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# Thin-film silicon solar cells: A review and selected trends

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## Abstract

A case is developed for considering silicon as the prime medium-term candidate for semiconductor photovoltaic cells; the argumentation is based on other materials not being abundantly available, highly toxic and/or very expensive.

Crystalline silicon solar cells have excellent efficiencies, however, according to data presented by the authors on material fluxes and energy consumption there are serious bottlenecks for this technique with respect to future large-scale applications both from an economical as well as from an ecological point of view.

Thus, the authors consider thin-film silicon solar cells as the main option for large-scale energy applications in the foreseeable future. Thin-film silicon solar cells are either polycrystalline or amorphous. The first category is gaining in interest at this moment, but major technological problems remain unresolved, e.g., growth of a high-quality crystalline structure on foreign (low-cost) substrates, reduction of deposition temperature and increase of deposition rate. The second category has so far yielded only limited stable efficiencies, although progress has been recently achieved in improving the stability of solar cells using stacked or tandem/triple structures. Novel approaches to further improve the stable efficiencies, such as using low-level doping profiles within the i-layer of the p-i-n solar cell, are listed. Entirely microcrystalline p-i-n solar cells that are stable and can be deposited at low temperatures (220° C) with rates up to 1 Å/s by the VHF plasma deposition technique are described as further, recent contribution to thin-film silicon photovoltaic technology.

## 1. Introduction

In a conventional photovoltaic solar cell, two basic operations are performed by the same semiconductor material:

(1) absorption of sunlight and generation of pairs of negative and positive charge carriers,

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(2) separation of negative and positive carriers (electrons and holes) by an internal electric field.

Due to the fact that the same semiconductor is used for both operations, severe constraints are imposed on the choice of the material. Electrochemical cells [1] generally work in a basically different way: they use a dye (or sensitiser) to absorb the sunlight and they then transport the carriers in different material(s) such as, in [1], the semiconductor $TiO_2$ as well as a liquid electrolyte. This separation of the two operations permits an easier adaptation of the absorber to the solar spectrum, but it is so far often associated with other severe problems such as long-term stability and leakage/evaporation problems in the case of liquid electrolytes, as e.g. used in Ref. [1].

Besides these purely physical limitations, there are, however, ecological, technological and economical constraints for large-scale energy applications; these certainly merit full attention in view of photovoltaic technology assessment.

## 2. Choice of material: The case for silicon

In planning for the future scaling-up of photovoltaic power generation it is important to carefully choose the semiconductor material of which the solar cells are to be made. Important criteria for the choice are, on one hand, the maximum achievable efficiency but, on the other hand, also economical and ecological aspects. These become even more important if one considers in future to cover large areas with solar modules. A first category relates to the availability of the raw material as well as to the nature of the production technology used; these two factors determine the feasible minimum costs of solar cells. A second category are environmental and safety aspects; thus some of the candidates that are very promising from the efficiency point of view contain highly toxic elements (As, Cd,...), and one must consider it a problematic choice to cover substantial areas of the world's surface with them.

Table 1 shows some of the main solid state materials used today for photovoltaic applications and their availability. As an (inverse) measure for toxicity we give the so-called MAK-value. Efficiencies are in each case today's best values for modules. In calculating the required amount of material we have omitted here sawing and other fabrication losses of material. These losses can be anywhere between 30% (wafer sawing) and 90% (thin-film deposition). Furthermore, we have not considered material requirements for substrates, encapsulation and interconnection here.

It is undisputed that GaAs solar cells are highly efficient devices but much too expensive for terrestrial large-area applications. The efficiency of GaAs solar cells has exceeded 30% (for concentrator laboratory cells), but there is still no market. Furthermore, arsenic has a large toxic potential; it should certainly not be placed in large amounts into the biosphere.

We state that CdTe, also, is not a reasonable choice for widespread use; Cd is again highly toxic; a further question is whether it will be possible to mine Te (60

Table 1
Today's solid state semiconductor materials for solar cell applications, their availability and costs

| | Si | | CIS | | | CdTe | | GaAs | |
|---|---|---|---|---|---|---|---|---|---|
| | c-Si | a-Si | Cu | In | Se | Cd | Te | Ga | As |
| Concentration in earth's crust in ppm | 277000 | | 70 | 0.1 | 0.09 | 0.15 | 0.002 | 15 | 5 |
| Toxic concentr. "MAK"-value [a] (mg/m$^3$) | - | | 1.0 | 0.1 | 0.1 | 0.05 | 0.1 | – | 0.2 |
| $\eta_{\text{module}}$ | 20.8 [2] | 10.2 [3] | 11.1 [4] | | | 10.1 [4] | | 21 [5] | |
| Area for 1 GW$_p$ (m$^2$) | $4.8\times10^6$ | $9.8\times10^6$ | $9.0\times10^6$ | | | $9.9\times10^6$ | | $4.8\times10^6$ | |
| Thickness (μm) [b] | ≈ 300 | ≈ 1 | ≈ 2 | | | ≈ 2 | | ≈ 5 | |
| Specific weight (g/cm$^3$) | 2.33 | 2.33 | 4.75 | | | 5.86 | | 5.31 | |
| Mass for 1 GW$_p$ (t) | 3355 | 22 | 86 | | | 116 | | 127 | |
| | | | 16.3 | 29.4 | 40.3 | 54.1 | 61.9 | 64 | 69 |

[a] "Maximale ArbeitsplatzKonzentration"; maximum admitted concentration in the air for workplaces during up to 45 hours per week, according to Schweizerische Unfallversicherungsanstalt [6].
[b] assumption made by authors.

tons of Te need to be incorporated in 1 GW$_p$ of solar modules) on a larger scale and at reasonable costs.

Projecting the costs one has to consider market factors: any element that is not largely available or whose industrial application is limited to some special sectors is subject to speculative operations. As an example, we investigated the development of the indium-price on the world market during the last 20 years and compared it to that of the silver price (cf. Fig. 1 [7]). Indium production is relatively low (estimated mining world-wide about 130–140 tons [8]) and known resources are comparable to those of silver (0.08 ppm in earth's crust). It should, therefore, be possible to enhance mining of indium up to the value for silver (≈ 8500 t/year). As

