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"Mikromorphe" Solarzellen

Basierend auf amorphem und mikrokristallinem Silizium

ausgearbeitet durch
Prof. Dr. A. Shah und Mitarbeiter
Institut de Microtechnique (IMT), Université de Neuchâtel
Rue A.L. Breguet 2, 2000 Neuchâtel

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Summary

The central subject of this project phase was to continue research on the "micromorph" solar cell concept: a new solar cell concept based on the combination of microcrystalline and amorphous solar cells in a tandem configuration and pioneered by IMT in 1994; the general goal was to demonstrate the potential of this new type of thin-film silicon solar cells. Hereby, different subtasks have been studied in order to obtain a better understanding of the individual problems that need to be solved in order to fabricate, in an economically acceptable way, high-efficiency "micromorph" tandem solar cells. While in the precedent project phase ('94-96) IMT was basically the only group doing active and successful research on microcrystalline silicon solar cells, there has been during the last three years the establishment of an "international community" working intensively on microcrystalline silicon and on "micromorph" tandem solar cells. On the other hand, many research groups have also started to try out the VHF-GD (Very High Frequency Glow-Discharge) deposition technique, an original deposition method that was introduced by IMT in 1986. The VHF technique is indeed convincing more and more groups, because of its potential for high deposition rates both, for microcrystalline as well as amorphous silicon and because of its usefulness in the growth of high-quality microcrystalline silicon layers. The success of microcrystalline silicon as low-band gap material goes today so far, that different groups (e.g. Canon Corp.) have now substituted their former research activities on silicon-germanium alloys by work on microcrystalline silicon. Thus, the justification of this project is certainly given: It is today clear that the concepts proposed by IMT have a high potential for use in the next generation of low-cost solar cells.

Within this period we **achieved** the following **individual results** which are all related to the micromorph concept:
1.) TEM (Transmission electron microscopy) investigations have revealed that *microcrystalline silicon* (μc-Si:H) does not constitute a single standard microcrystalline material but is, on the contrary, a *semiconductor with a large variety of different microstructures or microtextures*. These forms of microstructure depend essentially on the applied deposition conditions and on the properties of the substrates and underlying layers.
2.) Systematic studies on different microcrystalline films have shown that the observed *absorption enhancement* for VHF-deposited μc-Si:H with respect to crystalline wafer silicon is mainly due to the as-grown *surface texture* of plasma-deposited μc-Si:H films. To obtain even higher effective absorption one needs to improve the surface roughness, while still keeping the sub-bandgap absorption (defect absorption) low.
3.) *Electronic transport* measurements suggest that the behaviour of the mobilityxlifetime products (μτ-products) in μc-Si:H material is *similar to that of μτ-products in amorphous silicon (a-Si:H)*. We therefore conclude that electronic transport in μc-Si:H layers is governed by the amorphous phase present at the grain boundaries.
4.) Intensive deposition studies on *microcrystalline single-junction devices* have led to an *improvement of the open circuit voltage* V_{oc} *to values clearly above 500 mV*. Thereby, a p-i-n cell with an efficiency of 8.5 % (V_{oc} = 531 mV, FF = 69.8 %, J_{sc} = 22.9 mA/cm^2) could be achieved; in the case of n-i-p μc-Si:H cells we have reached, for single-junction cells, an efficiency of 7.8 %.

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5) *Deposition rates for individual microcrystalline silicon* layers with reasonable quality could be increased up to *16 Å/s*, reasonable n-i-p solar cells (η = *6.9%*) could be fabricated at deposition rates as high as *10 Å/s*.

6.) For high-rate deposition of amorphous silicon layers, with reasonable stability and good $\mu\tau$-products, both DC deposition (as used by BP-Solarex Inc.) and VHF deposition (as introduced by IMT) give excellent results, provided the *hydrogen dilution ratio* used during deposition is carefully *optimised*. Traditional RF deposition at 13.56 MHz gives clearly lower deposition rates. Thereby, the most important deposition parameter that controls the quality of the amorphous silicon obtained is the substrate temperature: With higher temperatures the $\mu^0\tau^0$-product in the light-soaked state increases.

7.) It is possible to obtain *with hot-wire (HW) deposition* individual intrinsic (<i>) a-Si:H layers with excellent quality (high value of the $\mu\tau$-product in the light-soaked state), it is also possible by combining this deposition method with VHF-GD to achieve high deposition rates (26 Å/s) for individual intrinsic µc-Si:H layers. However, hot-wire deposition leads to additional technical problems when fabricating full p-i-n or n-i-p solar cells. Because of lack of time and resources, IMT has abandoned investigation on hot-wire deposition.

8.) *Applying the hydrogen dilution* technique to the deposition of the intrinsic (<i>) layer within p-i-n single-junction amorphous silicon solar cells leads, indeed, to an *improved stability* of these cells. Combining hydrogen dilution with increased substrate temperatures leads to higher short-circuit currents but lower open circuit voltages.

9.) By *CO_2 and H_2 treatments* of the i-p interface of *n-i-p a-Si:H solar cells* an *improvement of both the open circuit voltage and the fill factor FF* could be achieved. On flat stainless steel substrates V_{oc}-values over 900 mV and FF-values of up to 74 % have been obtained.

10.) Besides our sputtered ITO and ZnO layer deposition technology we have built up an *in-house LP-CVD ZnO technology* which is a high-rate deposition process and which allows us to directly prepare rough TCO layers. Our work here was concentrated sofar mainly on the building up of the process system and on achieving process reproducibility.

11.) *Patterning techniques* for p-i-n based solar cells have been developed based on both the *pad printing* technique and on the *laser scribing method*. Well-defined areas of the test cells are required for the short-circuit current determination and the verification of the efficiencies of our p-i-n type solar cell. A substantial effort was undertaken by us to reequip and install a laser scribing system (λ = 1064 nm) borrowed from the firm Phototronics-Solartechnik GmbH (D). This laser system is at present used to scribe the front ZnO layers of our micromorph cell modules. For scribing the silicon layers, a Nd:YAG laser (λ = 532 nm) originally acquired for light-induced degradation is used at present (low pulse frequency of only 20 Hz.). Using both laser wavelengths it now becomes possible to apply the well-established integrated series connection method also to our micromorph p-i-n devices.

12.) Our *micromorph* p-i-n-p-i-n tandem cells could be improved so as to obtain *stabilized efficiencies* of *11.0 to 11.6 %* for a cell area of 0.25 cm^2. A discrepancy observed between indoor simulator and outdoor (clear sky condition) characterisations may be due to a loss in the blue part of the spectrum present in our "artificial light source" (solar simulator). A larger number of micromorph cells with well-defined cell areas are needed so as to obtain full efficiency verification by the Fraunhof ISE (Institut für solare Energiesysteme) Freiburg.

13.) A *first micromorph mini-module* (23.6 cm^2) was fabricated, thereby *applying the integrated electric series connection concept*, a concept already well-established for amorphous silicon modules. An initial module aperture *efficiency of 9.2 %* could thereby be achieved, the relatively high value obtained thereby for the module FF (70 %) proves that the laser scribing technique used here is indeed applicable not only for amorphous silicon, but also for our thicker micromorph tandem cells. The application of the integrated electrical series connection concept based on laser-scribing can be considered to be a key factor for cost reduction in PV.

14.) *Infrastructure*: Over the past 3 years the photovoltaics and thin-film silicon laboratory of IMT has undergone very important developments. Until 1996 exclusively test solar cells of small areas (< 1 cm^2) could be realised on research-type equipment. Now, however, under the influence of more application-oriented projects and by stepwise addition of substantial new equipment, this has considerably changed: IMT will soon own and operate a comprehensive technological infrastructure allowing the development of amorphous, microcrystalline and micromorph solar cells from small test cells for research upto 30x30cm size modules for testing and demonstration.

It is to be wished that in Switzerland or at least elsewhere in Europe there will soon be an industrial company that takes serious interest in the micromorph concept - as is already happening at present in Japan. Pilot production of micromorph tandem cells would be the next step before mass production can be envisaged. This step is planned in Japan (Kaneka Corp.). All efforts have to be undertaken in Switzerland/Europe to keep up our present leading position in this sector.

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2. Starting-point and goals

Thanks to its pioneering work on the technology of Very High Frequency Glow Discharge (VHF-GD) deposition of thin-film silicon and thanks to the introduction of microcrystalline silicon as new optoelectronic absorber material, the Institut de Microtechnique (IMT) of the University of Neuchâtel has obtained international recognition in the field of plasma-deposited silicon thin-film solar cells. While in 1996 IMT was the only group which fabricated microcrystalline silicon single-junction and "micromorph" (microcrystalline/amorphous) tandem solar cells, there is now an "international community" of University groups and industries which consider, on one hand the "micromorph" tandem cell to be the most suitable candidate for the next generation of thin-film silicon solar cells and which, on the other hand, consider the VHF-GD technique to be the ideal fabrication process for obtaining increased deposition rates for amorphous as well as for microcrystalline silicon.

The main focus points of IMT in this project period (1997-99) were: to further explore the potential of microcrystalline silicon solar cells, to increase the deposition rate of this material and to obtain a better control and understanding of the whole "micromorph" deposition technology. The development and fabrication of amorphous solar cells by the hot-wire technique, a tool that had originally been included in the project proposal, was, on the other hand, abandoned because of lack of manpower.

The **goals of this project** are described in detail in the project proposal and **are summarized** in **short below.** (An overview of the achieved results during this project period is given in Appendix A). *The overall goal of the project was the achievement of a stable tandem cell efficiency of 12%.*

a) Optimization of microcrystalline silicon layers for single-junction cells

Sub-bandgap absorption $\alpha(0.8\ \text{eV}) \leq 5\ \text{cm}^{-1}$, $E_{02} \leq 1.15$ eV, absorption in the visible $\alpha(2.5\text{eV}) \geq 3\text{x}\alpha(\text{c-Si at } 2.5\text{eV})$, deposition rate in collaboration with the CRPP ≥ 10 Å/sec, low oxygen content $[\text{O}] < 2\text{x}10^{18}\ \text{cm}^{-3}$, $\mu^0\tau^0 = 3\text{x}10^{-7}\ \text{cm}^2\text{Vs}^{-1}$.

b) Improvement of the microcrystalline p-i-n solar cell

Open circuit voltage $V_{oc} \geq 500$ mV; Fill factor FF ≥ 70 %, $J_{sc} \geq 25\ \text{mA/cm}^2$, leading to a µc-Si:H cell efficiency $\eta > 9$ %.

c) Hydrogen dilution of amorphous films and cells

oxygen content $[\text{O}] \leq 1\text{x}10^{18}\ \text{cm}^{-3}$ for diluted layers, defect densities $N_{defect}(\text{dilution}) = {}^1/_2\ N_{defect}(\text{standard a-Si:H})$, amorphous p-i-n solar cells with stabilized V_{oc}-values of 1 V; furthermore if possible layers and cells with i-layers belonging to the transition region between µc-Si:H and a-Si:H with $N_{defect} = 3\ \text{cm}^{-1}$ and an energy gap of 1.4 to 1.5 eV.

d) Improvement of contact and reflector layers with respect to light-trapping properties

ZnO layers by sputtering and by the CVD technique with the properties: transmission > 85 % in the visible range at a sheet resistance of 2Ω/É, a Haze factor > 35 % and a deposition rate >5 Å/sec..

c) Improvement of the tunnel junction

Improvement of the contact interface layers between the top and the bottom of a tandem solar cell with the goal to enhance the V_{oc} and the J_{sc} of the entire tandem cell.

