, with sunlight concentration (5)] are demonstrated in complicated setups that have, however, no importance for commercial modules. On the other hand, tandems and triple junctions are at present used in amorphous silicon solar cells, with the goal of reducing the effect of light-induced degradation observed there.

Finally, concentration of sunlight also results in a higher theoretical efficiency limit: The balance between photogeneration and recombination described above becomes more favorable; thereby, V_{oc} and FF are increased. The use of higher light intensities is associated, however, with serious practical problems: Higher current densities and higher temperatures have to be handled. Moreover, the optical concentrator itself and the mechanical light tracking add to the complexity and cost of the system. Thus, concentrator solar cells have not found a large field of practical application.

Figure 3 shows the evolution of record laboratory efficiencies for small-size solar cells for different technological options over the past 45 years. All thin-film technologies show an efficiency evolution curve that is similar to that of crystalline silicon, but with a delay of ~ 10 years. Ribbon silicon (actually a bulk crystalline silicon technology) has not achieved any substantial lead over thin-film technologies. No stabilized efficiencies can be given for dye cells, as their stability problems are not yet fully solved.

PV Technologies

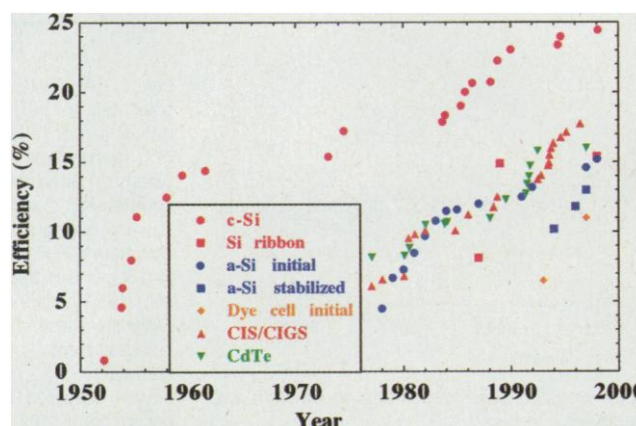
Crystalline silicon solar cells: The trend toward thin-film crystalline silicon. As $>80\%$ of solar cells produced at present are crystalline silicon solar cells (6) and the remaining

20% are mostly amorphous silicon solar cells (which are mainly restricted to consumer electronics), almost all PV systems with >1 -kW peak power rating (kW_p) are fitted with crystalline silicon solar cells. These solar cells were until very recently exclusively based on the use of silicon wafers. Alternative structures, such as silicon ribbons, are just being introduced into the market.

Wafer-based crystalline silicon solar cells have relatively high efficiencies, with commercial modules having efficiencies between 12 and 16% and laboratory cells having a record efficiency of 24.4% (7). These cells have already proven their excellent stability and reliability, operating under outdoor conditions without any deterioration in their performance over several decades. The main disadvantage associated with this technology is, however, the resulting high module price (presently about \$4.50 per 1-W peak power rating). This high price has set the amount for PV modules in general, as (until very recently) cheaper modules based on other technologies were simply not available. The high production cost is a consequence of several factors: (i) the low production volume of present manufacturing plants [recent studies indicate, that about a factor of 2 could be gained in cost reduction if the production volumes were upscaled by an order of magnitude (8)], (ii) the complex production steps involved in cell manufacturing and in module assembly, and, especially, (iii) the large amount of highly purified silicon feedstock required (20 kg of feedstock for every 1 kW_p of module production). The feedstock problem limits the cost reduction potential of wafer-based silicon technology. Until 1995, the PV industry mainly used rejects from the microelectronics industry; it could, thus, obtain silicon feedstock at reduced prices. With the growth of the PV industry, this source of feedstock supply became insufficient. Silicon feedstock supply will remain a serious bottleneck until production plants for directly supplying "solar-grade silicon" are set up: These plants would then be able to supply a cheaper and less pure form of silicon than what is currently used for the microelectronics industry.

The fact that wafers have to be cut from an ingot with a mechanical saw creates other serious impediments for wafer-based technology: It is expensive, involves considerable material loss, and can result in the breakage of thin wafers. Furthermore, wafers are limited in size and must be externally assembled and series connected to form larger modules. In this context, square-shaped "multicrystalline" wafers cut from cast polysilicon ingots are more convenient to assemble than the circular-shaped monocrystalline wafers. Multicrystalline wafers are also cheaper, but they generally result in cells and modules with

Fig. 3. Record efficiency evolution of small-size laboratory solar cells of various technologies [see (5) and references cited in (5)].



conversion efficiencies that are 2 to 4% lower than those obtained with monocrystalline wafers. Wafer-based silicon technology has the potential to be ecologically acceptable (9), but it implies a substantial amount of fabrication energy, so-called "gray energy" (10).