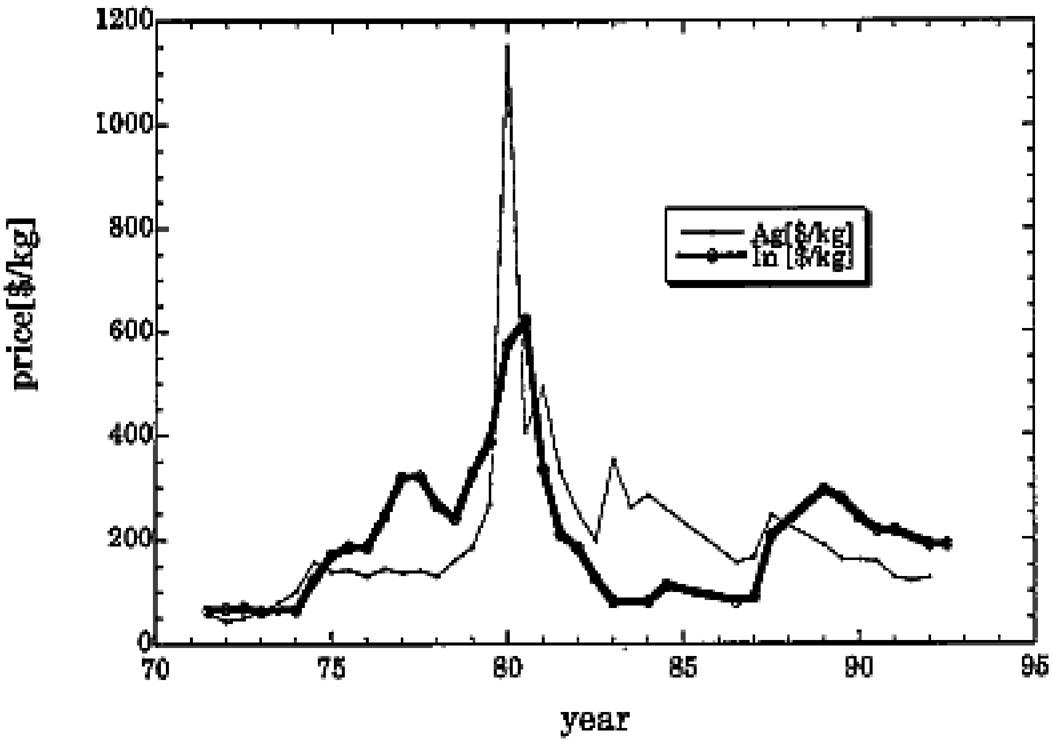


Fig. 1. Indium and silver price development on the world market 1973–1993 [7].

can be seen from Table 1, one needs for 1 $GW_p$ of module power made from CIS, 40 tons of indium (assuming an optimistic production efficiency of 75%) which is nearly 30% of the present annual production. The peak in the indium price in 1980 is due to speculative purchases as reaction to the announcement of a new potential market. When this market did not appear, the price fell down again. In the years 1986–1987 Japan doubled its demand for indium to 60 tons/year (mainly due to production enhancement of ITO, indium-tin-oxide) which explains the second peak in the indium price. The example shows that a market demanding supplementary 30 tons of indium can cause a multiplication of the price by a factor of 4. The subsequent slow decrease of the indium price is due to new sellers on the market. At present the relative fraction of the indium price within the total costs of CIS cells is low; however, variations in the indium price up to a factor of 10 due to speculative activities (which have taken place in the past and cannot be excluded for the future) can change the situation drastically.

As mentioned, an element which has about the same concentration in earth's crust as indium but which is industrially used to a much larger extent is silver. Even here enormous variations in price can appear due to speculation. In 1980 such speculative purchases took place and increased the silver price by a factor of 10.

As a conclusion, one should take into account a possible substantial increase in indium prices if one projects the production of CIS modules on a larger scale.

Considering, thus, only materials which are abundantly available in the earth's crust, which are non-toxic and which have already reached technological maturity, one is left with silicon as the only realistic medium-term candidate for semiconductor photovoltaic solar cells.

Silicon is perhaps the best-known semiconductor material and the technology for handling silicon is certainly very well developed.

## 3. Silicon solar cells: Present options

*Crystalline silicon* is undoubtedly a mature photovoltaic technology, yielding high efficiencies and excellent stability, proven through long-term field use. At present, however, the high production costs of crystalline silicon solar cells constitute a major barrier to the widespread use of photovoltaic energy conversion. These are essentially linked to the use of wafer processing (see Section 6 and Fig. 5 for details). Thus, there is a very strong motivation for developing a viable thin-film silicon solar technology.

Unfortunately, crystalline silicon (c-Si) is a semiconductor with an indirect gap; this has as consequence that its absorption in the interesting spectral range of maximum solar power is relatively poor; thus, solar cells made from crystalline silicon have to be relatively thick (30 μm of monocrystalline silicon to absorb $\approx 80\%$ of the sunlight without light-trapping). A very favourable candidate for thin-film solar cells is hydrogenated *amorphous silicon* (a-Si:H) which has basically higher absorption (due to the structural disorder of the material, the quantum mechanical selection rules for optical transitions do not act in the same way).

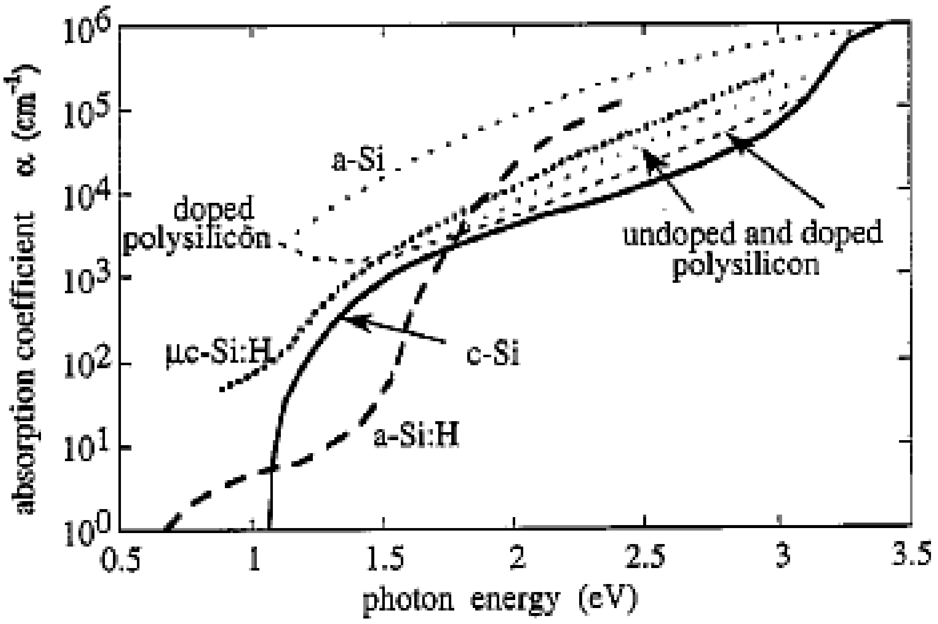


Fig. 2. Absorption coefficients for different silicon-based photovoltaic materials [48].

Practically, it has an absorption in the "useful" spectral range (cf. Fig. 2) that is higher by an order of magnitude than crystalline silicon. Therefore a-Si:H can be used as a "true" thin-film solar cell material, with thicknesses down to $< 1$ μm, provided one has suitable light-trapping structures (the latter are always used for a-Si:H solar cells). *Polycrystalline* and *microcrystalline silicon* (μc-Si:H) have absorption curves lying in between those of monocrystalline silicon and of a-Si:H (see Fig. 2). μc-Si:H has a relatively high absorption; with cell thicknesses of 2 to 4 μm it could become a promising new candidate for solar cell applications.

At present, widespread efforts are being undertaken to combine the good electronic transport properties of crystalline or polycrystalline silicon with the production advantages of *thin film technology*. Some approaches first deposit the films in an amorphous form and crystallise the deposited films subsequently: thus, Matsuyama et al. [9] deposit an a-Si:H film and crystallise it by annealing for up to 600 min at 550–650° C. With a 10 μm thick polycrystalline cell they reach a conversion efficiency of 8.5%. M. Cuniot et al. [10] crystallise magnetron sputtered amorphous films for solar cell applications by heating the material for 65 hours at 600° C. Other methods do not pass via the amorphous phase. Some recent examples thereof: J. Cifre et al. [11] deposit directly polycrystalline silicon by hot-wire CVD at substrate temperatures between 280 and 500° C and at deposition rates of 9.5 up to 35 Å/s. Other groups [12,13] use liquid phase epitaxy (LPE) to grow polycrystalline or crystalline samples. Very good efficiencies are attainable by this method. However, it is up to now still difficult to make good cells on substrates other than single crystal or polycrystalline silicon wafers. This seems to be a major problem because processing temperatures are, in general, very high; thus, impurity outdiffusion from the underlying substrate becomes an issue. AstroPower reports quite good 100 μm thick cells (14.9% [14]) on ceramic substrates, however to our knowledge details about the deposition process have not been reported. Low deposition rates are often a further limitation. Thus, high temperatures, long deposition/annealing times and the necessity for relatively thick samples constitute at present major handicaps.