3. Main results

3.1 Introduction

Plasma-deposited hydrogenated microcrystalline silicon (µc-Si:H) was pioneered as a new photovoltaic thin-film material by our group in 1993/94. We were subsequently able to demonstrate that glass-TCO p-i-n type solar cells with reasonable efficiencies could be fabricated using this material. As the bandgap of µc-Si:H thin-films is identical to that of wafer-based crystalline silicon (c-Si), solar cells fabricated with µc-Si:H are – in contrast to those fabricated with hydrogenated amorphous silicon (a-Si:H) – receptive to the near infrared part of the solar spectrum. Microcrystalline silicon solar cells with their bandgap of 1.1 eV are, thus, an ideal partner for constituting tandems together with a-Si:H solar cells and their bandgap of 1.7 to 1.8 eV. We have named this new type of thin-film tandem solar cells the "**micromorph**" (**micro**crystalline/a**morph**ous) silicon solar cell.

In order to fabricate p-i-n type solar cells with satisfactory efficiency values, the individual intrinsic µc-Si:H layers used must be "midgap" (Fermi level in the middle of the gap): this is obtained by reducing the oxygen content. They also have to possess a "reasonable" electronic quality, i.e. a low defect density and high mobility x lifetime (µτ) product, so as to keep recombination losses low. We are able to monitor the defect density by measuring the sub-bandgap absorption, with such techniques as PDS (photothermal deflection spectroscopy) and CPM (constant photocurrent method). Microcrystalline silicon material with very low defect densities, i.e. layers with very low values of sub-bandgap absorption can be deposited, under certain conditions, by the VHF-GD (very high frequency glow discharge) technique introduced by our group. The mobility x lifetime (µτ)-product of µc-Si:H layers can be measured using a novel method introduced by our group and described in more detail below (see section 3.2.2 hereunder). However, one must realize that µc-Si:H layers are anisotropic and have a very complex microstructure. This means that the µτ-product (which is measured sofar in a direction perpendicular to the direction of the transport collection in actual solar cells) does not give complete information about layer quality. On the other hand, thanks to electron microscopy, we are now able to gain more insight into the microstructure of µc-Si:H layers. We hope, thus, to obtain tools and "deposition recipes" to produce even better µc-Si:H solar cells. We are already learning a lot more about our individual µc-SiH layers (see section 3.2.1 hereunder).

Our best microcrystalline solar cells are produced in the "superstrate" configuration (glass-TCO-pin structure) and have efficiencies between 8 and 9 % (see section 3.2.3 hereunder). The open circuit voltage values which were relatively low in our first cells (370 – 450 mV) have been increased to presently around 550 mV. Whereas our main work here has been, as mentioned, with the classical superstrate structure, we have also looked at the so-called "inverted" ("substrate" or "n-i-p" type) structure; the work done here was carried out within the framework of an European R&D project (see section 3.2.4 hereunder). Finally, we are trying to improve and complete the methods for analyzing entire µc-Si:H cells, with the hope of providing better tools for cell characterization. This part of our work was financed by the Swiss National Science Foundation (Schweiz. Nationalfonds).

As described in section 3.3 hereunder it is indeed possible to further improve amorphous solar cells w.r.t. stability and to the same time to adapt them to the specific requirements of micromorph tandems, i.e. to obtain a lower optical gap, i.e. a higher optical absorption coefficient and, thus, a higher short circuit current. It turns out that the best layers are made at higher temperatures (300 to 350°C). Further optimisation of these amorphous top cells, especially in the n-i-p configuration is underway. All this fine-tuning work is not possible without adequate tools for layer and cell analysis. This part of our work has been mainly financed by the Japanese government through the NEDO (New Energy Development Organisation). In fact our grant from OFEN / BfE during the period '97-99 would not have been sufficient to allow us to carry on effective research in this sector.

A very important part of all thin-film solar cells that is often decisive w.r.t. module performance and cost is constituted by the transparent contacts, i.e. by the transparent conductive oxide (TCO) layers. Because of limited funding only a strongly reduced program with a minimum amount of staff could be executed (see section 3.4). In order to progress further with our micromorph tandem cell concept, it becomes imperative to now intensify our efforts in this sector. One should take note of the fact that in certain other countries (Germany, Japan) ZnO materials research has become a priority topic and that specific R&D programs with financial volumes of several million U.S. dollars each, have been launched. Even though our financial possibilities at IMT are much more limited, we will certainly continue to take up this challenge, and we are very confident of achieving excellent results.

Patterning of thin film solar cells is an issue that cannot be avoided, if one wants to fabricate test cells with well-specified areas and certainly also if one wants to produce mini-modules for test and demonstration purposes. The problem of patterning microcrystalline, amorphous and micromorph tandem cells has been studied and partly solved by IMT with relatively expensive and slow laboratory methods (section 3.5 hereunder).

Section 3.6 finally describes the results obtained for full micromorph tandem cells and mini-modules. Small-area tandem cells with stabilised efficiencies between 11 and 12 % have been obtained. Finally, a micromorph mini-module was fabricated by IMT Neuchâtel with 9.2 % aperture area efficiency demonstrating thereby the full compatibility of our micromorph tandem cell concept with laser-scribing of monolithic (integrated) electrical series connection. This is an important first step towards micromorph module pilot fabrication.

In section 3.7 hereunder, the present technological and characterisation facilities for thin-film silicon solar cells built up, over a period of 15 years, at IMT Neuchâtel are described, with special emphasis on recent extensions. One may note thereby that in spite of very limited equipment funding, IMT has implemented one of the world's most complete and most adequate laboratories for further research on plasma-deposited thin-film solar cells.

3.2 Microcrystalline silicon (µc-Si:H)

3.2.1 Microcrystalline silicon layers – microstructure

During 1998 and 1999, we have started a systematic study, based on Transmission Electron Microscopy (TEM), of the microstructure of a series of microcrystalline samples deposited at variable silane concentrations in a VHF plasma reactor. TEM studies give us information about the shape, size and crystallographic orientation of the crystallites (or grains) in microcrystalline silicon, as well as on the presence of cracks or of amorphous silicon zones at the grain boundaries.

Indeed, w.r.t. characterization of the material produced at IMT we were sofar lacking reliable information about the shape, size and crystallographic orientation of the crystallites, as well as on the possible presence of voids or amorphous tissue between the grains. The aim of this part of our work is to gain a fundamental understanding of the relationship between the grain boundary density (which, in its turn, is related to the grain shape), the anisotropy of the structure and the electrical transport properties of layers.

A study of the size and shape of the silicon crystallites has been made using TEM, whereas a study of the average crystallographic orientation of the grains within the layer was conducted with X-Ray Diffraction (XRD) measurements. Atomic Force Microscopy (AFM) has been used for the observation of surface topography (roughness). Surface topography plays an important role in device performance, because of its effect on light scattering.

The main result of our study on a series of samples deposited at various silane/hydrogen concentrations in the plasma phase is the presence of a surprising variation of microstructure as a function of this parameter. We show in Fig. 1, as an example, the complex microstructure encountered in a sample deposited with 2.5% silane diluted in hydrogen.

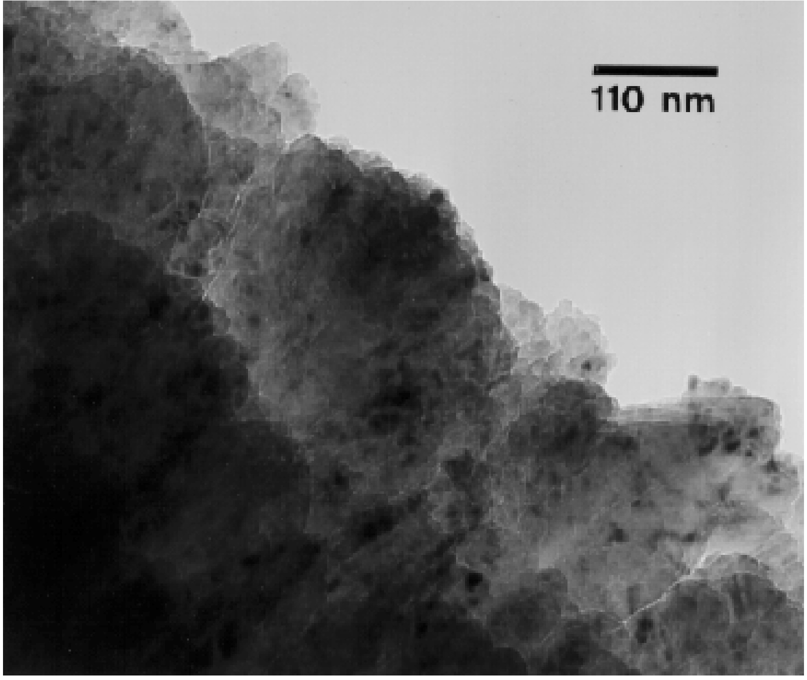

Fig. 1: Bright field cross-section micrograph of a 2.5% dilution sample. The observed surface is the growing surface. Pyramidal and "cauliflower-like" grains are typical of this sample. The pyramidal grains pointing out of the sample lead to a surface roughness of about 60 nm (peak to valley), whereas the "cauliflower"-like grains are much less rough.

A schematic picture of the evolution of the microstructure of intrinsic microcrystalline layers deposited at variable silane concentrations in the plasma gas phase is represented in Fig. 2.

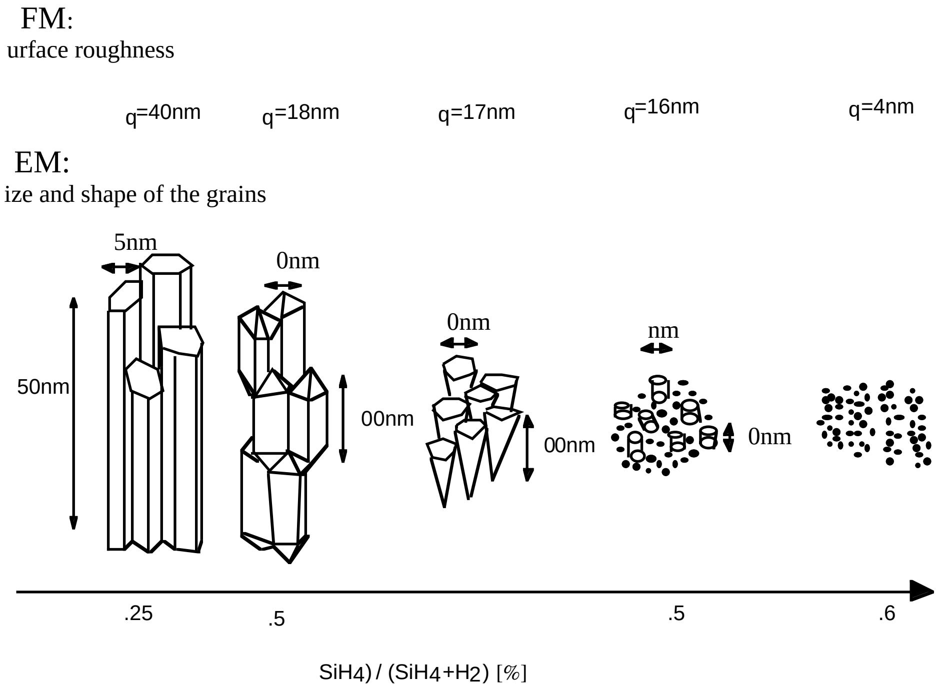

Fig. 2: Schematical picture of the evolution of the microstructure with increasing dilution of silane (SiH_4) in hydrogen (H_2). The small black dots represent amorphous material. The main information about microstructure obtained by each measurement technique is also indicated: S_q is the root mean square surface roughness as determined by AFM; the average dimensions and characteristic shapes of the crystallites determined by TEM are given on the drawings.

