The "Micromorph" cell: a New Way to High-Efficiency-Low-Temperature Crystalline Silicon Thin-Film Cell Manufacturing?

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Abstract. Hydrogenated microcrystalline Silicon (μc-Si:H) produced by the VHF-GD (Very High Frequency Glow Discharge) process can be considered to be a new base material for thin-film crystalline silicon solar cells. The most striking feature of such cells, in contrast to conventional amorphous silicon technology, is their stability under light-soaking. With respect to crystalline silicon technology, their most striking advantage is their low process temperature (220°C). The so called "micromorph" cell contains such a μc-Si:H based cell as bottom cell, whereas the top-cell consists of amorphous silicon. A stable efficiency of 10.7% (confirmed by ISE Freiburg) is reported in this paper.

At present, all solar cell concepts based on thin-film crystalline silicon have a common problem to overcome: namely, too long manufacturing times. In order to help in solving this problem for the particular case of plasma-deposited μc-Si:H, results on combined argon/hydrogen dilution of the feedgas (silane) are presented. It is shown that rates as high as 9.4 Å/s can be obtained; furthermore, a first solar cell deposited with 8.7 Å/s resulted in an efficiency of 3.1%.

1. INTRODUCTION

In recent work (1), hydrogenated microcrystalline silicon (μc-Si:H) has been successfully introduced as active semiconductor in entirely μc-Si:H p-i-n solar cells. The present paper will first review the development from the first "mid-gap" layers to entirely microcrystalline solar cells and the extension to the so-called "micromorph" tandem cell concept. Thereby these micromorph cells have already achieved, after 1000 hours light-soaking a stabilized efficiency of 10.7% (confirmed by ISE Freiburg, Germany).

The Very High Frequency Glow-Discharge (VHF-GD) technique has so far played a key role in obtaining "solar grade" μc-Si:H material. With this technique...
μc-Si:H can be deposited at temperatures as low as 220°C, a fact that permits the use of low-cost substrates such as plastic, glass, aluminium etc., in the field of crystalline silicon. One may generally argue that due to that further cost reduction for future solar cell manufacturing can be achieved.

At the present state of development, μc-Si:H and micromorph solar cells have two main problems to overcome: first, their stable efficiency has to be further increased; second, the deposition rate of high-quality material has to be increased from presently 1-2 Å/s to more than 10 Å/s. It will be shown in the second part of this paper that by diluting silane in argon and hydrogen, deposition rates up to 9.4 Å/s can basically be obtained. The use of argon/hydrogen dilution increases the parameter space for optimization of the material quality. Thus, the full optimization of deposition will take more R&D time and is not yet completed. A first μc-Si:H solar cell deposited at 8.7 Å/s with an efficiency of 3.1% has already been achieved.

2. SOLAR CELLS BASED ON MICROCRYSTALLINE SILICON: REVIEW OF PAST WORK

Hydrogenated microcrystalline silicon is generally obtained in a plasma using silane strongly diluted with hydrogen (2). Apart from few isolated papers (3-5), μc-Si:H was in the past generally not seriously taken into account as a candidate for becoming an active semiconductor for solar cells. The novel inputs that have lead to the successful use of μc-Si:H in solar cells as reported in recent work (1, 6-9), can be reduced to two main characteristics:

1. The absorber material in μc-Si:H solar cell must be "mid-gap" material.
2. The material used must have a low grain-boundary trap density and a low defect density within the grains.

"Mid-gap" material

The deposition of "mid gap" μc-Si:H is not straightforward; as-deposited intrinsic μc-Si:H turns out to be slightly n-type; this is basically due to oxygen impurities, as reported by Veprek et al. (10). Two possibilities have in the past been used to overcome this problem:

1. The compensation technique: Small traces of diborane compensate the n-type behaviour (7). The compensation technique leads to surprisingly good results for layers and solar cells but it turns out to be technologically delicate.
2. The purifying technique: A gas purifier (oxygen getter) installed close to the reactor removes oxygen-containing impurities (8). Thereby, low dark conductivities and μc-Si:H single-junction solar cells with 7.7% efficiency could be obtained (6, 11). The purifying technique can completely replace the compensation technique.
Low grain-boundary trap density