Table 2 gives a very brief overview over some of today's research efforts in the c-Si thin film sector. Table 2 only represents selected trends, a more complete overview can be found in Ref. [15].

## 4. Efficiency limits as a function of bandgap energy $E_g$ (for AM1.5 conditions)

The efficiency of a solar cell is determined by the short-circuit current density ($I_{sc}$), the open-circuit voltage ($V_{oc}$) and the fill factor of the cell (FF)

$$\eta = \frac{I_{sc}V_{oc}FF}{100\ \mathrm{mW/cm^2}}. \tag{1}$$

The upper limit for the short-circuit current density $I_{sc}$ is given by the solar spectrum and the bandgap energy of the semiconductor ($E_g$); assuming that each incoming photon with an energy $h\nu > E_g$ creates a single free electron-hole-pair one thus obtains:

$$I_{sc} = e\Phi\big|h_{\nu > E_g} \tag{2}$$

where $\Phi$ is the incoming photon flux per unit of time and area. Quantum efficiencies $> 1$ due to impact ionisation are limited to very special conditions [22] and are, therefore, neglected here.

The situation is not so straightforward for the open-circuit voltage $V_{oc}$; solving the (illuminated) $I(V)$ equation for $V$ and setting $I = 0$ one obtains

$$V_{oc} = \frac{k_B T}{q}\ln\left(\frac{I_L}{I_0} + 1\right), \tag{3}$$

where $k_B$ is Boltzmann's constant, $I_L$ the light-induced current density and $I_0$ the diode saturation current density. It would, however, be of physical interest to transform Eq. (3), in such a way as to express $V_{oc}$ as a function of $E_g$. To do this, we have to examine $I_0$. In classical semiconductor device theory [23], $I_0$ is given in form of material- and device-dependent parameters such as diffusion lengths, diffusion constants, doping densities and carrier densities. This approach does not directly lead to any physical insight. On the other hand, M.A. Green [24] gives a semi-empirical function relating $I_0$ to the bandgap. This function is based on practical experience and reads:

$$I_0\left[\frac{\mathrm{mA}}{\mathrm{cm}^2}\right] = 1.5 \times 10^8 \exp\left\{\frac{-E_g}{k_B T}\right\}. \tag{4}$$

Thus, one obtains as semi-empiric formula for $V_{oc}$, by combining Eqs. (3) and (4):

$$V_{oc} \approx \frac{k_B T}{q}\ln\left(\frac{1}{1.5}\cdot\frac{I_L}{10^8\ [\mathrm{mA/cm^2}]}\right) + \frac{E_g}{q}, \tag{5}$$

Table 2
An overview of some selected thin-film c-Si research efforts

| Cell | Substrate | Single-c-Si | Polycrystalline silicon | High-$T$ foreign substrates | Low-$T$ foreign substrates |
|---|---|---|---|---|---|
| *CVD* | comment | | | subst.: $SiO_2$ ZM-recrystallisation | subst.: fussed silica hot-wire CVD |
| | $d$ | 50 µm | 35 µm | 60 µm | |
| | $T$ | 1150° C | 1150° C | 1200° C | 280–500° C |
| | $R$ | 0.7 µm/min (?) | 0.7 µm/min (?) | | 9.5–37 Å/s |
| | $\eta$ | 17.3% (l.t. [a]) [13] | 12.1% [13] | 14.2% [16] | no cells reported [11] |
| *PECVD* | comment | | subst.: plasma-spayed polycryst. Si | plasma spraying on carbon fiber/ glassy carbon | subst.:glass/TCO |
| | $d$ | 15 µm | | | 1.7 µm |
| | $T$ | 200° C | | | 220° C |
| | $R$ | | | | 1 Å/s |
| | $\eta$ | 11.4% [17] | 8.4% [17] | 4.3% [18] | 4.6% (l.t. [a]) [19] |
| *LPE* | comment | | | | |
| | $d$ | 16.8 µm | 20 µm | | |
| | $T$ | 600–900° C | 950–825° C | | |
| | $R$ | | | | |
| | $\eta$ | 14.7% [20] | 11.9% [13] | | |
| *SPC* | comment | also on glass and $SiO_2$ | | substrate: textured metal | |
| | $d$ | 30 µm | | | 10 µm |
| | $T$ | 600° C | | | 550–650° C |
| | $R$ | 1–5 µm/h | | | |
| | $\eta$ | no cells reported [10] | | | 8.5% [9] |
| *Ion-assisted dep.* | comment | | | subst.: ceramics and glass partially coated with Mo or Ti | |
| | $d$ | 7 µm | 4 µm | 4 µm | |
| | $T$ | 550–700° C | 550–700° C | 300–700° C | |
| | $R$ | up to 10 µm/h | | | |
| | $\eta$ | 6.4% [21] | no eff. reported [21] | | no efficiencies reported [21] |

[a] l.t.: light trapping

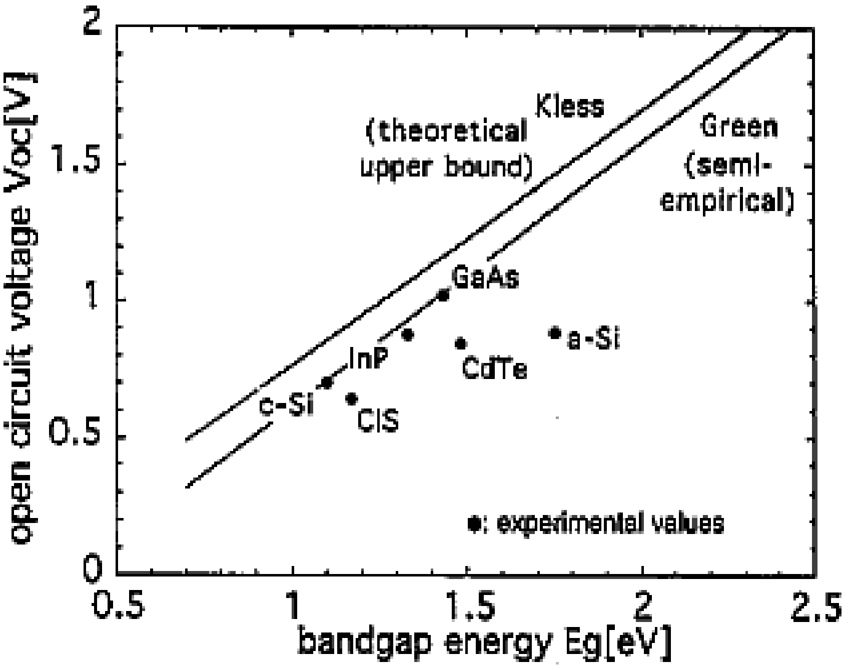


Fig. 3. Open-circuit voltage $V_{oc}$ according to Eq. (5) and experimentally reached values according to M.A. Green [49], all for non-concentrator cells. The value for CIS is reported in [50], an independently confirmed value is 0.644 V [49].

which fits the maximum values so far experimentally reached in the laboratory surprisingly well (cf. Fig. 3). The prefactor $1.5 \times 10^8$ in Eq.(4) was determined based on past experience with various crystalline materials. Recombination via deep traps (dangling bonds) is very important for amorphous semiconductors; this substantial contribution to recombination is certainly one of the main reasons why the $V_{oc}$-values obtained so far for a-Si:H solar cells are so much lower than the "limit" given by Eq.(5).