3.2.2 Electronic transport in microcrystalline silicon layers

The "device-quality" µc-Si:H layers produced by our laboratory and successfully incorporated into p-i-n and n-i-p solar cells, as intrinsic, photovoltaically active layers, are characterized by the following general properties:

(a) They have a "midgap" nature
(b) They have an enhanced effective optical absorption in the near infrared
(c) They have a high degree of grain boundary defect passivation
(d) Their electronic transport properties are similar to those of a-Si:H

A broad set of characterization techniques has been applied to measure the opto-electronic properties of these layers (see Tab. I).

In particular, a close collaboration with the group of Dr. M. Vanecek in Prague has allowed us to gain better understanding on the relationship between the light-scattering effects (related to the surface roughness of the as-grown layers) and the short-circuit current of the solar cell. There are, however, still several unsolved questions especially w.r.t. the transport anisotropy; these have now to be further investigated. A part of the work here was carried out thanks to a parallel Swiss National Science Foundation project which deals with the more basic aspects of our research (see e.g. [Goerlitzer, Ph.D. 1998]). Let us now look at some further insights that have been obtained w.r.t. the four topics mentioned above.

Table I: Measurement techniques applied to our series of microcrystalline silicon layers for the characterization of various transport properties.

	Measurement technique	Physical parameter evaluated	Experimental correlation with solar cells performance
Optical properties	Absolute Constant Photocurrent Method (A-CPM)	Interband absorption, surface light scattering, defect absorption	Short-circuit current, efficiency
Electronic transport properties	Photoconductivity (σ_{photo})	Lateral coplanar majority carrier $\mu\tau$	efficiency
	Steady-State Photocarrier Grating (SSPG; ambipolar length L_{amb})	Lateral coplanar minority carrier $\mu\tau$	efficiency
	Surface Photovoltage (SPV)	Transverse minority $\mu\tau$	efficiency

(a) Midgap character of layers and oxygen content

Our μc-Si:H layers have a "midgap" nature, i.e. their Fermi level is near the middle of the gap; this shows up, in individual layers, by a low value of dark conductivity σ_{dark} (typically 10^{-7} $\Omega^{-1}cm^{-1}$) and a high value of the activation energy E_{act} (typically 0.5 eV). As drift (and not only diffusion) play an important role for carrier collection in p-i-n-type cells, the midgap nature of the i-layer is necessary to sustain an electrical field, and thus to produce efficient cells.

While characterising the transport properties of individual layers, we were, however, faced with a major surprise: even if our as-deposited layers, now have little residual oxygen, they are very rapidly subjected to a postoxidation process, which leads, for some samples, already within hours to a drastic increase in the dark conductivity, i.e. to a shift of the Fermi level towards the conduction band. Detailed observations relating to this postoxidation process have been published [1997, ref 32]: oxygen content (measured by SIMS) rises to levels around 5×10^{20} atoms/cm^3 at the surface of the samples after several months. Furthermore, the extent and nature of the postoxidation process seems to depend on the specific nature of the individual μc-Si:H layer (i. e. on the deposition conditions). On the other hand, complete p-i-n or n-i-p cells do not show any change in characteristics that could be attributed to postoxidation (see section 3.2.3 for further details). Possibly, this is partly due to the sealing effect of the contact layers (metal/transparent conductive oxide/doped layers). In a first approach, we thought that we should develop techniques to protect our individual layers before we can pursue the study of their transport properties. However, in a next step, we were able to show that this is not necessary: by introducing the parameter *b* (which indicates the position of the Fermi level (E_F); see section (d) hereunder), we can represent our transport measurements in such a way that the problem of postoxidation no more affects their interpretation.

(b) Enhancement of optical absorption in the near infrared and in the visible spectral region

Our µc-Si:H layers have a higher "effective" optical absorption coefficient in the near infrared, as compared to crystalline silicon (c-Si); this is easily seen in optical absorption measurements performed by PDS (Photothermal Deflection Spectroscopy) and especially in the absorption curves measured by the group of Dr. M. Vanecek in Prague with the more sensitive CPM (Constant Photocurrent Method). The value of the absorption coefficient is specially important (in the context of solar cells) around 1.5 to 1.8 eV, as in this range only an enhanced absorption coefficient allows one to absorb enough of the sun's spectrum within a few microns of i-layer thickness (2 to 3 µm can then become sufficient to absorb a large part of the solar spectrum, and to photogenerate enough carriers so as to obtain high short circuit currents). Thanks to work done by Dr. M. Vanecek and his group - in collaboration with us and on our µc-Si:H layers - one can now identify the likely reason for the enhancement of the effective absorption coefficient (by a factor of about 3): it is (mainly) optical scattering by the rough surface and by the columnar structure of our µc-Si:H layers. Fig. 3 shows typical results.

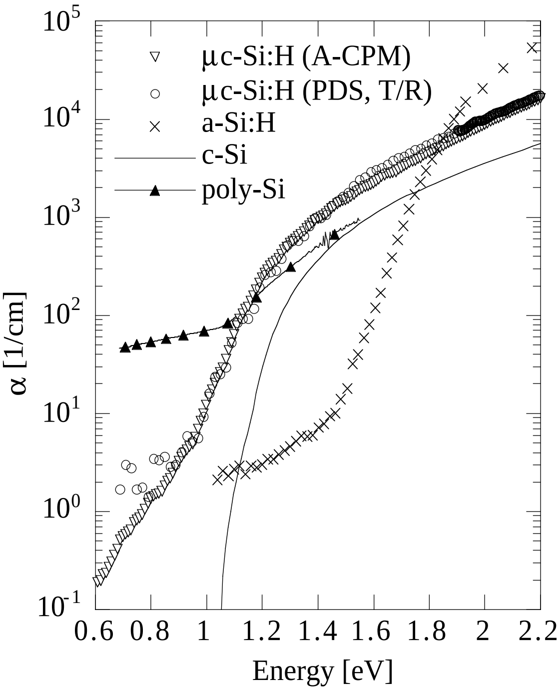

Fig. 3: Optical absorption of "device-quality" µc-Si:H layers as measured by absolute - CPM (A-CPM) and PDS. For comparison, the absorption curves for a-Si:H, c-Si and poly-Si are also shown. Note that µc-Si:H shows an enhanced absorption as compared to c-Si and also that the defect-connected absorption at 0.8 eV lies here about an order of magnitude below the absorption limit of PDS (here about 2 cm^{-1}). In contrast, usual poly-Si (without defect passivation by hydrogen) has a high defect connected absorption at 0.8 eV.

(c) Defect densities of the intrinsic layers

Our µc-Si:H layers have a high degree of grain boundary defect passivation. This can be seen by the very low values (< 0.1 cm^{-1}) of sub-bandgap absorption (around 0.8 eV) as measured by CPM and connected for surface roughness effects. This passivation, which reduces carrier losses, is an essential requirement for making p-i-n or n-i-p cells with satisfactory collection. Such low values obtained for the densities of midgap defects means a relatively high lifetime "τ", as these defects act as recombination centers. However, the exact nature of the defects and their precise effect on the transport properties has yet to be clarified. Note that the value of the actual defect density in µc-Si:H layers is not yet known precisely, since we need a calibration value to establish the link between optical defect absorption and defect density.

(d) Electronic transport properties

In contrast with the encouraging results already obtained for entire µc-Si:H solar cells, very little is known so far on the electrical transport properties of this novel photovoltaic material.

However, it would indeed be useful to know more about electrical transport and carrier collection. It would, in fact, be especially important to find a parameter that is indicative of the "electronic quality" of individual μc-Si:H layers.

In order to characterize transport and collection, we need to access not only the densities of recombination centers (and thus indirectly the lifetime "τ"; see section (c) above), but we want to measure the entire mobility × lifetime ($\mu\tau$) product. This $\mu\tau$-product is, in fact, the essential quantity that influences drift and diffusion lengths, and, thus, also collection in p-i-n or n-i-p cells. In order to obtain information about the $\mu\tau$-product, we have performed, in a similar manner as for a-Si:H, measurements of the photoconductivity (σ_{photo}; giving access to the $\mu\tau$-product of majority carriers) and of the ambipolar diffusion length (L_{amb}; giving access to the $\mu\tau$-product of minority carriers); the latter was measured by the SSPG technique [Ritter 1987, Sauvain 1992], which was shown to be still valid for the case of μc-Si:H [Goerlitzer 1996].

Because of the postoxidation of the μc-Si:H layers (as discussed in section (a) above), an effect that strongly depends on deposition conditions, the position of the Fermi level (E_F) is consequently changed and the interpretation of the transport properties can be problematic [1997 ref 32]. In order to overcome this problem, we introduced the parameter b, which reflects the position of E_F, and which is defined in the same way as for a-Si:H [Sauvain 1992, 1997 ref 21]. It is experimentally deduced from σ_{photo} and L_{amb}. It is then possible to directly compare electronic transport in a-Si:H and in μc-Si:H, at a chosen value of b, and to compare different μc-Si:H layers between themselves, since b takes into account the shift in E_F due to postoxidation. The outcome of this study was that the behaviour of the $\mu\tau$-products are similar in μc-Si:H and in a-Si:H [1999 ref 7]. Moreover, electronic transport (i.e. $\mu\tau$-products) in μc-Si:H are only slightly better than in a-Si:H. Evaluation of the $\mu\tau$-products by Time-of-Flight measurements gives, by the way, similar results [1997 ref 32]. These similarities suggest that electronic transport in μc-Si:H layers is governed by the amorphous phase present at the grain boundaries of μc-Si:H. The main goal was, in fact, to find a parameter related to the "electronic quality" of individual μc-Si:H layers, in such a way that it can link the material quality with solar cell performance (as far as the latter is limited by the intrinsic layer). We claim to have found such a parameter by extending the approach already introduced by our group for a-Si:H to the case of μc-Si:H. It turns out that this extension works surprisingly well. The approach consists of defining a "normalised" mobility × lifetime product, $\mu^0\tau^0$ [Beck 1996] (based on the recombination model for a-Si:H [Hubin 1995]), that is experimentally deduced from σ_{photo} and L_{amb}, and which is independent of E_F of the considered sample. The parameter $\mu^0\tau^0$, as measured in individual μc-Si:H layers, was compared with efficiencies of n-i-p solar cells incorporating the same intrinsic μc-Si:H layers as the photovoltaically active layer. As Fig. 4 indicates, the $\mu^0\tau^0$ product seems to show, even in μc-Si:H, a rather good correlation with the cell efficiency. A number of problems remain still unsolved regarding the understanding of transport and collection in μc-Si:H. The most striking problem is the fact that in individual layers, the measured electrical transport properties are similar in μc-Si:H and a-Si:H, but that in solar cells the collection is far better for μc-Si:H ($d = 3\ \mu m$) than for a-Si:H ($d = 0.3\ \mu m$). Another enigma is the fact that the transport model for a-Si:H works surprisingly well for the case of μc-Si:H layers but that the structure of these layers is clearly different due to the presence of the crystallites. Indeed, we still have a lot of further work to do before we can understand transport and collection in μc-Si:H.