It can be assumed, that μc-Si:H deposited by VHF-GD has a very high fraction of crystalline silicon. The amorphous fraction is thereby essentially reduced to the grain boundaries. Using the grain boundary trapping model developed by Seto et al. (12), Meier et al. (13) estimated a grain-boundary trap density that is approximately 100 times lower than that what has been reported for polysilicon deposited by CVD, with roughly the same grain size (12). Infrared spectroscopy performed by Kroll et al. (14) showed that bonded hydrogen in VHF-GD μc-Si:H is preferentially located at crystallite surfaces. Thus, one may tentatively conclude that an efficient grain-boundary passivation due to "excess" atomic hydrogen takes place.

VHF-GD deposited μc-Si:H shows a pronounced absorption edge; thereby a gap-energy as low as 1 eV could be deduced (8). As a surprising fact, the overall absorption within the whole near-infrared range is higher than that obtained with monocystalline silicon. This particular feature makes μc-Si:H an attractive candidate for thin-film silicon solar cells.

Selected properties of entirely microcrystalline cells

The most striking features of entirely microcrystalline solar cells as produced by VHF-GD are:
1. Complete stability under intense, long-time light-soaking (8).
2. As can be predicted by the absorption spectra, entirely microcrystalline solar cells show a spectral response that is strongly extended towards the infrared, when compared with amorphous silicon solar cells.
3. The manufacturing technique of microcrystalline silicon is compatible to that of amorphous silicon, i.e. the process temperatures do not exceed 250 °C.

The "Micromorph" Concept

The combination of an entirely microcrystalline solar cell with an amorphous silicon solar cell results in a "true" tandem cell with different gap-energies for the top (1.76 eV) and the bottom cell (1.0 eV). This type of tandem cell has been called by the authors the "micromorph" cell. The stabilized efficiencies obtained sofar are summarized in Tab. 1:

<table>
<thead>
<tr>
<th>cell type</th>
<th>η [%]</th>
<th>$I_{sc}$</th>
<th>$V_{oc}$</th>
<th>FF</th>
<th>area [cm$^2$]</th>
<th>light-soaking procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>μc-Si:H p-i-n</td>
<td>7.7</td>
<td>25.3</td>
<td>0.448</td>
<td>67.9</td>
<td>0.33</td>
<td>10 suns, 48°C, 400 h</td>
</tr>
<tr>
<td>Micromorph</td>
<td>10.0*</td>
<td>11.3</td>
<td>1.34</td>
<td>65.5</td>
<td>1.22</td>
<td>AM 1.5; 50°C 1000 h</td>
</tr>
<tr>
<td>Micromorph</td>
<td>10.7*</td>
<td>11.9</td>
<td>1.34</td>
<td>66.7</td>
<td>0.13</td>
<td>AM 1.5; 50°C 1000 h</td>
</tr>
</tbody>
</table>

* Confirmed by the Fraunhofer ISE PV- Kalibrationslabor
Limits and potential for further improvements

The $V_{oc}$-values obtained so far for entirely microcrystalline cells (micromorph bottom cell) are substantially lower (448 mV) than the $V_{oc}$-values of typical a-Si:H (top) cells (890 mV). Due to this fact, the top cell produces, within the micromorph tandem cell, two thirds of the total power of the cell (9). Because of this, the stability of the top cell will remain a key feature as long as the open circuit voltage of the bottom cell remains limited to such low values: One may conclude that a further increase of the $V_{oc}$-value of the bottom cell alone is the most important individual factor for further improvement in the stable efficiency of the micromorph cell.

The most striking limitation in the future industrial potential of any kind of thin-film crystalline silicon solar cell is, at present, the too long manufacturing times (recrystallization and/or deposition rates). Looking at the deposition rates of µc-Si:H, the VHF-GD process in itself brings so far at least some improvement, as reported by Finger et al. (15). Attempts at obtaining yet higher deposition rates are described by Torres et al. (16). In this paper we present an alternative approach using argon plus hydrogen dilution of silane.