In a more fundamental approach H. Kiess [25] gives as expression for $V_{oc}$; an equation which considers only radiative recombination and thus leads to a purely theoretical upper bound. He obtains for $V_{oc}$:

$$V_{oc} = \frac{E_g}{q} + \frac{k_B T}{q} \ln \left\{ \frac{1}{E_g^2} \cdot \frac{h^3 c^2}{2\pi k_B T} \cdot \Phi \Big|_{h\nu > E_g} \right\} \tag{6}$$

Note that Eq.(6) strictly only contains basic physical constants. As is shown in Fig. 3, Eq.(6) results in a curve for $V_{oc}(E_g)$, which is, over the whole range of $E_g$, markedly higher than the curve based on M.A. Green's semi-empiric formula (our Eq.(5)).

For the case of an "ideal" p-n-junction, the fill factor can be easily expressed as a function of the open-circuit voltage; using the diode quality factor $n$ and the normalised voltage $v_{oc} = V_{oc}/(nk_B T/q)$, the following semi-empirical formula fits the numerically found FF values [24] for $v_{oc} > 10$ with an accuracy of about 4 digits:

$$FF = \frac{v_{oc} - \ln(V_{oc} + 0.72)}{v_{oc} + 1}. \tag{7}$$

If one now expresses $V_{oc}$ as a function of $E_g$ according to Eq.(6), one obtains a curve for FF as function of $E_g$. This semi-empirical limit curve [26] once again fits

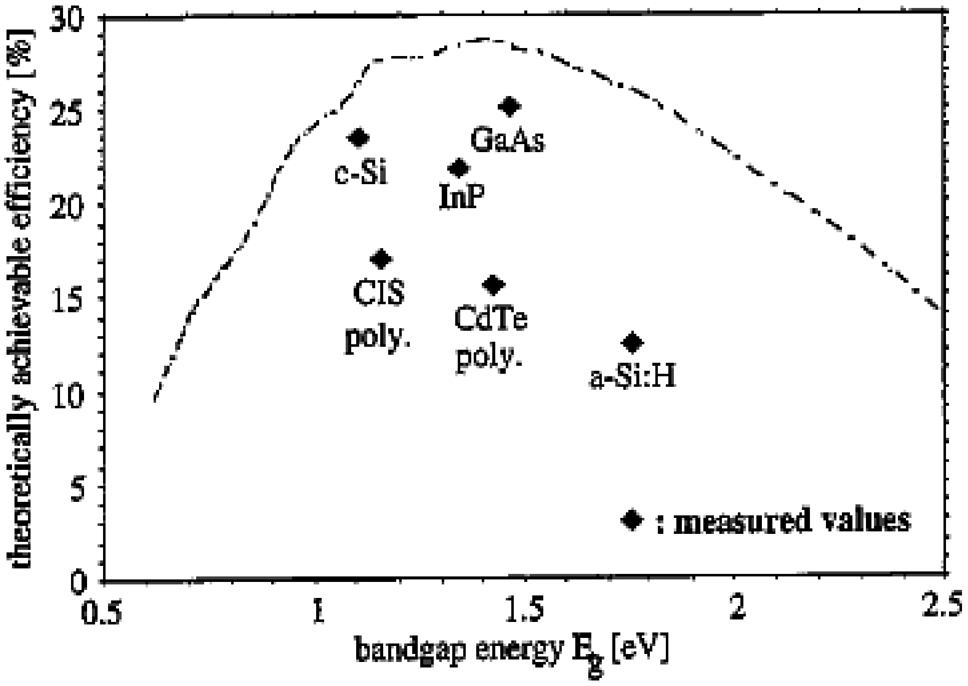


Fig. 4. Theoretically achievable efficiency as a function of the bandgap as calculated with our Eqs. (1,2,5,6) and comparison with measured values according to M.A. Green [49]; all for non-concentrator cells, i.e., for one sun. The value for CIS is reported in [50], an independently confirmed value is 13.9% [49].

the maximum values experimentally obtained so far surprisingly well. Again, amorphous silicon is well below the semi-empirical limit curve. This can be traced back to three main reasons: (1) the low value of $V_{oc}$ so far obtained for a-Si:H (see above), (2) the excess recombination in a-Si:H due to dangling bonds leading to a higher diode quality factor and even invalidating Eq.(7), and (3) — possibly most important — the additional series resistance introduced through the transparent conductive oxide (TCO) used in a-Si:H cells as front contact.

On the other hand, a more basic development based on thermodynamic considerations yields theoretically achievable fill factors up to 0.99 which is again markedly higher than the values from the semi-empiric formula (7).

Fig. 4 shows the maximum efficiency which is "theoretically" achievable as calculated with the semi-empirical approach of Eqs. (1,2,5,7) and the AM1.5 solar spectrum, as well as measured maximum values obtained so far for cells made from different materials. Three points should be noted as the message contained in Fig. 4:

- the optimum bandgap is around 1.5 eV
- even though the bandgap of c-Si is markedly lower (1.1eV) and that of a-Si:H somewhat higher (1.75eV), these "offsets" result only in very small sacrifices with respect to the obtainable limit efficiency.
- c-Si solar cells are already rather near to the limit efficiency, but a-Si:H have still a "long way to go".

Further, more precise and detailed theoretical work is necessary to indicate how far the practical efficiencies for a-Si:H have a scope to be further increased (e.g., by improving various technological parameters, material quality and dangling bond densities) or, would rather be basically limited at some lower value due to the amorphous nature of the material itself.

## 5. Drift versus diffusion and the p-i-n structure

Amorphous silicon solar cells always use a p-i-n diode structure in contrast to the classical p-n diode structure used in virtually all crystalline solar cells so far. Although there are "technological" reasons for using a p-i-n structure in the case of a-Si:H (difficulty of doping, decrease of layer quality with doping), the p-i-n structure also offers some basic advantages with respect to collection. Here, we wish to discuss these basic advantages as they may be of general interest for all types of thin-film silicon solar cells. For wafer-based c-Si solar cells collection is not a major problem as the minority carrier diffusion length $L_{\mathrm{diff}}$ is usually sufficiently large that minority carriers are transported by diffusion to the junction, where the actual separation between holes and electrons takes place, thanks to the internal field in the depletion region. This depletion region is typically much thinner than the total cell thickness and the electrical field extends only over this very thin region. Amorphous silicon, in contrast, has relatively poor transport properties, i.e., low carrier mobilities $\mu$ and short carrier lifetimes $\tau$ so that the diffusion length, which can quite generally be written as

$$L_{\mathrm{diff}} = \sqrt{D\tau} = \sqrt{\frac{k_{\mathrm{B}}T}{q}\mu\tau} \tag{8}$$

would be very small (in the best intrinsic material $L_{\mathrm{diff}}$ is about 0.2 μm [27]). Therefore, collection certainly is a major problem in a-Si:H based solar cells; diffusion alone is not sufficient as transport mechanism. In order that the major part of the generated free carriers do not recombine within the amorphous silicon solar cell, it is imperative to have drift-assisted transport, based on an internal electric field $E$ extending over most of the cell, i.e., over the whole of the i-layer. The drift length $L_{\mathrm{drift}}$ in an intrinsic (i) layer is quite generally given by

