Microcrystalline silicon and ‘micromorph’ tandem solar cells


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Abstract

The case for thin-film silicon as one of the main future options for cost-effective photovoltaic solar cells is outlined. The limitations of present amorphous silicon (a-Si:H) solar cells are briefly mentioned. Hydrogenated microcrystalline silicon (µc-Si:H) deposited by PECVD (plasma-enhanced chemical vapor deposition) at low substrate temperatures (approx. 200 °C) constitutes a new and additional possibility for solar cells. Properties of intrinsic µc-Si:H layers deposited by PECVD at VHF (very high frequency) excitation frequencies are listed, together with the necessary conditions for obtaining device-grade material. Performances obtained so far with µc-Si:H solar cells are given; the latter are compared with estimated limits for p-type devices with $E_g = 1.1$ eV. Finally, present performances and future perspectives for ‘micromorph’ (µc-Si:H/a-Si:H) tandem solar cells are discussed.

Keywords: thin-film silicon; photovoltaic solar cells; c-Si:H layers; micromorph

1. Introduction

For photovoltaic (PV) solar energy conversion to become a substantial contributor to the general production of electricity, a massive increase in module production volume over the present value of approximately 300 MWp/year is needed. Indeed, it is only at world production levels in the order of magnitude of 100–1000 GWp/year that PV solar modules will have a noticeable effect in the substitution of fossil fuels or in the replacement of nuclear power stations on a global level. This will take, even at the present impressive growth rate of approximately +40%/year, approximately 2–3 decades more (Fig. 1). In the authors’ view, it is, therefore, necessary to choose a PV cell technology that can cater to such a massive production volume. Wafer-based crystalline silicon, with its relatively large requirements of ultra pure monocrystalline or polycrystalline silicon base material (10–20 tons per MWp of solar cells) and its relatively high energy payback time (several years for Central European climates), hardly seems to be a viable candidate. Even though this technology presently accounts for over 80% of PV modules produced, and even though it has in the past two decades contributed to a substantial decrease in PV module prices, its further price reduction potential can be considered to be relatively modest. Indeed, at this moment, prices of PV modules fabricated from crystalline silicon wafers are stagnating at a level of approximately US $4/Wp (Fig. 1).

There is, therefore, growing interest in thin-film PV technologies [1].

Amongst these, cadmium telluride (CdTe) and copper indium (gallium) diselenide (CIGS) constitute two thin-film options that have given rise to considerable interest, especially as the corresponding performances of small-size (approx. 1 cm² surface area) laboratory cells made from these two materials have, in recent years, undergone remarkable improvement and now reach conversion efficiency levels in the 15–20% range. Mass production of corresponding modules is, however, only gradually taking off, and this because of several reasons: (1) lack of adequate industrial/technological experience; (2) so far low production yields; (3) production hazards (especially for CdTe modules); (4) necessity for production processes at relatively high temperatures (400–500 °C); (5) additional problems with substrates

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and transparent contacts, as needed for these cells; and (6) difficulties in passing the ‘damp heat test’ required of PV modules (especially for CIGS). Now, many of these problems may be considered to be temporary (with the exception, possibly, of the high process temperatures and of the hazardous, toxic raw materials involved). In the long run, however, basic material availability constitutes an even more serious problem. Table 1 gives the figures for material availability, for various PV materials, as used in thin-film solar cells.

It is quite evident from Table 1 that at a future world PV module level of 100–1000 GW/year, both CIGS and CdTe technologies will run into serious problems w.r.t. (with respect to) raw material availability.

Thus, the motivation for developing a high-performance, viable thin-film solar cell technology, based on silicon, can be clearly perceived.

A first attempt at creating such a thin-film solar cell technology was based on hydrogenated amorphous silicon (a-Si:H).

Amorphous silicon solar cells are relatively cheap (present module prices are approx. $3/Wp), account for 10–15% of the world PV solar cell market and have an almost total monopoly for low-power ‘gadget’-type applications (calculators, watches, etc.). Laboratory cell record efficiencies in excess of 13% (stabilized values, after light-induced degradation) have been achieved [3], using a triple-cell configuration and involving amorphous silicon–germanium alloys (a-SiGe:H). Corresponding commercial module efficiencies are, however, only approx. 6–8%, which is rather low for many energy-relevant applications. Amorphous silicon has the advantage of being deposited at relatively low substrate temperatures (180–300 °C); thus, it allows for the use of very low-cost substrates, such as cheaper forms of glass, stainless steel, aluminium, and especially polymers (polyimide, possibly also PET [4]). Deposition times are still relatively long (approx. 30–60 min for a full a-Si:H cell), but could be further reduced by the use of newer deposition techniques, such as VHF-PECVD [5].