3. USE OF ARGON AS DILUTION GAS: GENERAL CONSIDERATIONS

Argon dilution and mixtures of Ar, H$_2$, and silane have often been reported in literature for a-Si:H deposition with the attempt to obtain more stable material (e.g. (17)). As a further beneficial effect, Kroll et al. (18, 19) report on significant silane savings using argon dilution. In another work, an increase of the deposition rate of a-Si:H is reported by Hautala et al (20). Sansonnens et al. (21) report on molecular quenching via metastables that leads to enhanced dissociation of silane. In all these cases, the authors used merely Ar/SiH$_4$ mixtures without hydrogen. Other authors report on properties of µc-S:H layers obtained using strongly argon-diluted silane plasmas (22). Further results on the increase of the deposition rate of µc-Si:H are reported by Imajyo et al. (23): they used a DC plasma gun for their experiments at high DC discharge currents. In this last case a mixture of Ar, H$_2$ and SiH$_4$ was applied.

In our work we have varied the composition of the diluting gases argon and hydrogen; thereby the VHF-GD technique was applied. In doing this, we emphasize on two aspects:

1. Reduction of the peak energy of ions that impinge on the growing layers; this constitutes, thus, an attempt to further improve the material quality,
2. increase of the deposition rate of VHF-GD µc-Si:H.
The full potential of µc-Si:H silicon to play a role in PV energy conversion gives still rise to speculations. One may assume that the plasma control parameters, that can lead to desirable growth mechanisms, are not fully optimized as yet. Looking at the "ideal" µc-Si:H layers with respect to an application in solar cells the following goals can be formulated:

a) The grains should be as large as possible (low grain boundary density).

b) The grains should have low defect densities (lattice defects and impurities).

c) Low grain-boundary trap density (highly passivated grain-boundaries).

d) No grain-boundaries perpendicular to the photocurrent.

The points a) and b) can be considered interdependent in the following way: High particle energies from the plasma create defects in the growing grains that lead, if the lattice damage is pronounced, to loss in the "information" as required for continuous "epitaxial-type" growth within the grains. A reduced grain-size with a higher grain-boundary density has then to be expected.

We should therefore look at the peak energies of particles to be found typically in a plasma used for µc-Si:H deposition. Due to the strong dilution of silane in hydrogen, the mean free path of silicon-based radicals (Si, SiH, SiH₂, SiH₃ etc.) is in the range of centimetres; for hydrogen atoms tenths of millimetres are typical values. Silicon-type radicals can therefore not contribute to thermalization of silicon type ions (Si⁺, SiH⁺, SiH₂⁺, SiH₃⁺, etc.) that are accelerated across the sheath. Now, for a sheath potential higher than the threshold energy Eₜₜh = 16 eV, defect formation occurs in the growing layer, according to Veprek et al. (24). Values as high as 16 eV are easily obtained in a 13.56 MHz discharge, whereas the ions in a 70 MHz discharge have typically maximum ion energies that are just around this value (25, 26). Note, that the collisions between Si-type ions and hydrogen atoms randomizes only several ppm of the energy of the ion. In order to thermalize efficiently the high peak-energies of Si-type radicals one can therefore envisage diluting the plasma with argon as an inert gas; note, that argon has about the same mass as silicon-based radicals.

The points c) - d) deal with the aspect of increasing diffusion- (or drift) lengths for electronic transport; these lengths are affected either by defects in the grains or by trap-assisted recombination at grain-boundaries. Furthermore, charged traps in grain-boundaries have the tendency to screen locally the built-in field; this leads again to enhanced recombination and to a loss in the efficiency of the cell (27).

Looking at our demands (a-d) pronounced columnar grown i.e. crystalline silicon columns throughout the thickness of the cell would be ideal. Meier et al. (8) have shown, using SEM and TEM micrographs and X-ray measurements, that VHF-GD µc-Si:H layers possess, indeed, a pronounced columnar structure in the (220) direction. At present there are no experimental tools at hand that allows one to quantify the characteristics c)-d) in a microscopic way giving thereby the possibility to "tune" the deposition conditions for obtaining an "ideal" µc-Si:H as sketched above.
4. EXPERIMENTAL PROCEDURES USED FOR ARGON/HYDROGEN DILUTION

All the experiments were undertaken using the VHF-GD technique at 70 MHz. Three series were deposited, as shown in Table 2.