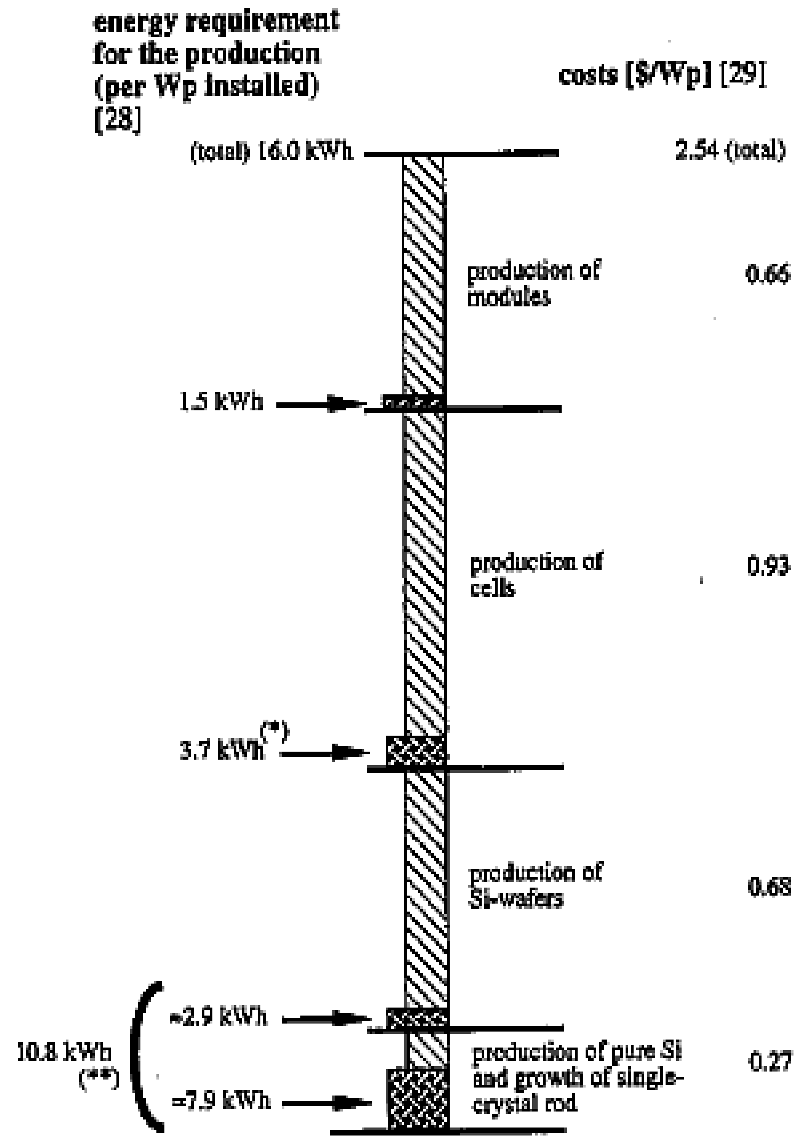
$$L_{\mathrm{drift}} = \mu\tau E \approx \mu\tau\frac{V_{\mathrm{bi}}}{L_i}, \tag{9}$$

where $V_{\mathrm{bi}}$ is the built-in voltage and $L_i$ the thickness of the i-layer. If we define $\kappa$ by setting $L_i = \kappa L_{\mathrm{drift}}$ we obtain with $V_{\mathrm{bi}} \approx 1$ V ($V_{\mathrm{bi}}$ depends on the gap)

$$\frac{L_{\mathrm{drift}}}{L_{\mathrm{diff}}} = \sqrt{\frac{V_{\mathrm{bi}}}{k_{\mathrm{B}}T/q}\cdot\frac{1}{\kappa}} \approx \sqrt{\frac{40}{\kappa}}\,. \tag{10}$$

For $\kappa \leq 0.5$ (which is certainly not unreasonable in order to obtain satisfactory collection) one obtains that the drift length is roughly a factor 10 (or more) larger than the diffusion length.

We have to remark that the built-in electric field according to Eq.(9) is fully operational under short-circuit conditions only, whereas at open-circuit ($V_{\mathrm{oc}}$) there remains a much smaller potential gradient, i.e., we tend towards "flatband" conditions and the contribution of drift to transport is here reduced; this may be a further reason why $V_{\mathrm{oc}}$ is well below the semi-empirical limit for a-Si:H solar cells



(*): Energy for buildings and installation of production line (≈1.3 kWh) not taken into account.
(**): 1.5 kWh of heat can be re-used.

Fig. 5. Energy requirements and costs for the production of polycrystalline-Si PV modules (450 μm). Energy requirements were calculated using the data of Hagedorn [28] and assuming an efficiency of 14%. All values are converted into primary energy (conversion factors: for electricity 0.35, for fuels 0.85 and for non-energetic consumption 0.8, as already used by Hagedorn). Costs are according to Strese [29]. Values are given by Strese in DM; conversion to $ is done using a factor 1.80DM/$ (exchange rate 1988). The pure silicon is assumed to be available as "waste" from the semiconductor industry, its price is therefore very low. When scaling up the production in future, this point could change drastically when such "waste" feedstock becomes insufficient.

(Fig. 3). Maximum power conditions are somewhere in between, the factor of ten between drift and diffusion lengths being reduced to a smaller value.

## 6. Ecological and economical aspects

The main advantage of amorphous technology as compared to crystalline wafer-based technology lies in the energy and raw material requirements for the production of modules; this, in its turn, leads to potentially cheaper production and to a better ecological balance sheet.

As presented in Fig. 5, crystalline silicon solar modules based on wafer technology require an energy investment of about 16 kWh per $W_p$ and have estimated costs of 2.5 $/$W_p$. Our Fig. 5 is based on data published by G. Hagedorn [28] (for