An important newcomer in the field of PV cell materials is plasma-deposited hydrogenated microcrystalline silicon (µc-Si:H). First µc-Si:H layers were

### Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Material presence in earth’s crust [2]</th>
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<tbody>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>Ga</td>
<td>Gallium</td>
</tr>
<tr>
<td>As</td>
<td>Arsenic</td>
</tr>
<tr>
<td>Cd</td>
<td>Cadmium</td>
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<tr>
<td>In</td>
<td>Indium</td>
</tr>
<tr>
<td>Se</td>
<td>Selenium</td>
</tr>
<tr>
<td>Te</td>
<td>Tellurium</td>
</tr>
<tr>
<td>Concentration [ppm]</td>
<td>282 000</td>
</tr>
<tr>
<td></td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
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<td></td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
</tr>
</tbody>
</table>

Fig. 1. Past and estimated future evolution of PV world production volume and of PV module prices (at current $/Wp), from Shah et al. [1], completed with new data.
deposited by Veprek and Maracek in 1968 [6]. However, it was only in the early 1990s that actual μc-Si:H solar cells were fabricated [7,8].

Pioneering work was done at IMT Neuchâtel by Flückiger et al. [9], Meier et al. [10] and Torres et al. [11], resulting within a short time in the fabrication of pin (or nip)-type μc-Si:H solar cells with fully stable AM 1.5 conversion efficiencies in excess of 7% [12].

The purpose of the present paper was four-fold:

● to discuss the requirements of intrinsic μc-Si:H layers for their incorporation into efficient pin/nip solar cells and to describe results obtained, with this goal, by VHF-PECVD;

● to give an indication on the performance so far obtained for μc-Si:H pin and nip solar cells;

● to indicate estimated limits for such cells; and

● to outline the perspectives for so-called ‘micromorph’ tandem cells, i.e. tandems involving a microcrystalline silicon (μc-Si:H) bottom cell and an amorphous silicon (a-Si:H) top cell.

2. Intrinsic μc-Si:H layers for pin/nip solar cells

2.1. General list of requirements

For intrinsic μc-Si:H layers to be useful in the context of pin (or nip)-type solar cells, the following requirements have to be fulfilled:

(a) The material should be ‘truly’ intrinsic, with the Fermi level position $E_F$ at midgap, i.e.:

$$E_F = \frac{1}{2}(E_c - E_v)$$

where $E_c$ and $E_v$ denote the energy levels of the conduction and valence band-edges, respectively.

As usual, μc-Si:H layers have a pronounced n-type behavior, this type of ‘midgap’ material can be obtained, either by low-level doping [7,9], or else, preferably, by a reduction in the inherent oxygen content of the material [13] to values below 10¹⁹ atoms/cm³. The Fermi level position can be monitored either by measuring the dark conductivity activation energy $E_{act}$ (should be higher than 0.5 eV) or the dark conductivity $\sigma_{dark}$ itself (should be lower than $10^{-6} \text{S/cm}$).

(b) The grain boundaries and other defects should be well passivated by hydrogen, resulting in defect absorption at 0.8 eV of less than 3 cm⁻¹, but preferably considerably less than 1 cm⁻¹ (see also Fig. 7).

(c) The layer surface should be rough (standard deviation, S.D. $\sigma_{AFM}$ of surface roughness as measured by AFM should be at least approx. 15 nm, but preferably higher).

(d) The crystalline volume fraction $\varphi_c$ should be 70% or more.

Using VHF-PECVD at plasma excitation frequencies of 70–200 MHz, and subjecting the input gas mixture (SiH₄ and H₂) to a SAES getter-type gas purifier [14], the following layer characteristics are routinely obtained by our group [15]: $E_{act} \geq 0.4 \text{ eV}; \sigma_{dark} \leq 10^{-5} \text{ S/cm}; \alpha(0.8 \text{ eV}) < 3 \text{ cm}^{-1}; \sigma_{AFM} > 10 \text{ nm}; \varphi_c > 70\%$, at gas phase ratios [SiH₄]/([SiH₄]+[H₂]) of 5–7%.