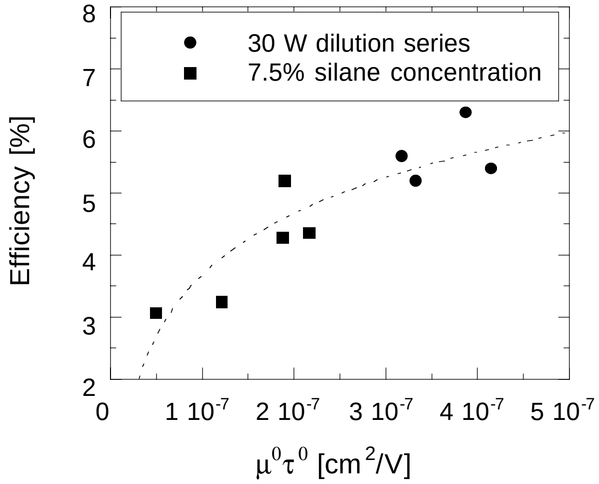

Fig. 4: Cell efficiencies as a function of the i-layer $\mu^0\tau^0$ product, for a power series (at 7.5% silane concentration) and a dilution series (at 30 W). The dashed curve indicates the observed (or "suspected") correlation for μc-Si:H samples.

3.2.3 Microcrystalline p-i-n solar cells

One of the main subjects of this 3-year project was the exploration of the further efficiency potential of our new microcrystalline silicon material. Especially, the improvement of the open circuit voltage of μc-Si:H single-junction solar cells was a major challenge to be taken on, because the efficiency of the micromorph tandem cells is directly linked with the V_{OC} of the μc-Si:H bottom cell. The status at the end of 1996 was given by μc-Si:H cells with an open circuit voltage of around 440 mV, whereas "theoretical predictions" claimed that open circuit voltages over 500 mV would be impossible to attain with this grainy material. Nevertheless, by further optimisation of our deposition technology, we were able to increase the V_{OC}-values of our microcrystalline silicon cells, to well over 500 mV (a main goal of this project).

Table II shows indeed that V_{OC}-values over 500 mV combined with satisfactory fill factors (FF) are obtainable for μc-Si:H single-junction solar cells. Sofar, a cell efficiency of 8.5 % could be achieved as maximum value by our group for an entirely microcrystalline silicon p-i-n solar cell. Our experiments even show that open circuit voltages of almost 600 mV can be obtained with microcrystalline absorber material. Hence, it seems that there is a realistic potential for obtaining usable microcrystalline silicon cells with open circuit voltages of around to 560 to 580 mV and reasonably high fill factors. Further extensive work and further optimisation, especially with respect to light-trapping properties, will be necessary in order to tap the full efficiency potential of the μc-Si:H solar cell device. In the next step we have also to obtain a better reproducibility of such high-V_{OC} cells in order to incorporate them into entire micromorph cells.

Table II: Results achieved in this project for μc-Si:H single-junction p-i-n solar cells.

η [%]	8.3	7.7	8.1	**8.5**	7.3	5.7	6.3	6	5.6	4.1
J_{SC} [mA/cm^2]	25.2	21.5	23.2	22.9	20.2	15.9	17.5	16	14.8	15.5
FF [%]	68.2	71.1	68	69.8	66.7	65.2	64	66	64.5	38.7
V_{OC} [mV]	**483**	**503**	**512**	**531**	**539**	**550**	**560**	**569**	**582**	**689**

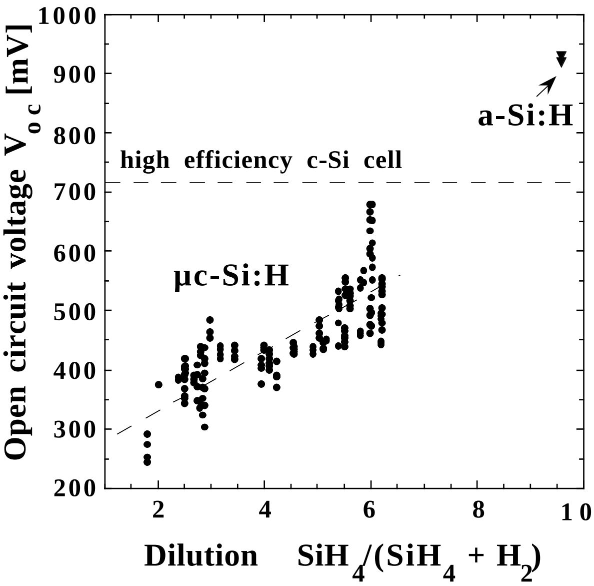

Fig. 5: V_{OC}-values for a large number of different p-i-n µc-Si:H solar cells in function of the silane to hydrogen dilution parameter ($[SiH_4]/[SiH_4+H_2]$).

From a more basic point of view, one has to wonder how the different microcrystalline films as described in section 3.2.1 behave in full solar cell devices. The performance of an individual µc-Si:H layer within an entire p-i-n device may be affected not only by its own complex microstructure but also by the electronic and optical properties of other layers, and even further by contact problems. A decisive influence on the ongrowing structure certainly originates also from the first initial doped layer (i.e. from the "seeding" layer); in the case of the p-i-n solar cell structure, this is the p-window layer. Doped µc-Si:H p-type layers can, however, be prepared under very different conditions; furthermore, the exact properties of all films depend on the substrates used and on the underlying layers. This means that films on bare glass substrates (as used sofar for the samples analysed by TEM, mentioned above) may have different structural features than films deposited (in actual cells), under the same conditions, on a glass/TCO substrate covered by a p-type doped µc-Si:H window layer. This is especially decisive in the case of the p-i-n structure, because the properties of the photovoltaically important p/i-interface are formed at the beginning of the nucleation zone.

At the present stage we are not able to give a full picture of the microstructure-related behaviour of our µc-Si:H solar cells: Various parameters such as light-trapping, layer thicknesses, structural inhomogeneities vs. thickness were not always the same, masking, thus, the effects due to a variation in the microstructure of our intrinsic absorber layer. However, one may already now observe a certain confirmed tendency for the open circuit voltage V_{OC} of our single-junction µc-Si:H cells: In Fig. 5, the V_{OC}-values of a large number of p-i-n cells deposited under a wide range of different deposition conditions are plotted as a function of the silane dilution parameter of the incorporated intrinsic µc-Si:H absorber layer. All cells, except for the amorphous one (deposited at a dilution of 9.5 %) show a clearly enhanced infrared response in the region above 750 nm and therefore can be classified as being microcrystalline. There is a general trend for a V_{OC} to increase with decreasing silane dilution, as one approaches the transition to amorphous silicon, which is located somewhere between 7 and 8 %.

In order to obtain more insight into the complex structure of the grains and its relation to solar cell properties, further broad-based TEM investigations have now to be performed directly on different types of µc-Si:H cells: We hold that this is the best way to obtain a better understanding of the structure-related effects in microcrystalline solar cells.

Chemical stability / Postoxidation study

As reported by us [1997 ref 32] and by other groups, systematic studies on isolated µc-Si:H films deposited on glass substrates have revealed a strong increase in dark conductivity, by a factor of 1000, after 40 days of air exposure; obviously, postoxidation takes place, leading to a chemical deterioration of the layers, accompanied by an increase in dark conductivity. Our initial apprehension was that entirely µc-Si:H solar cells may also be subject to such chemical instability; this was, however, fortunately disproven: Fig. 6 shows the dramatic increase observed for the dark conductivity of a thin film, compared with the corresponding curve for the efficiency of a glass-TCO-p-i-n solar cell with an intrinsic layer deposited using the same parameters as for the film. As already observed on other solar cells in the past, the full p-i-n solar cell turns out to be completely stable. We are led to assume that the phosphorous-doped n-layer as well as the whole back contact protect the cell efficiently from postoxidation.

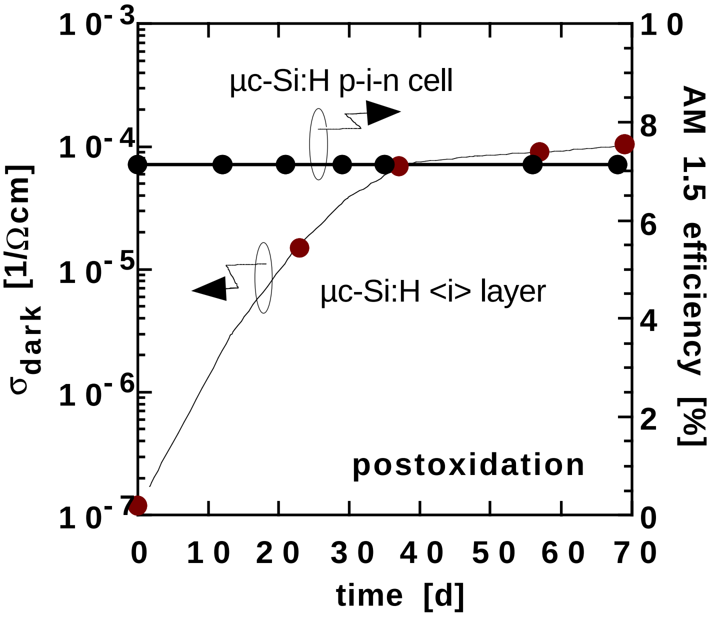

Fig. 6: Comparison of an intrinsic µc-Si:H film (dark conductivity) and of the corresponding p-i-n solar cell (efficiency), in function of air exposure time after deposition.

3.2.4 Microcrystalline n-i-p solar cells

The research work on "inverted" µc-Si:H silicon solar cells (n-i-p type) was mainly carried out in the context of our **E.U. project NEST (New and Enhanced Silicon Thin-film solar cells**); its results are therefore described in the annual and final reports of that project (Project Nr. OFES 96.0340).

The three-year E.U. project period started with an exploration of suitable conditions to produce inverted (n-i-p) solar cells. One aim was to increase deposition rates from the range far below 1 Å/s towards 10 Å/s by using the VHF-GD at an excitation frequency of 130 MHz.

In order to study µc-Si:H silicon, several series of thin-films were deposited on glass and characterized: By increasing the plasma power, at the fixed dilution ratio of 7.5 % silane/(silane+hydrogen), we observe a morphological transition from a-Si:H to µc-Si:H (as confirmed by optical and crystallographic measurements and Raman spectroscopy), as well as an increase in deposition rate (up to 16 Å/s in this case). Crystallographic properties and solar cell efficiencies vary thereby in a significant manner. For this study, solar cells were deposited in the metal-n-i-p configuration. The results for solar cell performance and deposition rate in function of VHF-power are shown in Figs. 7 and 8:

We observed a correlation between the photocurrents for these n-i-p cells with the preferential growth of the i-layer crystallites in the 220 direction (observed by X-ray diffraction). One should note that the rough surface morphology which gives rise to light trapping by scattering has, indeed, a direct impact on the photocurrent of the cells.