Among all the methods investigated for the further improvement of wafer-based crystalline silicon technology, only two schemes will be mentioned here. The first scheme consists of forming the solar cell within a high-quality epitaxial layer grown on top of a silicon wafer. Although high efficiencies ($>19\%$) (11–13) and high deposition rates (0.5 $\mu\text{m}/\text{min}$) for epitaxial growth at temperatures of $\sim 500^\circ$ to 600°C (14) have been demonstrated with laboratory methods, the transfer of these techniques to economically viable schemes [for example, multiple reutilization of the original silicon wafer or, alternatively, growth of an epitaxial layer on top of a laser-crystallized hydrogenated amorphous silicon (a-Si:H) layer on glass] has resulted in cell efficiencies that are only ~ 10 to 12% (15, 16).

The second scheme is based on the deposition of a doped amorphous silicon layer on the crystalline wafer to form a heterojunction (17). Another amorphous silicon layer can be deposited on the opposite side of the wafer (18, 19) to form the back surface field and obtain back-side passivation, increasing the efficiency to 20.0% for laboratory cells. Corresponding pilot production of cells and modules has been announced (20). The advantage of this scheme is simplified cell processing combined with a relatively high efficiency.

Crystalline silicon ribbons and crystalline silicon layers (on substrates) do away completely with the need for producing wafers by sawing. Research on these ribbons and layers has been under way for ~ 20 years and is only now entering the production phase. These cells are based on multicrystalline silicon material obtained directly from the liquid phase. The temperature of ribbon or layer formation is thus given by the melting point of silicon and is $\sim 1412^\circ\text{C}$. Such a high temperature limits the choice of substrates. These ribbon-forming schemes also suffer from a problem of thermal and mechanical stress, because of the high thermal gradients (on the order of $500^\circ\text{C}/\text{cm}$) present near the solid-liquid interface. In addition, the feedthrough rates for forming ribbons with satisfactory material quality are relatively low (around 18 mm/min) (21).

Several megawatt peak power ratings (MW_p) of solar modules based on ribbons are currently being produced with the edge-film growth method (22). Laboratory efficiencies have been as high as 14%. In an alternative approach, the string ribbon method is being modified so that substrates are no longer required, and an efficiency of 15.4% has been demonstrated for laboratory cells (23); but, commercial modules are not yet available.

Researchers at the Institute of Energy Conversion at the University of Delaware have developed modules based on a 50- μm -thick silicon layer deposited on a ceramic substrate (24). They use a method for integrated monolithic series connection of submodules that is similar to the one developed for amorphous silicon and other thin-film modules. Efficiencies reported recently for a 320- cm^2 module are 9.79% (25). It can be expected that these methods will yield some cost advantage as compared to conventional wafer-based crystalline silicon modules, but at the price of reducing the efficiency.

Since the past few years, there has been a strongly increasing interest in thin-film crystalline silicon solar cells with film thicknesses of $<10\ \mu\text{m}$. Of all the methods tested for depositing crystalline silicon thin films from the gas phase, probably the most interesting are those that operate at low temperatures (typically 200° to 500°C); they allow for the use of low-cost substrates, such as glass, stainless steel, aluminum, or sometimes even polymers. They also permit, in principle, efficient grain-boundary passivation by hydrogen incorporation into the growing crystalline layer. Thus, even at grain sizes well below 1 μm , satisfactory layer properties can be obtained. To keep the required total thickness of the solar cell as low as possible (preferably $<2\ \mu\text{m}$), one must employ an efficient form of light scattering or light trapping. This is achieved with surface texturing of the silicon layer as it is deposited and of the contact layers, especially of the transparent conductive oxides (TCO) used in our examples. So far, the most promising results have been obtained by plasma-enhanced chemical vapor deposition (PECVD). Deposition temperatures as low as 220°C can be obtained with the very high frequency (VHF) plasma deposition method (26). Efficiencies of up to 8.5% were reached with a cell thickness of 2.7 μm . With standard PECVD at 13.56 MHz and for deposition temperatures of 500° to 550°C , an aperture cell efficiency of 10.1% was obtained for a 2.0- μm -thick cell (27).