2.2. [16,17] Variety of microstructures observed in PECVD-deposited μc-Si:H

Unlike monocrystalline silicon or even unlike amorphous silicon (a-Si:H), microcrystalline silicon is a highly complex material that can take on very different microstructural forms, depending upon the exact deposition conditions. Only certain forms of microcrystalline silicon are suitable for solar cells. This has already been extensively treated by the authors in a previous paper at the E-MRS Symposium in 1999 [16], where conditions were detailed w.r.t. intrinsic device-quality μc-Si:H as-deposited by VHF-PECVD. Fig. 2 schematically indicates the large microstructural variety observed. It would seem that the best solar cells are (so far, at least) produced with those intrinsic μc-Si:H layers, which are deposited at deposition conditions near the μc-Si:H/a-Si:H phase transition. Details of HR-TEM (high-resolution transmission electron microscope) observations on μc-Si:H layers can be found in Vallat-Sauvain et al. [17].

Note that the type of μc-Si:H layers deposited depends critically on the underlying layers and/or on the substrate used: microcrystalline layers deposited on glass or an amorphous silicon tend to have a larger amorphous volume fraction than those deposited on underlying crystalline material (see, e.g. [18]). The initial growth phase of a microcrystalline layer is especially delicate and is currently under study [19].

3. Microcrystalline silicon (μc-Si:H) solar cells of pin/nip-type

3.1. Results currently obtained

Fig. 3 shows typical J/V characteristics of a ‘good’ p-i-n type μc-Si:H solar cell, as currently fabricated by our laboratory; Fig. 4 shows the corresponding spectral response curve, as compared to the spectral response curve of a typical a-Si:H solar cell.

The performance of a μc-Si:H solar cell can be characterized by three solar cell key parameters:

● Short-circuit current density $J_{SC}$;

● Open-circuit voltage $V_{OC}$; and

● Fill Factor $FF$.

At least six laboratories worldwide are in the process of producing, at present, ‘state of the art’ μc-Si:H solar cells:
As for the short-circuit current density $J_{SC}$, the values obtained are in the range between 20 and 30 mA/cm$^2$, depending upon i-layer thickness, and especially on the light-trapping scheme within the solar cell also.

The open-circuit voltage $V_{OC}$ of μc-Si:H cells had in the first cells been approximately 350–400 mV, but presently values between 520 and 560 mV are obtained by virtually all laboratories mentioned above. $V_{OC}$ depends surprisingly, to a large extent, on the silane/hydrogen gas phase ratio used for i-layer depositions. High $V_{OC}$-values are obtained for cells deposited near the μc-Si:H/a-Si:H phase transition boundary (Fig. 5): This is, so far, a necessary but insufficient condition for a high $V_{OC}$. The p/i interface (through which light enters into the μc-Si:H cell) is another critical factor. Further research is under way here (see also [18,19]).

Fill Factors (FF) currently obtained for best μc-Si:H cells are between 70 and 77%. The fill factor FF is a complex parameter: it depends essentially on three quantities that can be identified in the electrical equivalent circuit of a pin solar cell (Fig. 6):
1. the series resistance $R_s$ should be minimized; high $R_s$ values are caused by insufficiently doped p- and n-type layers, and especially by excessively resistive (transparent) contact layers: a highly conductive transparent oxide (TCO) is, indeed, definitely needed to obtain a low value of $R_s$;

2. the parallel resistance $R_p$ which is given by shunts — either at the edge of the cell or within the cell, the latter type of shunts being presumably due to cracks in the intrinsic μc-Si:H layer (such shunts should be avoided to obtain high $R_p$ values which are, in fact, what is needed in order to maximize the $FF$-value); and

3. by additional recombination losses due to the pin (or nip) solar cell configuration, symbolized by the current sink $J_{\text{rec}}$ in Fig. 6.

Further research is needed to understand better the limitations w.r.t. $FF$ often encountered in practical μc-Si:H solar cells as well as in 'micromorph' tandem solar cells and modules: One should analyze the cells/modules carefully each time, by Variable Intensity Measurements (VIM) [21], so as to identify to which one of the above quantities (a), (b), (c), the limitation of $FF$ is due to in a given specific case.

With $J_{SC} \approx 30$ mA/cm$^2$, $V_{OC} = 518$ mV and $FF = 70\%$, a 10.9\% efficient μc-Si:H cell becomes possible. Such a record-efficiency single-junction μc-Si:H cell has been reported by Saito et al. of Canon Inc., at the 12th International PVSEC Conference in Jeju (Korea) 2001 (Table 2).

Can the efficiency of μc-Si:H solar cells be significantly increased over 10\%? To answer this question one may compare the key parameters of μc-Si:H solar cells with those obtained with the best monocrystalline silicon solar cells — a topic that will be addressed in Section 3.2.