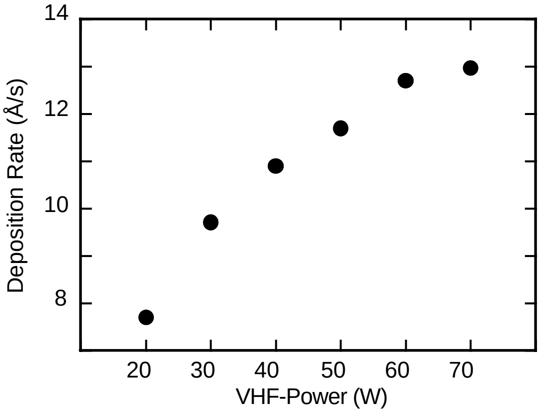

Fig. 7: Deposition rate in function of power at constant dilution of 7.5% silane in hydrogen.

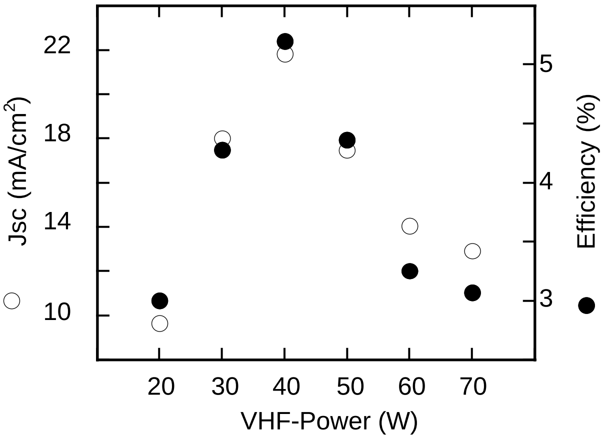

Fig. 8: n-i-p cell parameters obtained in function of VHF power at constant dilution, as on the left. Note the maximum conversion efficiency of 5.2 % is obtained at a deposition rate of 10.9 Å/s.

As an alternative method to obtain high deposition rates for µc-Si:H silicon, we investigated also a combination of the hot-wire (HW) and VHF techniques. We found a considerably increase for the deposition rate compared to the conventional VHF technique; deposition rates up to 25 Å/s have then been obtained with good material properties. This material has been integrated into a n-i-p cell, but resulted (in a first, brief exploratory phase) in yet rather low performances (V_{oc}=484 mV, FF=48%, J_{sc}=6.7 mA/cm^2 what gives η =1.5%).

Choice of substrates

For convenience, first inverted µc-Si:H silicon cells were deposited on metallic substrates (stainless steel or aluminum) or on Asahi type substrates (a high-quality Japanese TCO-coated type of glass).

Reduction of cell thickness can only be achieved with highly reflecting back reflector substrates. The development of these back reflectors was done within the NEST project by the research group in Jülich, and substrates with reflectors were then tested in Neuchâtel by depositing thereon full n-i-p cells. The best substrates are made with a chrome/silver/ZnO structure deposited on both, stainless steel and glass. Note, that substantial surface roughening of the ZnO was obtained with a wet chemical etch, obtaining, thus, the desired diffuse reflector.

High deposition rates

The motivation to increase deposition rates of the absorber layer (i-film) is similar to the motivation for using thinner µc-Si:H cells: The throughput must be high in a solar cell producing unit, e.g. a reduction of total production time is, in this respect, a key issue. Our single-junction n-i-p microcrystalline silicon cells could be further improved in the way of retaining the high deposition rates (around 10 Å/s) while generating substantially more photocurrent or open circuit voltage with thinner cells; two recently obtained solar cells with good performances may be outlined here:

- A first solar cell with 6.9 % conversion efficiency (V_{OC}=0.481 V, FF=67%, J_{SC}=21.5 mA/cm^2), deposited at a rate of 10 Å/s (4 µm thick)
- a second solar cell with improved near-IR response thanks to optimized interfaces and a highly scattering back-reflector, with a conversion efficiency of 7.8% (J_{sc}= 24 mA/cm^2, V_{oc}=445 mV, FF=70%), grown at 7.4 Å/s **with 2 µm thickness**.

Based on the results above, a full n-i-p-n-i-p micromorph tandem with 11.2 % initial efficiency (V_{oc}=1.4 V, FF=71%, J_{sc}=11.3 mA/cm^2) could be fabricated (note the high open-circuit voltage). The intrinsic µc-Si:H layer of 2 µm thickness was deposited at 6.8 Å/sec.

The remarkable achievements described above show the feasibility of obtaining reasonable n-i-p-n-i-p micromorph devices under the given circumstances (no double chamber deposition system available for doped and intrinsic layers; bottom and top cell of the tandem cell were deposited in two different, isolated systems). Thanks to the good back reflectors obtained from Jülich, such results were made possible within this project. A serious effort should be undertaken at IMT to develop equally good n-i-p back reflectors (on suitable substrates).

3.3 Amorphous silicon (a-Si:H)

3.3.1 Recent amorphous silicon technology developments

Hydrogenated amorphous silicon (a-Si:H) remains an extremely important and promising material for the whole field of thin-film silicon solar cells.

A large variety of solar cells for concrete applications can already be produced at economically viable prices (these range today from low-wattage solar cells for calculators and watches to large modules for façade and roof applications in the energy sector and will in future include light-weight space cells for satellites).

Amorphous silicon (a-Si:H) unfortunately suffers from a reversible initial degradation effect: this is the so-called "Staebler-Wronski effect (SWE)", or "light-induced degradation effect". Whereas it has sofar been impossible to overcome this effect, it is, on the other hand, quite feasible to reduce the extent of SWE-induced losses in a-Si:H based solar cells. To obtain such a reduction, two issues have to be simultaneously addressed: an individual intrinsic a-Si:H layers with better electronic quality in the degraded state (i.e. after the initial SWE process) and, at the same time, a-Si:H layers with a slightly lower bandgap, i.e. with higher optical absorption in the useful range. With such newly optimised layers it becomes possible to fabricate a-Si:H solar cells in p-i-n and n-i-p configuration that are thinner (i.e. less susceptible to losses due to the SWE) and still have sufficiently high short-circuit current densities J_{sc}. These cells are of interest both as single-junction solar cells as well as top cells within the "micromorph" tandem structure (see Tab. III).

Table III: Overview of the adequate optical gap as required for different solar cell configurations.

High E_{gap} (~1.8 eV)	Low E_{gap} (~1.6 eV)
• Top cell of amorphous tandem cell (a-Si:H/a-Si:Ge:H or a-Si:H/a-Si:H)	• Single junction solar cell • Top cell of “micromorph” tandem cell • Bottom cell of a-Si:H/a-Si:H tandem cell

The development of such novel layers is based on the utilisation of new tools for precise characterisation (the $\mu^0\tau^0$ product method developed by our group) and for rapid layer degradation (accelerated light-induced degradation based on a combination of laser pulses and of continuous bias light, also developed by our group). Thanks to the VHF-GD (Very High Frequency Glow Discharge) method and to a systematic optimisation of deposition conditions, excellent layer properties could be obtained by us. The results (for VHF a-Si:H layers) being at least as good as those obtained by the more "exotic" technique of "Hot Wire deposition" (which is probably difficult to master in large-area manufacturing situations), we have, at IMT Neuchâtel, abandoned the Hot Wire (HW) method and concentrated our efforts on VHF-GD.

The main solar cell work sofar has been with p-i-n type solar cells (section 3.3.3), but we are increasingly using n-i-p type solar cells (section 3.3.4); this is because this type of solar cells allows for the use of a great variety of substrates (incl. stainless steel, aluminum and polymers). n-i-p type a-Si:H solar cells also permit greater design flexibility, w.r.t. deposition conditions, especially w.r.t. the use of higher deposition temperatures T_{dep}. (It has now become quite evident that high T_{dep} leads to layers with higher optical absorption and even better stability). The work in this sector would not have been possible without the financial support of the **Japanese New Energy Development Organisation (NEDO).**

3.3.2 Amorphous silicon intrinsic layers with increased stability and higher optical absorption

3.3.2.1 Choice of deposition technique

Several deposition techniques have been explored in order to obtain intrinsic materials with improved stability against light-induced degradation (i.e. to obtain a material with a high value of $\mu^0\tau^0$ product after accelerated degradation). Three of them are based on the PE-CVD process, these are DC, RF (13.56 MHz) and VHF (70MHz) techniques, one of them was based on catalytic decomposition of gas (Hot-Wire, HW).

3.3.2.2 Moderately high deposition temperature without H_2-dilution

Within the framework of a Ph.D. thesis (Rainer Platz), our in-house and various external amorphous silicon materials were compared w.r.t. their use as top cell i-layer materials for micromorph tandem cells: Fig. 9 shows the results obtained for the "quality parameter" $\mu^0\tau^0$ (characterising the quality of electronic transport within individual intrinsic layers) after accelerated light soaking (i.e. in the degraded state): these results are given for three different deposition methods, i.e. for VHF-deposition, DC-deposition and Hot Wire deposition; in all three deposition methods reported on in Fig. 10, silane was used as source gas and no hydrogen dilution was employed. One clearly sees that one of the most important parameters controlling amorphous silicon layer quality (in the case of otherwise optimised deposition parameters) is the substrate temperature.

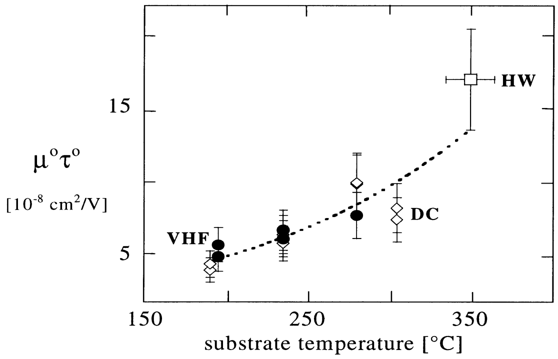

Fig. 9: $\mu^0\tau^0$-product in the degraded state for DC- and VHF-deposited films as a function of the deposition temperature. All samples are deposited from an undiluted SiH_4 plasma. For comparison we added the best value reported by Ziegler (in his Ph.D. thesis at the University of Neuchâtel) for a Hot-Wire deposited sample without H_2 dilution. Error bars indicate an estimated experimental error of ±20 %.

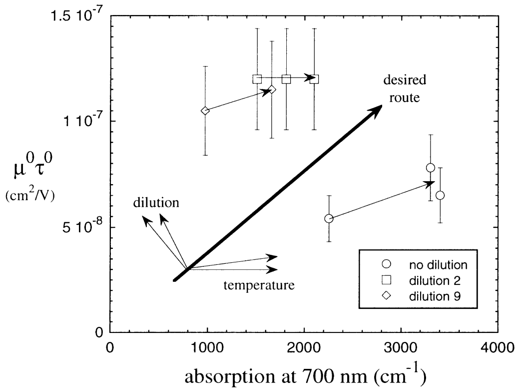

Fig. 10: Degraded state $\mu^0\tau^0$-parameter for a-Si:H films deposited by VHF-glow discharge at 70 MHz at various hydrogen dilution ratios. For no dilution and dilution 2, the substrate temperature setpoints are 220°C, 270°C, and 330°C, while for dilution 9 they are 220°C and 270°C.