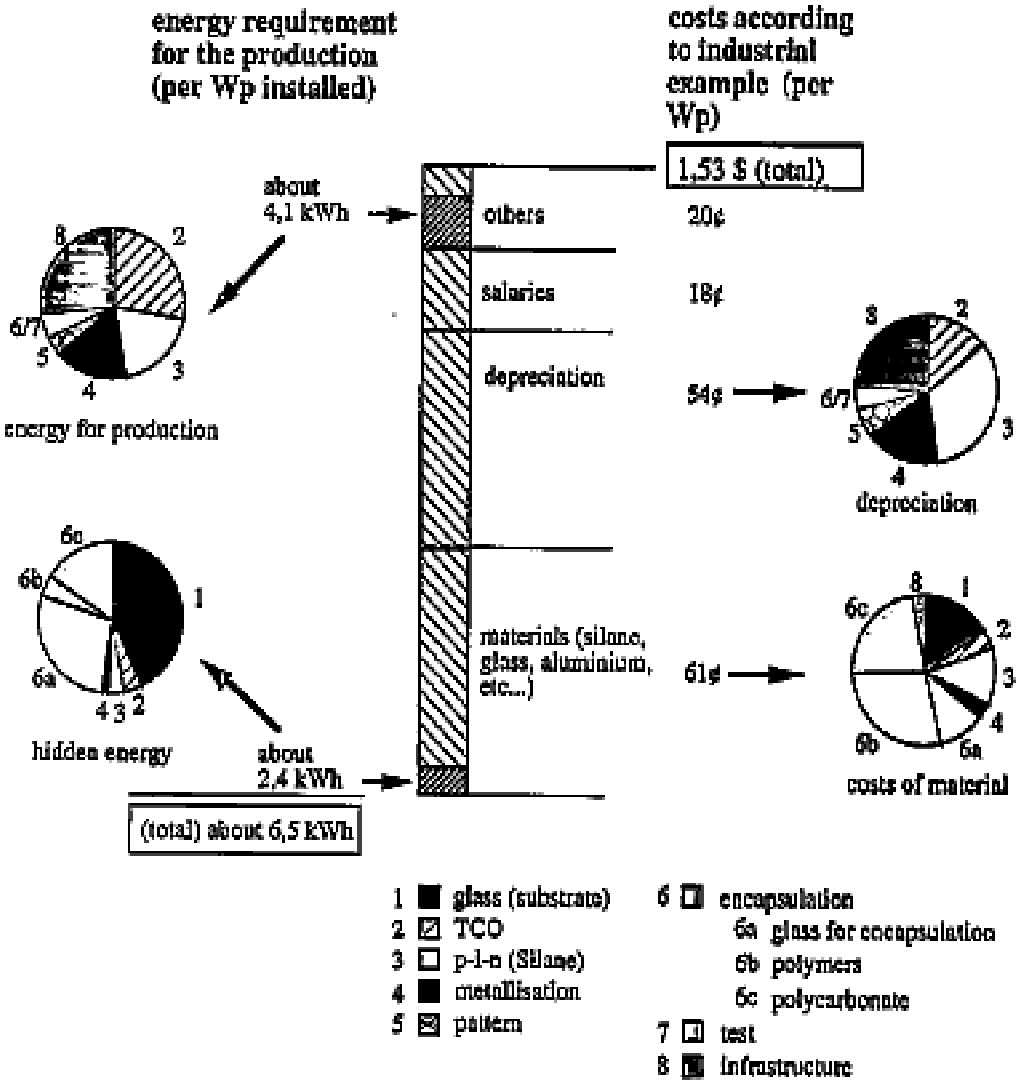


Fig. 6. Energy requirements and costs for the production of a-Si:H based PV modules according to an industrial example, as reported by Srinivas [32]. Assumptions underlying the study are: "conventional" RF (13.56 MHz) a-Si:H deposition, single-junction (p-i-n) solar cell structure, 5% efficiency and a conventional TCO technology.

the energy requirements) and by D. Strese [29] (for the cost factors). The assumed efficiency which underlies the data of Fig. 5 is 14%. The main energy factors are the production of highly clean silicon crystals and the production of the cells; both these steps contain high-temperature processes: the crystal itself is grown at ≈ 1420° C from a silicon melt and the pn-junction is made by diffusion at about ≈ 1000° C from the gas phase. Future technological progress, such as low-temperature plasma processing for formation of the p-n junction [30,31] should be able to reduce significantly the energy requirements as well as the costs. A thickness reduction of the cells would allow one, on one hand to use material of lower quality (as the ratio of diffusion length to thickness will here become the determining factor) and would, on the other hand, also reduce the energy payback time.

The production of photovoltaic modules from amorphous silicon is already much more favourable from the point of view of energy and of cost: for the production of 1 $W_p$ in a solar module, 6.5 kWh of energy have to be invested and the costs are 1.5 $/Wp, as reported by K.S. Srinivas [32] and shown in Fig. 6. In this case an efficiency of only 5% was assumed; this is a rather conservative estimation. Here again future technological progress — especially an increase in module efficiency, an improvement in TCO production and an increase in the

Table 3
Amount of silicon required to produce 1 $kW_p$ of photovoltaic cells/modules [33]. Assumptions are as follows: "Today": c-Si cell efficiency 14.2%, wafers of 440 μm thickness, cut by conventional technique. A-Si module efficiency 6%, silane deposition efficiency only 5%. "Near future": Same efficiencies, but optimised production. C-Si: wafers cut by wire technique, they are only 100 μm thick, the cutting loss of 150 μm is recycled. A-Si: silane deposition efficiency is 30%. "Future": optimised production methods (as described before) as well as higher efficiencies (18% for c-Si and 10% for a-Si)

| | Monocrystalline technology | Amorphous technology |
|---|---|---|
| Today | 30.5 kg Si/kWp | 350 grams Si/kWp |
| Near future | 4.4 kg Si/kWp | 52 grams Si/kWp |
| Future | 2.9 kg Si/kWp | 31 grams/kWp |

deposition rate of amorphous silicon (eg. by the VHF plasma deposition method, Section 8 of this article) — would affect the outcome favourably.

A very striking difference between crystalline and amorphous technology is the amount of silicon needed for a given power rating. This comparison is shown in Table 3, as based on a recent study [33].

We would like to emphasise the fact that all the studies quoted here have been undertaken by investigating existing production lines and extrapolating merely an increase in production volume; the uncertainty is therefore quite limited in contrast to the estimations for other solar cell technologies which have not yet left the laboratory state. For amorphous silicon the energy requirements for the production of the TCO (transparent conductive oxide) exceed those of the a-Si:H-deposition. Note that the costs and energy requirements for the TCO have often inadequately been taken into account when evaluating future thin-film technologies and this leads to unrealistically low cost predictions: e.g. present electrochemical solar cells [1] based on dye absorbers, $TiO_2$ and liquid electrolytes use glass + TCO on both sides and it is therefore difficult to see how they could (at least with their present design) be in any way cheaper than a-Si:H cells. Another important factor is the encapsulation and the glass protection panel which is relatively expensive and needs a lot of energy, but is indeed generally needed for all types of solar cells. An interesting application is therefore to cover those glass areas which are already planned for a new building (e.g. facades) with solar modules.

Because it requires less production energy and, furthermore, because it requires much less purified silicon (see Table 3), amorphous silicon technology is associated with far less $CO_2$ emission than is crystalline silicon technology. (Note, that the production of purified silicon is linked with a relatively high amount of $CO_2$ emission; 6kg $CO_2$ are emitted when producing 1kg metallurgical grade Si, considering only the chemical reduction process [34].) Thus, from the ecological point of view, also, amorphous silicon is superior to crystalline silicon.

On the other hand, crystalline silicon solar modules are superior to amorphous silicon considering the area requirements for a given installed power, as the efficiency of c-Si cells is at present significantly higher than that of a-Si:H based cells. Thus, crystalline silicon will still be the clear favourite, wherever the available surface area is scarce or whenever the modules have to be mounted on (expensive) dedicated concrete structures, such as in centralised photovoltaic plants. However, crystalline silicon solar modules need effective cooling (e.g. by ventilation from the back side) because of their large negative efficiency temperature coefficient; the efficiency temperature coefficient for amorphous modules is, in contrast, significantly lower.