### 3.2. Comparison between present μc-Si:H and best c-Si solar cells

The laboratory record efficiency for a wafer-based crystalline silicon (c-Si) solar cell has been reported by Green and co-workers [22] under AM 1.5 illumination, the following values have been obtained thus far (Table 2).

Note that it is generally accepted and can be theoretically confirmed (see also [23,24]) that the values obtained for c-Si laboratory cells are quite near the theoretical limit which it is physically possible to achieve with single-junction solar cells and a material having an energy gap of 1.1 eV. This means that Table 2 indicates the potential for further improvement in the performance of μc-Si:H cells.

As can be seen from Table 2, there is relatively little to be gained further, w.r.t. $V_{OC}$, $n$ and $FF$-values which are already quite near to those achieved for best c-Si cells.

The largest scope for further improvement is clearly w.r.t. $J_{SC}$. If one wants, however, to keep cell thickness reasonably low (in order to keep deposition time, and thus, also production costs reasonably low), this can only be done by optical means, i.e. by light trapping.

This is a complex optical problem: it requires suitably textured (i.e. rough) layers and very low optical absorption in all transparent layers.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Comparison between record-efficiency c-Si and μc-Si:H single-junction solar cells as obtained to date</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{SC}$</td>
<td>42.2 mA/cm$^2$</td>
</tr>
<tr>
<td>$V_{OC}$</td>
<td>706 mV</td>
</tr>
<tr>
<td>$FF$</td>
<td>82.8%</td>
</tr>
<tr>
<td>$\eta$</td>
<td>24.7%</td>
</tr>
</tbody>
</table>
3.3. Need for pin (or nip)-type configurations for μc-Si:H solar cells

Crystalline silicon is a material with an indirect bandgap, and therefore, the absorption coefficient \( \alpha(hv) \) for light wavelengths near the absorption edge (\( hv \)-values just slightly over \( E_g \)) is very low, for all forms of crystalline silicon (Fig. 7): we observe in monocrystalline silicon typical values of approximately 70 cm\(^{-1} \) for \( hv = 1.24 \text{ eV} \) or \( \lambda = 1000 \text{ nm} \). A similarly low value of \( \alpha(hv) \) is observed in μc-Si:H layers, even though the ‘effective’, as-measured value of \( \alpha(hv) \) is slightly higher here (approx. 200 cm\(^{-1} \)) due to surface roughness of the layer [25]. With such low values of \( \alpha \), photogenerated carriers will have to be collected from the whole depth of the thin-film solar cell and not just (as is the case for CIGS and CdTe solar cells, with their direct bandgap) from regions near the surface. On the other hand, the minority carrier diffusion length \( L_{\text{diff}} \) of doped μc-Si:H layers is (due to defects and grain boundaries) extremely small and can be estimated to be less than 1 \( \mu \text{m} \). This specific diffusion length can, in fact, be considered, in a first approximation, to be smaller or equal to the ambipolar diffusion length of intrinsic μc-Si:H layers, the latter having been measured by means of the surface photovoltage (SPV) and steady-state photocurrent grating (SSPG) techniques, with resulting values between 0.2 and approximately 0.8 μm [26].

As one definitely needs a solar cell thickness \( d_{\text{cell}} \) higher than 1 \( \mu \text{m} \) to absorb enough sunlight, one clearly sees that it is quite impossible to obtain satisfactory collection by diffusion alone, as \( d_{\text{cell}} > L_{\text{diff}} \). Thus, clearly pn-diodes, where the collection of the photogenerated carriers is by diffusion, cannot be used for μc-Si:H solar cells.

Therefore, in a similar manner as for a-Si:H, all successful research groups have used the p-i-n (or n-i-p) configuration to fabricate μc-Si:H solar cells.

Here, the carrier generation (photogeneration) is almost exclusively within the intrinsic (i)-layer and the carrier collection is by drift (Fig. 8).

Indeed, the drift length \( L_{\text{drift}} \) (or ‘Schubweg’) can be shown to be almost always higher than the diffusion length \( L_{\text{diff}} \).

One has:

\[
L_{\text{diff}} = \frac{\tau \cdot D}{\mu} \text{, with } D = \frac{kT}{q} \cdot \mu
\]

i.e.

\[
L_{\text{diff}} = \sqrt{\frac{kT}{q} \cdot \mu \cdot \tau}
\]

where \( \mu \) is the carrier mobility, and

\[
L_{\text{drift}} = \mu \cdot \tau \cdot E_i
\]

where \( E_i \) is the prevailing internal electric field, and is equal to \( V_{bi}/d_i \) for an ideal situation (no field deformation) and for short-circuit conditions, with \( V_{bi} \approx 1 \text{ V} \) (built-in voltage) and \( d_i \) is the i-layer thickness.