These cells have low V_{oc} values (~ 500 mV), which could possibly be increased by

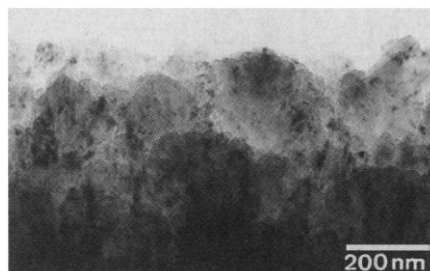


Fig. 4. TEM cross-section micrograph of typical intrinsic microcrystalline silicon layer as deposited by PECVD and used for p-i-n solar cells (26).

optimizing crystallite nucleation and growth and thereby reducing recombination. Figure 4 shows a transmission electron microscopy (TEM) photograph of a typical microcrystalline silicon layer incorporated in such a cell, indicating the complexity of structures involved.

From an economical point of view, present deposition rates of ~ 5 to $10\ \text{\AA}/\text{s}$ (28) must be increased. Combining this increase with a cell thickness reduction to $\sim 1\ \mu\text{m}$, deposition times of well below 1 hour would be possible.

Crystalline silicon thin-film solar cells deposited by PECVD can be easily combined with amorphous silicon solar cells to form tandem cells (Fig. 5); the bandgaps involved (1.1 eV for crystalline silicon and ~ 1.75 eV for amorphous silicon) are very close to the theoretically ideal combination. Resulting stabilized tandem cells with efficiencies of $\sim 12\%$ have been reported (27, 29, 30).

An interesting structure for multijunction crystalline silicon solar cells was proposed by the Photovoltaics Research Centre of the University of New South Wales (31). In this structure, the individual component solar cells are electrically connected in parallel (and not in series, as in the conventional tandem and multijunction structures). Numerical simulations (32) indicate that the efficiency potential of such a structure is $\sim 15\%$. It is, in principle, feasible to use a large number of individual junctions within this structure. Indeed, the delicate current-matching problem of conventional series-connected multijunction cells does not apply here. However, fabrication costs may become substantially higher again. A large R&D program is under way in Australia (33), but few experimental results have been published.

Amorphous silicon solar cells. Hydrogenated amorphous silicon was introduced as a material with a potential for semiconductor devices in the mid-1970s and is the first thin-film solar cell material that has reached

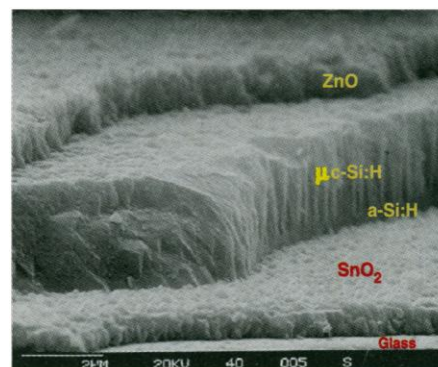


Fig. 5. Microcrystalline and amorphous silicon tandem solar cell, as introduced by the IMT (so-called "micromorph" solar cell) (26) Scale bar, 2 μm .

the stage of large-scale production (~ 20 MW_p/year at present). Amorphous silicon has, in the visible range of the spectrum, a higher optical absorption coefficient than crystalline silicon and, thus, can have thicknesses much less than 1 μm . In order to reduce recombination losses, a-Si:H solar cells use the p-i-n structure, consisting of a thin p-type doped layer, a central intrinsic i-type layer (which is the photovoltaically active layer), and a thin n-type doped layer. The electrical transport in the i-type layer is assisted by an electric field.

The deposition of amorphous silicon layers for solar cells is generally carried out with PECVD, which allows for deposition of large areas (up to 1 m² or more); generally, the a-Si:H solar cell is deposited on glass coated with a TCO; the TCO layer is either SnO₂ or ZnO and acts as a front contact. In an alternative structure, the amorphous silicon solar cell is deposited on an opaque substrate, such as stainless steel or even a polymer. The stainless steel or polymer substrates can be obtained as thin flexible foils, allowing a roll-to-roll deposition process (Fig. 6) (34). At present, industrial processes for amorphous silicon are limited by low deposition rates (~ 1 Å/s) and the resulting high deposition times (~ 1 hour) for a solar cell. The cost of producing high-quality TCO layers is another bottleneck, shared also by other thin-film solar cells. Thus, the price of amorphous silicon solar modules is, at present (for a given power output), only marginally lower than that of crystalline silicon solar modules. There is, however, ample scope for future

price reductions. Deposition rates can be increased fivefold with the VHF plasma method (35); TCO costs can be reduced by using ZnO instead of SnO₂ and by streamlining the whole TCO fabrication process (36).