For the M-series (Mixing-series), the mixture of the diluting gases Ar and H₂ was varied at constant silane flow (6 sccm). The sum of flows of the diluting gases (Ar + H₂) was kept at 150 sccm.

For the D-series (Dilution-series), the mixture of the two diluting gases was kept constant, at 90 sccm H₂ and 60 sccm Ar, whereas the silane flow was varied.

For the P-series the Power of the plasma was varied for a fixed silane flow of 8.4 sccm in 90 sccm hydrogen and 60 sccm Argon.

TABLE 2. Strategy of H₂ / Ar dilution experiments for deposition of µc-Si:H.

<table>
<thead>
<tr>
<th>Serie</th>
<th>Φ(SiH₄) [sccm]</th>
<th>Φ(H₂) [sccm]</th>
<th>Φ(Ar) [sccm]</th>
<th>Power [W]</th>
<th>Pressure [mbar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>6</td>
<td>140 - 0</td>
<td>10 - 150</td>
<td>30</td>
<td>0.8 mbar</td>
</tr>
<tr>
<td>D</td>
<td>6-12</td>
<td>90</td>
<td>60</td>
<td>40</td>
<td>0.9 mbar</td>
</tr>
<tr>
<td>P</td>
<td>8.4</td>
<td>90</td>
<td>60</td>
<td>10 - 70</td>
<td>0.9 mbar</td>
</tr>
</tbody>
</table>

For our Ar / H₂ dilution experiments, looking at the above goals a)-d), we tried to quantify the columnar growth of the µc-Si:H layers using X-Ray diffraction.

![Typical X-Ray diffraction pattern of a µc-Si:H thin-film grown by VHF-GD deposition using Ar/H₂ dilution. The points refer to the powder sample according to the JCPDS (28).](image)

FIGURE 1. Typical X-Ray diffraction pattern of a µc-Si:H thin-film grown by VHF-GD deposition using Ar/H₂ dilution. The points refer to the powder sample according to the JCPDS (28).

To this end we suggest using a formula (1) that can serve to roughly indicate the preferential columnar growth of µc-Si:H layers; this formula is based on
corresponding X-Ray diffraction parameters as found in the JCPDS (28) chart for isotropic powder samples.

\[
F = \frac{A_{(220)}}{A_{(111)}} \cdot \frac{A_{\text{powder (111)}}}{A_{\text{powder (220)}}} = \frac{A_{(220)}}{A_{(111)}} \cdot 1.81 \quad [1]
\]

Here \(A(iii)\) represents the area under the respective diffraction; the values of the isotropic powder sample \(A_{\text{powder (iii)}}\) can be obtained from the JCPDS chart. A typical X-Ray diffraction pattern obtained for \(\mu c\text{-Si:H}\) is thereby given in Fig. 1.

From X-Ray measurements, the average grain-size was determined using Sherrer's formula. Doing this, one basically assumes that the crystallites have a spherical shape. As we know, this is definitively not the case, as the SEM, TEM and X-Ray diffraction patterns indeed confirm. One should consider the growth not to be spherical but in the form of a "cigar". Therefore, in addition to using the apparent grain-size as calculated by Sherrer's equation, we propose using the factor \(F\) (equation (1)), to roughly characterize structural properties.

5. RESULTS AND DISCUSSION.

5.1 Results on Layers.

The X-Ray diffraction pattern of the various samples of series M, D, P are similar to the one shown in Fig.1. As already observed in previous work (8) samples grown by H\(_2\) dilution also show a strong anisotropic columnar growth in the (220) direction.