From Eqs. (2) and (3), one can obtain the following relation:

\[
\frac{L_{\text{drift}}}{L_{\text{diff}}} = \frac{\gamma \cdot L_{\text{diff}}}{d_i}
\]

where \( \gamma = \frac{V_{bi} \cdot q}{kT} \approx 40 \) for μc-Si:H and \( T \approx 25 \text{ °C} \).

This ratio becomes higher if the material is of better quality (if \( L_{\text{diff}} \) increases) and also if the solar cell is thinner (\( d_i \) reduces). Even for a relatively unfavorable
been difficult to confirm under well-defined laboratory conditions with a solar simulator.

At present, a whole range of R&D groups are reporting stabilized laboratory tandem cell efficiencies in the range of 10–12%, as witnessed by many contributions at the PVSEC-12 Conference in Korea (June 2001).

For larger-sized modules, IMT Neuchâtel reported a stabilized active area efficiency of 9% for a 4×8-cm² mini-module [30]. Lately, Kaneka Corp. of Japan has successfully fabricated a large area (approx. 0.5 m²) module, closely following IMT’s original micromorph concept: stabilized aperture area efficiencies over 9% are claimed [31]. These modules are now available in small quantities on the European market and the efficiency claims of Kaneka could be partially confirmed, at least for the initial state.

4.3. Problems encountered at the moment with micro-morph tandems

The problems presently faced fall into three categories:

1. Interface and interdiffusion problems, especially w.r.t. the critical ‘tunnel (recombination) junction’ between the two partial cells. These are process- and reactor-dependent and not much can be said about them here.

2. Thickness-related problems: Because of the light-induced degradation (Staebler–Wronski effect) prevailing in a-Si:H solar cells, the amorphous top cell has to be kept thin (d_{top} ≤ 0.3 µm). In order to avoid prohibitively long deposition times (of more than 1 h), the microcrystalline bottom cell has also to be kept relatively thin (d_{bottom} ≤ 2 µm), as long as deposition rates for device-quality intrinsic µc-Si:H layers are not substantially over 10 Å/s. Thus, the short-circuit densities obtained are rather low.

3. Light trapping problems: It is especially difficult to obtain effective light trapping for the amorphous top cell, unless an ‘intermediate mirror’ (e.g. an intermediate ZnO layer) between the top and the bottom cell, could be successfully used. This is one of the reasons why most of the early micromorph tandems have been top-cell limited. On the other hand, it becomes important if one has optical paths that run at a small angle through the solar cell (and have in this manner been considerably lengthened) to keep the optical absorption coefficient α(hv) in the TCO layers very low, otherwise a lot of light will be lost through absorption in just these layers. However, because of free carrier absorption, it is very difficult to attain a low absorption coefficient in the near-infrared region — a region of the solar spectrum that is important for the microcrystalline bottom cell.

4.4. Module performance under field conditions

We have so far referred to cell and module performance under standard test conditions (STC): i.e. with light entering vertically onto the cell/module, for T = 25 °C cell/module temperature and for the AM 1.5 spectrum at one sun intensity (approx. 100 mW/cm²)

In actual field use, the light will be entering the module at an angle (≠ 90°), the temperature may go up into the 60° to 80 °C range; the spectrum may shift in the evening towards the orange (and in cloudy weather towards the blue) and light intensities may be substantially less than 100 mW/cm².

Work is under way to assess the effect of these factors on micromorph tandem modules and results will be reported later. Preliminary data tend to show that micromorph modules fare relatively well under actual field conditions, possibly quite a bit better than other types of thin-film photovoltaic modules.

5. Conclusions

Solar cells based on plasma-deposited hydrogenated microcrystalline silicon (µc-Si:H) as well as ‘micromorph’ (µc-Si:H/a-Si:H) tandem solar cells — both pioneered by IMT Neuchâtel — have opened up a whole new field of investigation for thin-film solar cell concepts. Japanese industrial research groups are now especially active here. A stabilized commercial module efficiency (total area efficiency) of 10% seems within reach during the next few years.

It can only be hoped that European Industries will take up the challenge and also become active in this field, as the micromorph tandem cell concept may well constitute one of the most promising future avenues for mass-produced low-cost photovoltaic modules. Low temperatures (≈ 200 °C), possibility of very low cost substrates (e.g. low-cost polymers such as PET, etc.), excellent material availability, absence of toxic/hazardous materials and proven large-area processing capacity all concur to make this option particularly attractive for the future.

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References