3.3.2.3 Moderately high deposition temperature combined with H_2-dilution

Figure 10 shows results for VHF-deposition only, but now including hydrogen dilution, the hydrogen dilution ratio being defined here in the usual way as the ratio of hydrogen gas flow to total (silane + hydrogen) gas flow, i.e. $[H_2]/([SiH_4] + [H_2])$. Here, the optical absorption coefficient (α) at 700 nm wavelength is also plotted. One sees that a combination of increased substrate temperature and a low value of hydrogen dilution leads to the best combination of a high $\mu^0\tau^0$-product and a high value of α. (A high value of α allows one to obtain a sufficiently high short-circuit current with a thin i-layer and that is very beneficial for solar cell performance in the degraded state. The goal we should here keep in mind, if we want to obtain the highest value of short-circuit current density J_{sc} in the degraded state, is to obtain the highest possible product α times $\mu^0\tau^0$).

Concerning the PE-CVD techniques (DC, RF and VHF), we can conclude that the hydrogen dilution method substantially improves the stability of the material. However, each technique behaves differently w.r.t. the hydrogen dilution ratio (see Figs. 11 and 12).

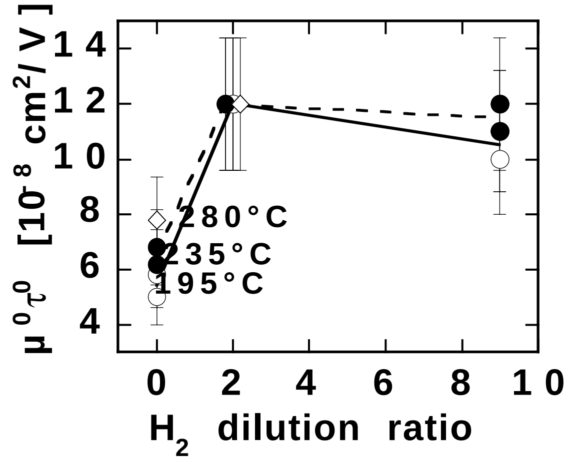

Fig. 11: $\mu^0\tau^0$-product in the light-soaked state as a function of the H_2 dilution ratio for VHF-deposited samples: T_s = 195, 235 and 280°C.

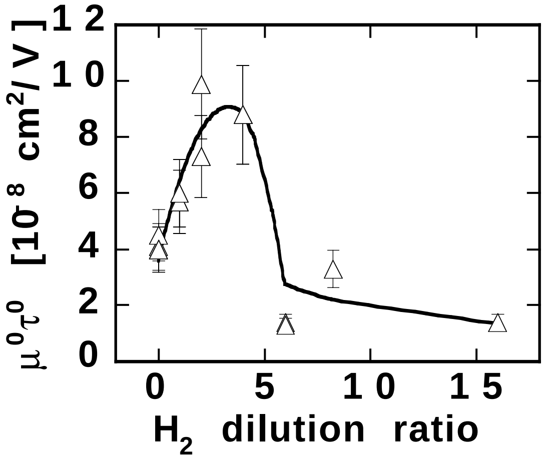

Fig. 12: $\mu^0\tau^0$-product in the light-soaked state as a function of the H_2 dilution ratio for DC-deposited samples. Substrate temperature T_s = 190°C.

3.3.2.4 Combined effect of the deposition temperature and H_2-dilution, second study

Based on the experience gained in 1997, a second study was undertaken in 1998. We deposited hydrogen dilution series at two different temperatures (300 and 350°C). The results are: First, it was confirmed that hydrogen dilution substantially improves the stability of the material (evaluated with the quality parameter $\mu^0\tau^0$ after our accelerated degradation method). Secondly, similar to the case of a-Si:H deposited without hydrogen dilution, the optical gap (evaluated from Tauc's plot) of diluted films is also reduced (i.e. the optical absorption coefficient increased) with increasing deposition temperatures. Finally, by choosing the appropriate hydrogen dilution ratio, the stability of the material can be further improved, even at 350°C. Table IV summarises results obtained in 1998 and gives a comparison with materials provided to us by other groups.

Table IV: Quality parameter $\mu^0\tau^0$ evaluated (in 1998) after our accelerated degradation procedure, as well as the optical gap of different materials deposited by our group (IMT) and by Prof. C.R.Wronski's group (Pennsylvania State University); one can observe the general tendencies that hydrogen dilution improves the stability of a-Si:H and that the optical gap decreases with increasing deposition temperature. Remember: What is desired for our micromorph tandem cells is a low value of the optical gap in the i-layer of the amorphous top cell.

Laboratory	Dep. parameters	$\mu^0\tau^0$ in degr. state [cm^2V^{-1}]	Optical gap [eV]
IMT	PE-CVD, standard 220°C	0.9×10^{-7}	1.75
IMT	PE-CVD, 250°C, dil. 2	1.9×10^{-7}	1.72
IMT	PE-CVD, 300°C, dil. 2	1.6×10^{-7}	1.7
IMT	PE-CVD, 350°C, dil. 2	2×10^{-7}	1.68
IMT	H-W, 350°C, dil. 1	1.6×10^{-7}	1.68
Pennsylvania (Wronski)	PE-CVD, standard 250°C	1.3×10^{-7}	1.73**
Pennsylvania (Wronski)	PE-CVD, 250°C, dil. 10	2.1×10^{-7}	1.76**

*** evaluated by Wronski et al.*

3.3.2.5 Amorphous silicon layers deposited by the Hot-Wire method

Our investigations on hot-wire deposition were based on first interesting results regarding stability and light-absorption in the years before the reporting period. In order to correctly assess the future potential of various deposition techniques, the method of accelerated light-soaking by pulsed laser illumination was further refined and applied to the different kinds of i-layers. (The solar cells fabricated by hot-wire are described in the following section.) The results are shown in Tab. V which recapitulates the quality parameter $\mu^o\tau^o$ after degradation as well as the absorption coefficient for red light for the different kinds of optimised materials. One can conclude that the hot-wire layers possess indeed an interesting combination of high stability (i.e. high value of degraded $\mu^o\tau^o$) with a high optical absorption coefficient. (In 1999 comparative results were also obtained for the plasma-CVD layers within our NEDO project see Table IV.)

Table V: Comparison of optimised layers produced with different deposition methods w.r.t. stability ($\mu^o\tau^o$ after degradation), and absorption coefficient for red light (values obtained in 1997, i.e. earlier than the values presented in Table IV)

process	T_S [°C]	hydrogen dil. [H_2/ (H_2+SiH_4)]	$\mu^o\tau^o$ degraded [10^{-7} cm^2V^{-1}]	absorption coef. at 633 nm [10^4 cm^{-1}]
plasma CVD	240	0	0.6	1.7
plasma CVD	240	2	1.2	1.4
plasma CVD	290	0	0.8	1.9
plasma CVD	290	2	1.2	1.6
Hot-Wire	290	-	1.4	1.8
Hot-Wire	320	-	1.8	2.0

3.3.2.6 Solar cells deposited by the Hot-Wire method

In our laboratory, we have obtained the most stable material by this deposition method for temperatures around 340°C (see above). However, even this substrate temperature seems too high for the incorporation of such layers into a p-i-n solar cell: The difficulty is mainly due to the diffusion of impurities into the intrinsic layer, near the p/i interface. Such a diffusion generally occurs for temperatures above 250°C. To avoid the problems introduced by deposition at higher temperatures, we decided at Neuchâtel to start off by incorporating, into a p-i-n structure, "device quality" hot-wire intrinsic layers obtained at the relatively moderate temperature of 270°C. The cell results of our group and of two other research groups are shown in Table VI.

Table VI: Summary of results obtained by the three more active laboratories working on amorphous silicon solar cells with intrinsic layers deposited by Hot-Wire. To reduce the problem of impurity diffusion, NREL adopts the inverted structure (n-i-p deposited on Stainless steel); the relative degradation obtained by them is quite low (~10 %), but the absolute value after degradation is still significantly lower than values for standard amorphous solar cells.

	NREL	**Kaiserslautern**		**IMT**
cell structure	n-i-p	p-i-n	p-i-n	p-i-n
T_{dep} [°C]	370	275	200	270
FF (initial)	**0.605**	**0.62**	**0.68**	**0.704**
V_{oc} [V] (initial)	0.88	0.8	0.87	0.838
J_{sc} [mA/cm^2] (initial)	12.8	13.7	16.8	14.85
$\eta_{initial}$ [%]	6.8	6.8	9.95	8.76
$\eta_{degraded}$ [%]	6.1	-	-	5.9

Conclusion: Due to the high substrate temperature levels involved, and to various specific technological difficulties associated with the hot wire deposition technique, the implementation of improved p-i-n solar cells, that could actually incorporated into micromorph tandem cells, appears to be still rather far away. Therefore, further investigations on the hot-wire method were stopped. On the other hand, plasma deposition at different substrate temperatures was to continued.

3.3.3 Amorphous silicon p-i-n solar cells

Micromorph tandem cells on glass constitute the main technology route pursued at IMT Neuchâtel. In this tandem cell, the amorphous silicon top cell is a p-i-n cell deposited on TCO-coated glass (a so-called ‘superstrate’ cell).

3.3.3.1 Hydrogen dilution (at standard deposition temperature) in p-i-n solar cells

In 1996, a clear efficiency improvement was obtained in our group for amorphous silicon solar cells thanks to the hydrogen dilution method. In fact, the hydrogen-diluted materials were found to have an improved stability, combined with an increased bandgap, leading to p-i-n cells with a better stability, and a high V_{oc} (880-900 mV). Thanks to the use of VHF-plasmas we even obtained relatively high deposition rates. However, due to the increased bandgap, the light absorption is decreased in these materials; thus, the cell yields a lower current. This turns out to be no problem when these cells are employed as top cells in an a-Si/a-Si tandem cell, because they are still capable to generate the required 7.5-8 mA/cm^2 at an i-layer thickness of less than 100nm, and one obtains the full benefits of increased V_{OC} and of good stability. This scheme enabled us in 1996 to obtain 9.0% stable a-Si/a-Si tandem cell efficiency.

In the micromorph tandem cell, however, in order to exploit the very large current capacity of the microcrystalline bottom cell, the amorphous silicon top cell must generate a higher current. Using the more stable but relatively weakly absorbing hydrogen-diluted materials, this is only possible with an excessively thick i-layer (about 400 - 500 nm), a fact that leads once again to unsatisfactory stability.

3.3.3.2 Combined effect of H_2-dilution and moderately high temperature in p-i-n solar cells

It was therefore decided to focus from 1997 onwards on low-gap, strongly absorbing amorphous silicon materials. These materials lead to thinner top cells and thus, in principle, have a better potential to increase the efficiency of a micromorph tandem cell, provided that the increased absorption does not compromise the material stability.