![Parameter graph](image)

**FIGURE. 2.** Parameters obtained from X-ray diffraction patterns of the M-series and the deposition rate from the same series. The F-values were calculated from equation (1). The apparent "grain-size" was calculated from the (220) diffraction signal using Scherrer's equation.
All samples of the M-series were found to be microcrystalline (Fig. 2). As the most striking result, a pronounced increase in deposition rate up to 5 Å/s was obtained for about equal parts of Ar and H₂ as dilution gases. The F-values show here a maximum: this leads us to assume that we have the most pronounced columnar growth under these deposition conditions. Looking at the "apparent grain-size" according to Scherrer's formula, a continuous increase can be found when increasing Ar dilution in the plasma. We assume that enhanced thermalization of high energy particles occurs and that this effect allows crystallites to obtain the highest "apparent grain-size" values in this study (250 Å).

For the D-series we applied the same dilution-values as those needed for obtaining the highest deposition rate within the M-series; however, we applied a slightly increased pressure (0.9 mbar). Fig 3. shows the results.

![Graph](image)

**FIGURE 3.** D-series: apparent "grain-size" as well as F-value and deposition rate in function of the dilution; thereby, the composition and the flow of the diluting gases was kept constant (90 sccm H₂, 60 sccm Ar).

All samples within the D-series were found to be microcrystalline. The F-values are roughly constant for all dilutions, whereas the "apparent average grain-size" (from Scherrer's equation) has a maximum at 4.5% silane. Adding more silane leads to a continuous decrease of grain-size. The deposition rate increases linearly up to the highest value of 9.4 Å/s obtained in this study.

In the P-series, the samples deposited at 10 and 20 W resulted in amorphous silicon. Surprisingly, the deposition rate of µc-Si:H obtained in this series has its highest value at 40 W and thereafter drops constantly for increasing power. The "apparent grain-size" shows a similar tendency. We can assume that a high value of ion peak-energy in the plasma creates defects which gives rise to an overall reduction in the growth of the crystallites. The anisotropy factor shows a sharp
maximum around 50 W i.e. for larger power values than those studied in series M and D.

**FIGURE 4.** "Apparent grain-size", F-value and deposition rate in function of VHF- power. Note, that for reduced power, the layers become amorphous.

### 5.2. Results on Solar Cells.

In a next step the Ar / H\(_2\) diluted layers that were deposited at high deposition rates, were incorporated in a solar cell with a i-layer thickness of 5.5 \(\mu\)m.

**FIGURE 5.** Spectral response and performance parameters of a first \(\mu\)c-Si:H n-i-p solar cell deposited at 8.7 Å/s.
Due to the strong tendency to peel off, an aluminium substrate and a n-i-p structure had to be used. Fig 5. shows the spectral response values and the solar cell parameters of this cell.

In contrast to the above individual layers of series M, D, and P, the entire cell was deposited using the purifying technique. It was found in a parallel study that this is crucial, because Ar-diluted μc-Si:H layers have the tendency to incorporate oxygen in a more pronounced manner than when using only H₂-dilution, according to Keppner et al. (29); a similar effect was already observed for a-Si:H layers by Kroll et al. (19). The cell presented in Fig. 5 shows a reduced spectral response in the near infrared; this is in agreement with PDS results (29) showing reduced infrared absorption around 1.2 eV. At this stage of the work it is not yet clear whether the reduced near infrared absorption is typical for layers produced at high rates with Ar-dilution or whether it is only due to the preparation techniques not being fully optimized.

6. CONCLUSIONS

A silicon-based tandem solar cell called the "micromorph" solar cell containing a microcrystalline bottom cell and an amorphous top cell has obtained a stable efficiency of more than 10 %. Because of the relatively low absorption coefficient in the near infrared, as obtaines in the μc-Si:H bottom cell, relatively high i-layer thicknesses are needed and the rather long deposition times remain a problem to be overcome. Argon / hydrogen dilution of silane, as the method was used here in combination with the VHF-GD process, basically provides the possibility to achieve deposition rates up to 10 Å/s. A first trial check with such high-rate material already result e.g. in a cell with 3.15 % efficiency. Argon / hydrogen dilution experiments show, furthermore, that the columnar growth structure and the average grain-size of the crystallites can, indeed, be controlled within a certain range. Thanks to the addition of argon as dilution gas, the parameter space that allows one to "tune" μc-Si:H w.r.t solar cell requierements is strongly expanded.

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REFERENCES


28. JCPDS International Centre for Diffraction Data; ASTM chart Nr. 27-1402.