The major handicap of amorphous silicon solar cells and modules is their low efficiency values. The present laboratory record for stabilized efficiency is 13%, obtained on a triple-junction cell (37); actual commercial modules have stabilized efficiencies between 4 and 8%.

One of the main reasons for the limitation in stabilized efficiency is the Staebler-Wronski effect (SWE) (38), or light-induced degradation (Fig. 7), in which the efficiency decreases to a stabilized but lower value after ~ 1000 hours of illumination. Subsequent annealing at 100° to 250°C can restore the original efficiency. It has become clear that the SWE is due to the creation of new defects (dangling bonds) that act as additional recombination centers. Despite massive research efforts, no way was found to manufacture amorphous silicon layers that do not possess such an effect. On the other hand, the SWE can be substantially reduced by diluting the silane (SiH₄) source gas used for plasma-assisted deposition of amorphous silicon with hydrogen (39).

By combining thin individual cells into a tandem or a triple-junction cell, one can reduce the detrimental effect of light-induced degradation (SWE) on cell efficiency. Thinner layers and thinner p-i-n cells suffer less from collection problems, even if the defect

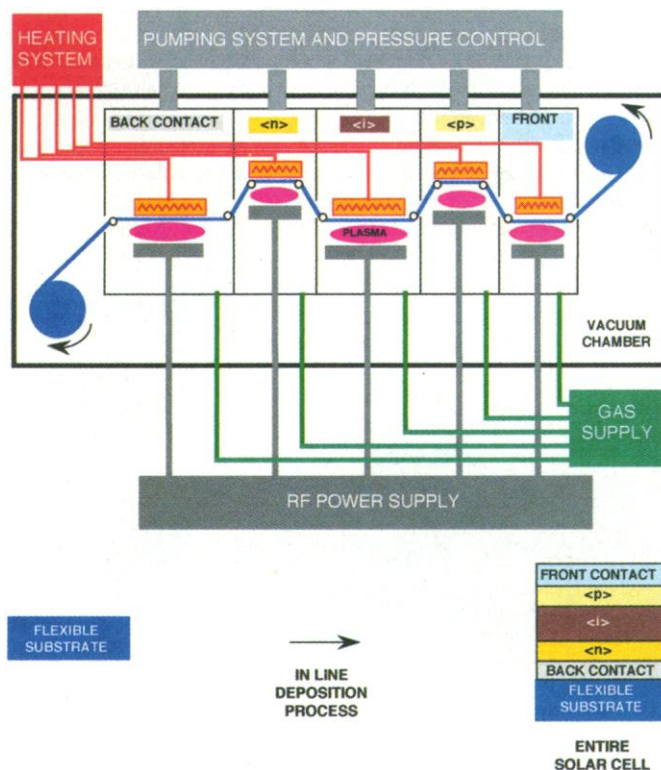
density is increased by the SWE; this is because, in thinner p-i-n-cells, the electric field prevailing in the i-type layer is enhanced, and collection is generally improved. Tandem and triple-junction cells also have the potential for a better use of the solar spectrum, provided that the bandgap energies of the individual component cells can be adjusted accordingly. This can be partly achieved if amorphous silicon is used with amorphous alloys of silicon and germanium. The latter have lower bandgaps than amorphous silicon itself; however, they also possess higher recombination center densities, especially for bandgaps < 1.4 eV (40, 41). Thus, although this combination provides somewhat higher efficiencies than tandem cells with amorphous silicon alone, there has not yet been a breakthrough here. A way out of this dilemma would be to combine amorphous silicon with both amorphous silicon and germanium alloys and with microcrystalline silicon; one could thus obtain bandgap energies that can be better spaced over the whole range from 1.1 eV (microcrystalline silicon) to 1.75 eV (amorphous silicon).

Advantages of amorphous silicon PV technology are as follows: the low deposition temperatures (typically 200° to 300°C), which permit the use of low-cost substrates; the possibility to easily integrate such modules into facades, roofs, and other structures; the option of implementing monolithically integrated electrical series connections within the solar cell structure itself; the relatively low production energy and low material quantities that need to be invested in the fabrication of a module; the abundance of all raw materials involved; the potential for realizing a large-scale manufacturing operation with an excellent ecological balance sheet; and, in the long run, the prospect of a substantial cost reduction (42, 43). Only a part of these advantages are shared by other thin-film technologies.