A first method applied here was "conventional" VHF-glow discharge (without hydrogen dilution), at increased substrate temperatures. At 330 °C we were able to deposit i-layers for amorphous silicon top cells that can generate 13 mA/cm^2 of short circuit current at an i-layer thickness of just 250 nm (Fig. 13). However, these high-temperature cells have reduced values of V_{OC}, at least in the p-i-n configuration used at present (Fig. 14). In fact, the p-layer is here deposited before the i-layer and therefore the p-layer and the p/i-interface are subject to the high i-layer deposition temperature of 330 °C, resulting in thermal damage of the p-layer and boron contamination of the i-layer near the p/i interface. Still, at 330 °C, the V_{OC} remained 60mV lower than that of p-b-i-n cells deposited at 270°C (Fig. 14).

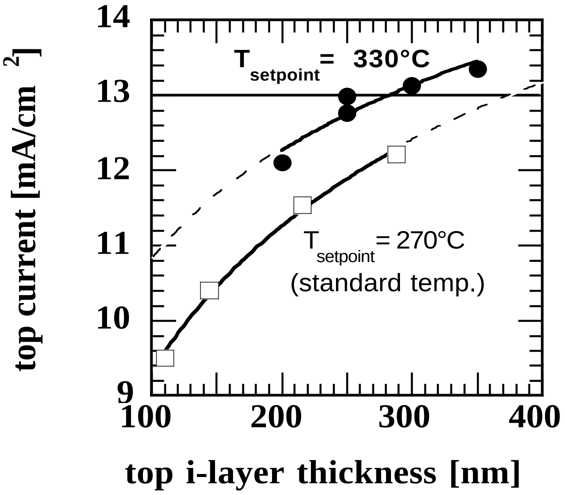

Fig. 13: Current density of an amorphous silicon top-cell within the micromorph tandem cell, as a function of i-layer thickness, for standard and high-temperature i-layers.

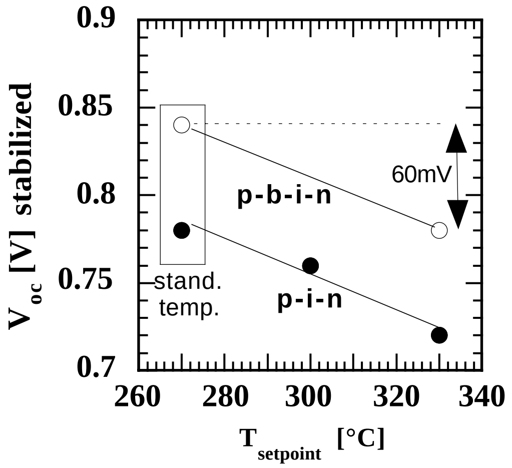

Fig. 14: Behaviour of V_{OC} in amorphous silicon p-i-n cells as a function of i-layer deposition temperature. The p-b-i-n cells incorporate a silicon carbide buffer-layer at the p/i-interface.

3.3.4 Amorphous silicon n-i-p solar cells

Within the three years' reporting period, n-i-p solar cells have evolved at IMT Neuchâtel from a 'niche' topic to an important part of the research activity. Much work was done in the framework of parallel projects: In our PSEL project [number 88] (on façade applications) the deposition on flexible polymer substrates and a sophisticated laser patterning technique have been introduced [see the PSEL final report]. Within our EU project 'NEST' (on n-i-p micromorph solar cells) the problems of the back contact have been addressed. Moderately high temperature deposition of a-Si:H layers and a-Si:H n-i-p cells, finally, were and continue to be subject of our NEDO project.

3.3.4.1 Detailed work on the upper part of the n-i-p cell

Our research on the upper part of the cell focused on the <i>/<p> interface and on the <p>-layer itself. (N.B. It is not single layers on glass that are of interest, but integrated layers observed w.r.t. their growth environment and to their function within the solar cell). The <p>-layer is one of the most important layers in the n-i-p configuration. It has the potential to generate a high V_{OC}: as in this configuration it is deposited at the end, there is here more freedom in the choice of deposition parameters (than in the case of p-i-n cells). In order to absorb here as few photons as possible (which are all lost for the cell), this layer must be very thin, but its upper part at least should be microcrystalline in order to obtain an ohmic contact to the TCO. It is not easy to grow a very thin microcrystalline layer on top of the amorphous <i> layer; a specific interface treatment has usually to be applied.

The effects of the interface treatments by H_2 plasmas and by CO_2 plasmas have been studied in detail and compared to the results without any treatment (see e.g. Fig. 15). The chemical changes of the interface due to these treatments (which can easily be made visible by the method shown in Fig. 16) were also studied by Auger Electron Spectroscopy (AES). In the case of the CO_2 plasma, the effect seems to be purely chemical: a silicon oxide layer favorises the microcrystalline growth. The H_2 plasma, on the other hand, seems to physically reorganise the surface and to create 'seeds' for microcrystalline growth.

This work on the upper part of the solar cell, combined with other optimisations of the deposition conditions, allowed us to surmount the 'landmark' value of 70% for the initial fill factor obtained on cells with flat substrates. For textured substrates, the fill factors are still slightly below 70%; our investigations continue.

This study will be the subject of a Ph. D. thesis to be completed in 2000 (P. Pernet).

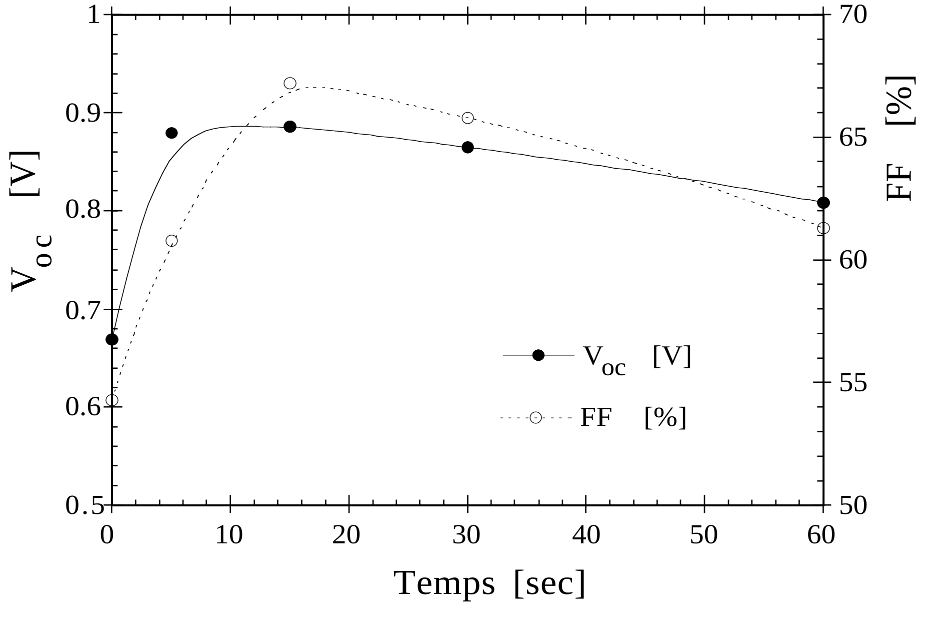

Fig. 15: Effect of a CO_2 plasma treatment at the i-p interface on V_{oc} and FF of the final a-Si:H n-i-p solar cells.

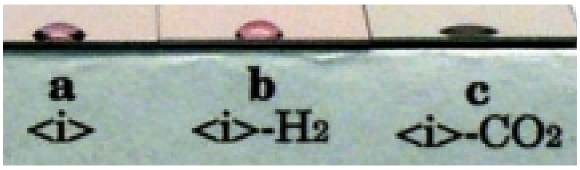

Fig. 16: A water droplet acts as indicator of a silicon oxide at the surface of the amorphous silicon layer. Without any treatment or after the H_2 *plasma, the surface is not oxidised, and the droplet stays round. After the* CO_2 *plasma treatment, the surface is oxidised and the droplet gets flatter, due to the affinity of SiO and* H_2O*.*

3.3.4.2 Work on V_{oc}

The combination of a new <p> layer and a slight dilution for <i> layer deposition allowed us to overcome the barrier of 0.9V for V_{oc} without the use of any buffer layer. A cell that has a V_{oc} of 911mV (and a fill factor of 74.3%) as single-junction cell (obtained on a flat substrate) could be successfully integrated into the micromorph structure (leading to an efficiency of 11.2% of the stacked cell).

3.3.4.3 Combined effect of H_2-dilution and moderately high temperature in n-i-p solar cells

Our new, more stable layers presented in section 3.3.2.4 were to be integrated in the actual n-i-p solar cells. Depositing at higher temperatures enhances the chemical interaction between substrate (or reflector layers) and the growing solar cell and also between the doped and undoped silicon layers. Any possible chemical diffusion will be enhanced and therefore a back contact which is compatible with the deposition at 250°C is not always compatible with the deposition at 350°C. To reduce the diffusion of phosphorus from the <n> into the <i>-layer, a specially designed high-temperature <n>-layer had to be realised.

In a light-induced degradation experiment, two n-i-p solar cells deposited at 250 and 350°C on a flat stainless steel substrate with both ZnO and ITO as front TCO have been compared (see Tab. VII). The final FF is, at least in the case of the cell with the ITO front contact, about the same for both temperatures. This is an indication that the degraded state value of FF is given by bulk degradation of the i-layer and not by chemical interdiffusion and interfaces problems.

Table VII: Performance of n-i-p solar cells deposited at 250 and 350°C on flat stainless steel substrates.

Contact		250°C				350°C			
Back	Front	Initial		Degraded		Initial		Degraded	
		V_{oc}	FF	V_{oc}	FF	V_{oc}	FF	V_{oc}	FF
Stainless steel	ZnO	0.908	71.5	0.899	64.2	0.75	64.6	0.788	58
Stainless steel	ITO	0.897	69.2	0.882	61.8	0.812	67.9	0.845	62.5

3.4 Transparent conductive oxides (TCO)

3.4.1 TCO technology development in our laboratory

Thin-film solar cells generally use Transparent Conductive Oxide (TCO) layers as front contacts, through which the light enters. They often also use a TCO layer, because of optical reasons, just in front of the non-transparent (metallic) back contact.

In the first years of our solar cell research work in Neuchâtel, our group did not have any TCO technology at all, but used commercially available SnO_2-coated glass substrates (from Asahi Glass Corporation) on which we deposited p-i-n type solar cells, the SnO_2-layer acting thereby as transparent front contact. At a later stage we introduced sputtered Indium Tin Oxide (ITO) as TCO for the "upper" side of the solar cell (i.e. for the back contact in p-i-n type solar cells). It became, however, increasingly evident that an in-house ZnO technology would be necessary in order to optimise our solar cells results. Sputtered ZnO and LP-CVD ZnO were therefore developed and characterised within the framework of a Ph.D. thesis (Anna Selvan 1999). Our first results obtained are encouraging, however, much more work has to be undertaken in this important sector of thin-film solar cells.

Within the development of TCO technology the following features are essential for the layers which we want to obtain:

(1) High optical transmission within the visible and near infrared spectrum (increase in J_{SC})
(2) High electrical conductivity in order to reduce the series resistance of the cell (increase FF)
(3) High optical scattering leading to efficient light trapping within the active, absorbing semiconductor.
(4) The TCO must be inert (no reaction with the ongrowing layers);
(5) The TCO should not be reduced by subsequent exposure to a hydrogen plasma;
(6) The TCO should act as antidiffusion barrier in order to be able to use a large variety of underlying low-cost substrates such as low-cost glass, stainless steel, polymers, aluminum;

Concerning optical scattering, we mainly focused on the surface roughness of the TCO. Indeed, as illustrated in Fig. 17, this roughness can lead to the scattering of incident light and, thus, increase the length of the optical path inside the active part of the solar cell. As a consequence, one can reduce the thickness of the cell, this being a very effective method of reducing the effect of light-induced degradation in amorphous silicon solar cells. By reducing the cell thickness, one also reduces deposition time, a parameter that is very critical for microcrystalline silicon solar cells.