## 7. Problems of a-Si:H based solar cells

As is well known, one of the main problems the amorphous silicon community still has to deal with is the *Staebler–Wronski effect* [35] (SWE), i.e., the so-called "degradation" of transport properties during e.g. illumination of the semiconductor. The recombination of free excess carriers as created by illumination or current injection causes the formation of new dangling bonds, i.e., of additional recombination centres; these affect the internal field distribution and, thus, the lifetime of the carriers. This process of defect formation is reversible, the material anneals if one heats the semiconductor for a certain time at moderate temperatures (≈ 180° C). The SWE affects the performance of devices made from this material; in particular the efficiency of amorphous silicon solar cells decreases under illumination. Fortunately, this is a self-limiting process, i.e., the cells' efficiency stabilises after a certain time at a value below the initial efficiency. The same effect can be shown for modules, after the 1st year the module output power stabilises with seasonal variations; these are shown in Fig. 7 for a typical outdoor test site as measured at TISO (Progetto Ticino Solare) [36].

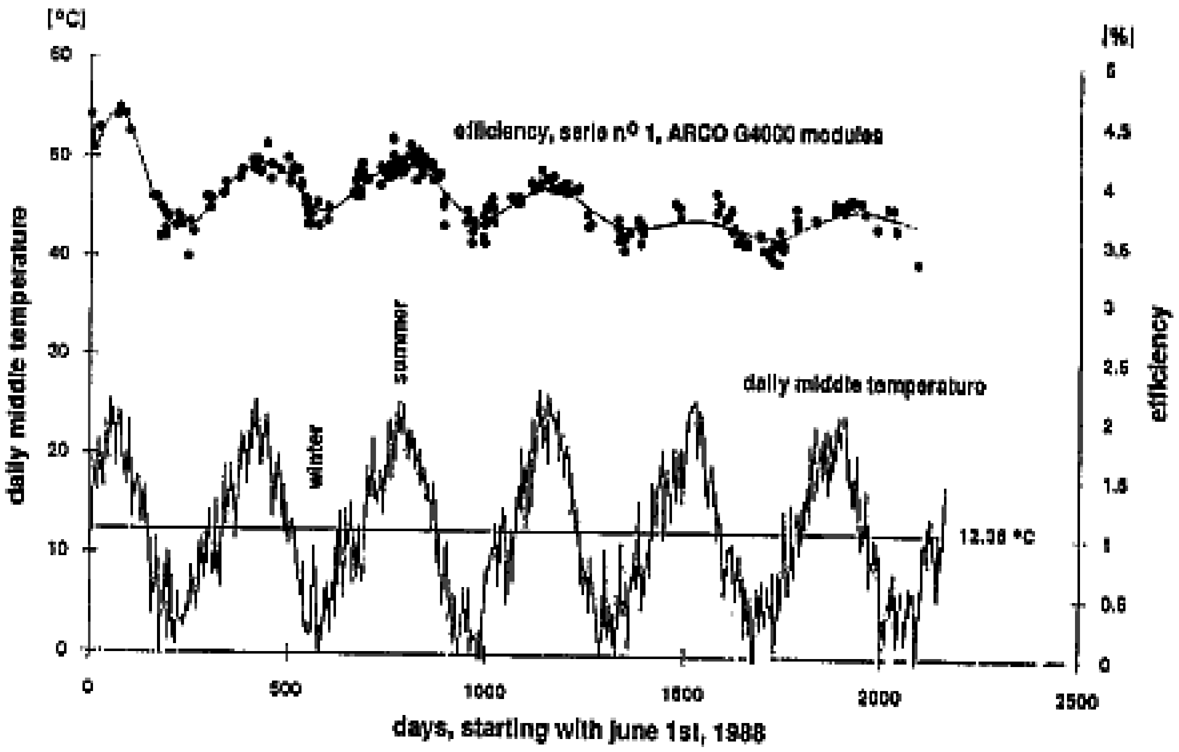


Fig. 7. Typical degradation of an a-Si PV module in an outdoor test site with seasonal variations in efficiency. Measurements provided by D. Chianese, TISO (Progetto Ticino Solare) [36].

Even without the SWE, the (initial) efficiency of a-Si:H solar cells is rather low and this is mainly a problem of low $V_{oc}$, at least for the TCO-p-i-n cell structure (see Section 4 above, especially Fig. 3). Further theoretical work is called for, so as to pinpoint exactly the main cell design factors and a-Si:H material parameters responsible for this low value of $V_{oc}$.

Another major problem of amorphous silicon is that *production costs* are not really as low as originally hoped for. There are two main reasons for this. (1) Current amorphous silicon production plants have rather low deposition rates (in the range of 1 Å/s). Deposition rates are at present most often limited by particle (powder) formation within the plasma reactors. Through further progress in plasma deposition techniques this limitation can be at least partly overcome. The VHF deposition process introduced at the author's laboratory is an example of a new method that can be used to overcome this limitation (see Section 8). (2) The semiconductor itself is only a part of the cell and, as already stated in Section 6 of this article, not even the most expensive part of a thin-film silicon module. Especially TCO technology needs further improvement both with respect to energy investment, cost and performance (optical transmission, haze factor, other means of light trapping, electrical conductivity).

## 8. Stacked cells and other recent R&D efforts

As we pointed out in the previous sector, the Staebler–Wronski-effect is one of the main problems for a-Si:H solar cells. After degradation the collection suffers from a strongly reduced internal electric field; field reduction is due to charged dangling bonds. There are several approaches to overcome or at least reduce this problem. One is to make the cells as thin as possible. New dangling bonds are created by recombination of free carriers. If the cell is very thin (small value of our parameter $\kappa$ in Eq.(10)), the internal electric field becomes large and drift is enhanced. Recombination is reduced and therefore also degradation. To compensate the current loss due to reduced absorption in thin cells, good light trapping by a hazed TCO and reflection from the back contact by a highly reflective contact is desirable. To make the i-layer even thinner and to absorb at the same time a major part of the sunlight, one has the possibility to deposit two (or three) thin cells in a *stack* and connect them thereby electrically in series. The top cell can be very thin (SWE will therefore not disturb the collection) and absorbs mainly the blue part of the spectrum, the bottom cell is moderately thicker and furthermore receives only filtered light so that here the SWE is less pronounced. For two stacked cells with the same bandgap energy the top cell will have to be extremely thin (to ensure current matching for the series configuration); this can cause severe problems with pinholes. Another possibility is to combine this concept with Si–C and Si–Ge alloys which have an "adjustable" energy gap: a wider gap or a narrower gap, respectively. Thereby one can make better use of the solar spectrum and avoid the large thickness variations between the individual cells. A persisting problem is the optoelectronic quality of these *alloys* which is at present not at all as good as that

Table 4
Stabilised efficiencies of amorphous silicon solar cells reached so far using the tandem/triple concept

| | With Si–Ge alloys | Without Si–Ge alloys |
|---|---|---|
| Cells | 11.16% (USSC [37]) | 10.0% (Fuji [38]) |
| Laboratory modules ($\approx 1000$ cm$^2$) | 10.2% (USSC [3]) | 8.9% (Fuji [39]) |
| Commercial modules (*best* values from production line) | 8.0% (Solarex [40]) | 6.3% (PST [41]) |
| Product specification (guaranteed values) | | 50 W/m$^2$ (PST)<br>54 W/m$^2$ (USSC [42]) |

of "pure" unalloyed a-Si:H. In this field there is still a lot of materials research to be done. Currently, development work is also done on varying the gap of "pure" (i.e. unalloyed) a-Si:H by changing the substrate temperature during deposition: a temperature variation causes incorporation of more or less hydrogen during film growth. Only very small variations in gap energy are possible by this method and the quality of the films deposited is lower, as in the case of alloys, the further one moves away from the "standard" gap energy i.e. the further one moves away from the optimum deposition temperature.