Amorphous silicon modules appear to be the ideal future candidate for those PV applications in which low cost is more important than high efficiency. They are especially suitable for solar pumps and building integration, where a sufficient surface area can be made available without high extra cost. In the sector of power supplies for small apparatuses, amorphous silicon has a dominant position and is not likely to be pushed out.

Copper indium diselenide and related materials. Copper indium diselenide (CIS) and copper indium gallium diselenide (CIGS) are direct-gap polycrystalline semiconductors with very high optical absorption coefficients and are presently being widely studied for application in solar cells, with the corresponding module technology just reaching the stage of pilot production. CIS and CIGS are p-type semiconductors and are always used in a heterojunction

Fig. 6. Principle of roll-to-roll deposition process for the deposition of amorphous silicon solar cells on flexible substrates (here, stainless steel) (34). The PECVD process is usually operated at the radio frequency (RF) of 13.56 MHz.



structure, mostly with very thin n-type cadmium sulfide (CdS) layers.

The efficiency record obtained to date for a small-size (0.449 cm²) laboratory cell is 18.8% (44), which is impressively high for a thin-film (3 μ m absorber thickness) polycrystalline solar cell. This is achieved with an effective bandgap of 1.1 to 1.2 eV for the absorber material. By partially substituting gallium for indium in CuInSe₂, the bandgap of this semiconductor can be increased, and the PV performance is optimized by increasing V_{oc} . A further degree of freedom is obtained by the partial substitution of S₂ for Se₂ (45). Other materials-oriented research efforts are directed at replacing the CdS window layer with a cadmium-free material, such as In(OH, S) (46). At present, the efficiencies of CIGS modules (30 cm by 30 cm) with integrated series connection, as fabricated in pilot production lines, are between 9 and 12% (47); this value is substantially lower than the laboratory record.

In terms of stability, CIS and CIGS solar cells do not have a problem of light-induced degradation; they generally show a slight increase in V_{oc} and in efficiency during the first hours of operation and can be remarkably stable, as was proven for periods up to 8 years (48). However, they do have a problem of instability in a hot and humid environment (49).

It is expected that CIS and CIGS cells should be substantially cheaper than wafer-based crystalline silicon modules (once production can be mastered on a large scale). However, if and when CIS and CIGS solar cell technology reaches a production volume on the scale of a few 100 MW_p/year, the availability and the price of indium will become a major issue: The availability of indium in Earth's crust is comparable to that of silver, and because of this relative scarcity, indium has been subject to erratic fluctuations in world market price. For example, a sharp price increase was registered around 1980, when Japanese liquid crystal display manufacturers started using large quantities of this material in their displays (4).

Cadmium telluride solar cells. Similar to CIS and CIGS, CdTe is a semiconductor with a direct bandgap, which almost fully absorbs the visible light within $\sim 1 \mu$ m. The bandgap energy, $E_{gap} = 1.45$ eV, is very near the optimum value for single-junction solar cells, simultaneously yielding both high current densities J_{sc} (up to 26 mA/cm²) and high voltages V_{oc} (up to 850 mV). Because CdTe is a binary compound, CdTe solar cells and modules are easier to fabricate than those from the CIS/CIGS system. A typical CdTe solar cell structure consists of a n-CdS and p-CdTe heterojunction deposited on a glass substrate coated with a TCO. Just as in CIS/CIGS cells, the highly doped CdS layer is a very thin n-type window layer used for barrier formation and is photoelectrically

inactive. The deposition of such a very thin CdS layer (to minimize the loss in blue light response) with sufficient uniformity is one of the critical issues for large-area devices. Similar to CIS/CIGS cells, most carriers are generated in the underlying p-type layer (here on the CdTe p-type layer, very close to the n-p interface), which means that, in the case of both technologies, the n-p heterojunction interface is a critical region that can cause efficiency, stability problems, or both, if the deposition technology is not fully mastered.

The efficiency record for CdTe solar cells is 16% on a 1-cm² laboratory cell (50). Interestingly, in 1992, researchers at the University of Southern Florida reported a laboratory cell with an efficiency of 15.8% (51). It appears, therefore, that progress with the efficiency of laboratory record cells is at present much less rapid in the case of CdTe technology than in the case of CIS/CIGS technology.

At present, at least two firms are building or completing large-scale manufacturing plants with a planned production capacity of 10 MW_p per year (52); many others have started or announced pilot production plants. Expected efficiencies for commercial modules are in the range of 8 to 9% for full sunlight and are somewhat lower at reduced light intensity because of current losses due to grain boundaries present in these polycrystalline solar cells.

An issue that has caused a considerable amount of debate is the toxicity of cadmium (53). On one hand, CdTe is, as a compound, very stable and probably nontoxic. There are, however, definite environmental hazards and safety issues related to the production of CdTe modules: the release of cadmium into the atmosphere in the case of fire, and the recycling of CdTe modules. Although these issues seem, in principle, manageable for a well-organized and politically stable industrialized country, this may not be the case for developing countries.

Thus, CdTe technology may not be a vi-

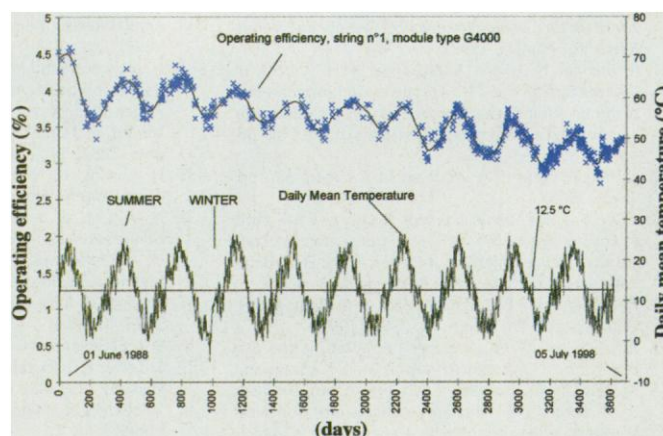
able option for the future large-scale worldwide application of PV modules. The same basically applies (albeit, to a lesser extent) to CIS/CIGS solar cell technology, in its present form, because of the thin CdS layer involved.

Dye-sensitized PV solar cells. An interesting solar cell design has been pioneered by Grätzel of the Ecole polytechnique fédérale de Lausanne (Switzerland) (54, 55): It is based on a rough TiO₂ layer covered by a light-absorbing dye and on a redox couple in a suitable electrolyte. Charge transport is realized by the conduction band of the TiO₂ on one side and by an ion flux within the electrolyte on the other side. This concept has the advantage of separating the tasks of carrier generation and carrier transport. Thus, recombination is minimized. So far, initial efficiencies of slightly more than 10% have been obtained at 100 mW/cm² light intensities on small (0.25-cm²) laboratory cells. The use of a liquid electrolyte, however, causes some serious additional problems: potential instability, limitation of maximum operation temperature, danger of evaporation, extra cost for forming an electrical series connection, and so forth (56, 57). These cells are, therefore, very far from the stages of commercialization and field use.

Conclusions

As the production volume of PV modules continues to increase, a stage will soon be reached at which the availability of raw materials, production aspects, ecological considerations, and operational reliability (rather than laboratory performance) become the prime issues in selecting and promoting a given technology. It is safe to assume that thin-film solar cells will play an increasing role in the future PV market. On the other hand, any newcomer to the production scene will, for obvious reasons, have a very hard time in displacing well-established materials and technologies, such as crystalline and amorphous silicon. One should not forget that, in the cases of crystalline and amor-

Fig. 7. Typical efficiency performance of amorphous silicon modules as measured at the TISO outdoor testing site near Lugano (Switzerland). Because of the SWE, the efficiency first decreases but recovers periodically (at least partly) during the warmer summer months; during a period of >10 years, the amplitude of these seasonal variations steadily decreases with efficiencies tending toward the lower value of the winter months (62). Blue crosses represent the average weekly operating efficiency.



phous silicon, PV technology profits from the wide experience base of the microelectronics and the display industries, respectively: However, no such synergy is present for CIS and CdTe. One should also look at the production risks and at the ecological balance sheet of these technologies. The case of silicon is very clear and well documented, whereas the PV community does not have access to the independent and in-depth studies of specialized ecotoxicological institutions for CIS and CdTe. Finally, because of the development of effective low-cost techniques for light trapping, it is no longer absolutely necessary to use a direct-bandgap semiconductor to obtain sufficient optical absorption in a thin-film PV solar cell. This again supports the case for silicon as the future prime PV material.

PV technologies cater to a very wide range of different requirements. One can therefore expect, especially with future growth in production and market volume, that at least two or three different PV technologies will coexist, each of them dedicated to a different sector of applications.

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