Stabilised efficiencies reached so far using the tandem/triple concept are listed in Table 4. One should point out that cells containing germanium are more expensive than others, because $GeH_4$ is relatively costly. Most of the efficiency values given here were certified by a neutral laboratory (NREL, ISES).

Note that according to Table 4, there is at present a factor of 2 between stabilised laboratory cell efficiency (11%) and stabilised commercial module efficiency (5.4%); this is in part due to active area losses by structuration for series connection and at the border of the module, it is also due to the larger series resistances for large-area modules as caused by the TCO.

## *8.1. Further research trends: (1) microdoping*

Another approach to produce more stable cells is to optimise the internal electric field not for the as-deposited state but for the degraded state. One possibility to do this is so-called "micro-doping" (low-level doping) [43,44]. The principle is illustrated in Fig. 8. With a graded doping profile it is possible to prevent the internal electric field from breaking down after light-soaking, because of the creation of new charged dangling bonds. Note that a large positive space charge is expected towards the p-side and a small negative space charge towards the n-side after light soaking; this generally results, after light-soaking, in a high electric field at the interfaces and a reduced electric field in the bulk. In the low-field region the recombination is strongly enhanced. The effect of the charged dangling bonds on the electric field can be offset through compensation with a suitable dopant profile. Experimentally, the stable conversion efficiency for homogeneously absorbed red light was thereby increased by about 1/5. Thus, pin cells

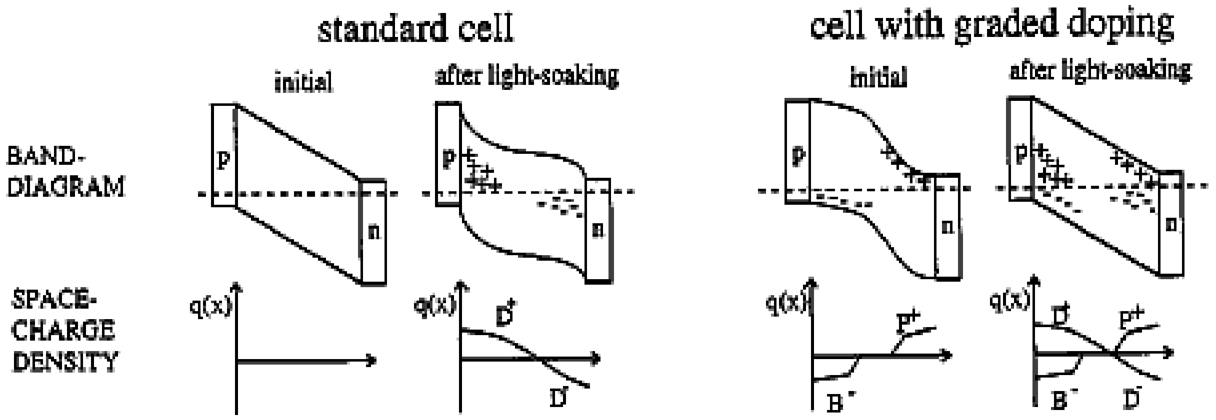


**Fig. 8.** Field profile in a p-i-n-cell before and after degradation and improvement of degraded electric field by micro-doping (schematic).

with graded boron doped i layers could certainly increase the stable efficiency of double-stacked amorphous silicon solar cells if employed as the red light converting bottom cell [44].

### *8.2. (2) Use of microcrystalline (μc) layers and cells*

Major progress has been made using μc doped layers (p and n). Activation energy can thereby be reduced, i.e., the Fermi level position more efficiently shifted and the built-in voltage enhanced. Conductivity is much better than for amorphous layers. The n/p contact in the middle of a stacked cell acts as a more effective tunnel junction if it is rendered microcrystalline (the grain boundaries are very effective recombination centres and enhanced recombination is beneficial here).

Microcrystalline silicon has also hopeful applications as an absorber of an entirely microcrystalline solar cell. A 1.7 μm thick entirely μc cell deposited by the VHF plasma deposition method (see below) at moderate substrate temperatures (170° C for $<p>$ and 220° C for $<i>$ and $<n>$) has reached an efficiency of 4.6% so far [19]. The i-layer consists of compensated μc-Si:H, the short-circuit current is increased due to enhanced infrared absorption, $I_{sc}$ is hence significantly higher than for any a-Si:H device (21.9 mA/cm$^2$). A very encouraging feature is that the cell so far does not show any degradation at all. The enhanced infrared absorption of μc-Si:H could be advantageously employed in the bottom cell of a tandem structure [45], replacing, thus, silicon–germanium-alloy bottom cells which suffer from strong degradation and are also relatively costly, due to the $GeH_4$ material costs.

N.B. The *VHF plasma process* [46], developed at Neuchâtel by the author's group is characterised by an increase in plasma excitation frequency from 13.56 MHz to around typically 70 MHz leading to a pronounced difference in plasma conditions, as compared to conventional RF plasma deposition. Thereby, deposition rates are strongly enhanced ($\approx 4$ times at otherwise equal conditions, and without causing powder formation). This has the potential to reduce costs especially for industrial applications as the throughput through expensive production installations can be increased. The VHF technique can be combined with Ar dilution to save on $SiH_4$ consumption [47]. Furthermore it favours the deposition of good quality microcrystalline silicon consisting of small crystalline grains (10–500Å) which are embedded in an amorphous silicon matrix. The crystalline volume fraction can be increased thanks to VHF deposition up to 80–90%. The VHF technique allows deposition rates up to 1 Å/s.

As a *general goal*, a stabilised commercial module efficiency of about 10% should be attainable within the next few years. Further goals of R&D are to reduce the silane ($SiH_4$) and especially germane ($GeH_4$) wastage, to improve the TCO deposition and to make the encapsulation cheaper. Costs per $m^2$ should thereby be reducible by about a factor of 2, making thus a-Si:H solar cells even more competitive.

## 9. Conclusions

Most of present photovoltaic technology is based on crystalline silicon *wafers*. Today's wafer-based silicon solar cell technology is associated both with high production temperatures and with substantial material fluxes (roughly 10 to 20 tons of ultrapure silicon is required, at present, per peak Megawatt of photovoltaic power installed). This leads to high prices, elevated energy payback times and non-negligible ecological problems (e.g., $CO_2$ emission during silicon purification).

Thus, there exists a strong motivation to develop a thin-film solar cell technology. Many different materials are now being investigated, but an analysis of their availability and toxicity indicate a very clear priority for a *thin-film* technology based on silicon. Within the thin-film silicon field, hydrogenated *amorphous silicon* solar cells are the forerunners. They have a major physical advantage due to their relatively high optical absorption. Further R&D work on *plasma-assisted deposition techniques* should lead, within the present decade, to improved performance of amorphous solar cells and to reduced costs. It is interesting to note that plasma-assisted chemical vapour deposition (plasma-CVD) from silane, cannot only be used to produce amorphous layers but also to deposit excellent microcrystalline silicon layers. Fully microcrystalline solar cells produced at the authors' laboratory already have stable efficiencies near 5% and are thus fast becoming interesting candidates for use as bottom cells in tandems and stacks. Ingenious combinations of microcrystalline and amorphous phases within the same cell or, even, within the same layer would offer interesting new options.

A current strong research interest lies in crystalline silicon deposition methods for solar cells. However, so far no method has been found here, that successfully combines high deposition rates, low deposition temperatures, a low-cost substrate and a high efficiency of the resulting solar cell.

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