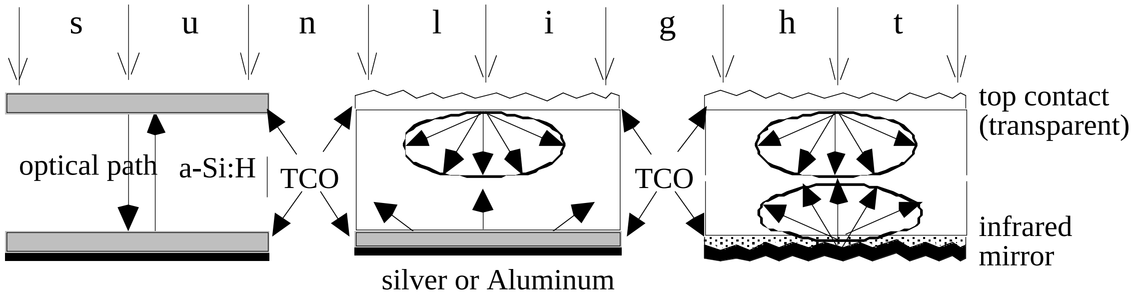

Fig. 17: Surface-textured TCO at front and back contact diffuses both the incoming light and the back-reflected infrared light, respectively. By that, the length of the optical path within the semiconductor is enhanced as compared to the real cell thickness.

3.5 Patterning of p-i-n solar cells

3.5.1 The need for cell patterning in p-i-n type cells

The goal of patterning p-i-n microcrystalline and p-i-n micromorph cells is to remove the peripheral effect of lateral carrier collection, an effect that is due to the high conductivity of the doped microcrystalline layers: this effect completely disturbs/falsifies I/V measurements on micromorph cells - it leads to wrong values for J_{SC} (too high) for FF (too low) and for η (not predictable). Another reason for patterning is to define precisely the solar cell's surface as shown in Fig. 18. Such a well-defined surface (of 1 cm^2) is required by ISE (Fraunhofer Institut für Solare Energiesysteme) to certify our cells.

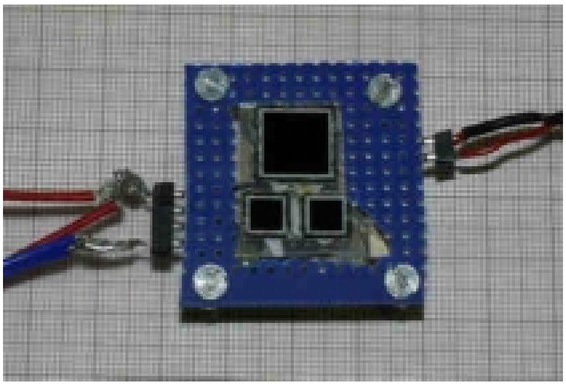

Fig. 18: Example of well-defined test solar cells in the p-i-n or ("superstrate") configuration.

3.5.2 Method of patterning

The method first developed by us was the pad printing technique, with which we obtain very good results; these results are, however, not always reproducible. Thanks to recent improvements in our set-ups we are now also able to use the laser-scribing technique. Laser-scribing is well-established in amorphous silicon module manufacturing. This method has carefully to be developed further and adapted to our thicker (2-4 µm) cells.

The micromorph cells are at present patterned by the Nd:YAG laser in frequency-doubling mode; this is, however, a particularly slow process. Generally we observed that micromorph tandem cells are much more sensitive for the laser pulses than single-junction microcrystalline p-i-n devices. This is mainly due to light degradation, recrystallisation other effects (see Figs. 19 and 20) that occur on the amorphous top cell at the zones of the laser cuts. Two ways of laser patterning, e.g. from the film and the glass side have been sofar investigated.

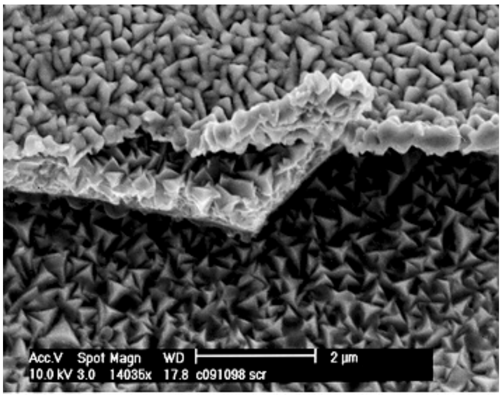

Fig. 19: Damage effect of laser structuration: view of the edge of an amorphous cell by Scanning Electron Microscope.

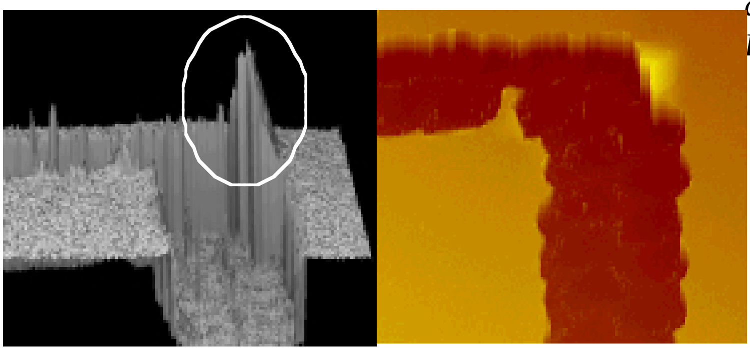

Fig. 20: 3D and 2 D view by AFM of a damaged laser-scribed edge of an amorphous cell.

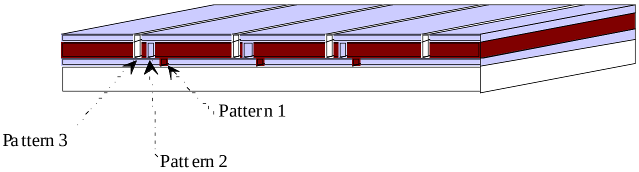

Fig. 21: Monolithic series connection of a micromorph minimodule; pattern 1 (λ=1064nm), pattern 2 & 3 (λ=532nm).

However, further detailed scribe studies have to be undertaken to indentify definitively the optimum for a defect-free patterning of our test devices.

Laser patterning allows (in contrast to the pad printing technique) for the fabrication of series-connected modules. The three different scribe steps involved for the fabrication of our first mini micromorph modul are given in Fig. 21.

3.6 Micromorph tandem cells

3.6.1 Measurement and calibration problems

The short-circuit current density (J_{SC}) of tandem cells depends sensitively on the light spectrum used for the I-V characterisation. Especially when semiconductors with large differences in the energy gap are involved, as in the case of our micromorph tandem cells (a-Si:H top 1.7 eV and µc-Si:H 1.1 eV), then the determination of AM1.5 conditions becomes critical. After having installed and applied a calibrated monocrystalline silicon reference cell (obtained in the meantime from ISE Freiburg) we now realise that the absolute spectral response (SR) measurements as applied for many years in our group for efficiency measurements (on our p-i-n "superstrate"-type solar cells deposited on glass), are very doubtful. This is mainly due to large-range (~cm) scattering effects being present in the front glass/TCO optical layer system. A further problem in absolute SR measurements is related to the nonlinearities (w.r.t intensity variation) prevailing in amorphous silicon and probably also in microcrystalline silicon solar cells. Because of these reasons our SR allows us, in fact, merely to analyse and understand certain limiting effects in the device; it should not at all be used for J_{SC}-calibration. These facts make the efficiency determination of the micromorph tandem cells even more difficult. They signify that only the I-V characterisation under STC (standard test conditions) can give reliable results regarding solar cell efficiency. A further condition imposed by ISE Freiburg is that solar cells to be certified by them must have at least an active area of 1 cm^2. Nevertheless, ISE Freiburg had certified once (before) an IMT micromorph small-area cell of 0.13 cm^2 as can be seen in Tab. VIII.

3.6.2 Outdoor Measurements

In order to check the influence of the spectral distribution on micromorph tandem cells we also performed outdoor measurements in Neuchâtel and compared them with indoor results obtained by our sun simulator (Wacom WXS-140S-10). To get a better statistical base, the outdoor measurements were performed on several days in the year. By that the influence of slightly different atmospheric conditions (dust, humidity) are better taken into account; this procedure also allows for a better evaluation of the measurements. Table VIII compares some of the results achieved sofar for indoor and outdoor characterisations made on stabilised micromorph tandem cells. The error bars include the inaccuracy of cell area determination, the errors of the reference detector and of the measurement set-up.

Tab. VIII: Achieved efficiencies of stabilized micromorph tandem cells for indoor conditions (under the sun simulator) and for outdoor (blue sky) conditions, in comparison with measurements at ISE Freiburg. As reference detector an ISE-calibrated monocrystalline solar cell was used.

Cell		Simulator (ISE calib.)	Outdoor	ISE Freiburg
Micromorph 1	1.22 cm^2	9.2 ± 0.5 %	10.0 ± 0.5 %	10.0 ± 0.5%
	0.13 cm^2	10.2 ± 0.8 %	10.8 ± 0.8 %	10.7 ± 0.7%
Micromorph 2	1.08 cm^2	10.2 ±0.5 %	10.6 ± 0.8 %	
	0.1 cm^2	10.4 ± 0.8 %	11.2 ± 0.8 %	
Micromorph 3	1 cm^2	10.4 ± 0.5 %	10.7 ± 0.6 %	
	0.25 cm^2	11.0 ± 0.6 %	11.6 ± 0.8 %	

The comparison shows that the micromorph cells generally possess slightly higher efficiencies under outdoor conditions than under the sun simulator. This is mainly due to an enhanced short-circuit current observed under clear sky conditions, as can be seen from Fig. 26. Additional spectral response measurements suggest that under clear sky conditions, the blue part of the spectrum must indeed be enhanced as compared to the artificial spectrum of our sun simulator. In order to evaluate more precisely the cell efficiency of our p-i-n type cells (i.e. for our "superstrate" configuration), we need to continue to fabricate well-defined cells and to compare also our measurements with measurements done at ISE Freiburg. Depending on the results a further check and calibration of our simulator light has then to be taken into account.
Outdoor measurements in function of different air mass (AM) values, as shown in Fig. 22, reveal a further very interesting behaviour of our micromorph cells. These tandem cells show only a weak dependency on the AM-value, e.g. a relative good tolerance with respect to spectral variations. This property is important for field applications, because under real outdoor conditions the sunlight deviates during most of the time from AM1.5 spectral conditions. An independent study (Durisch et al., Nat. Photovoltaiktagung 1999) attributes, to the micromorph tandem cell, a much better performance under variable outdoor conditions (variations in the AM-value, due to a variation in the position of the sun) than that obtained for the commercial a-Si/a-SiGe/a-SiGe triple-junction solar cell modules of Unisolar Inc. (USA). The weak "AM-dependency" of our micromorph solar cell is certainly an important advantage of this solar cell concept, as it influences directly the yearly energy production per installed W_p.

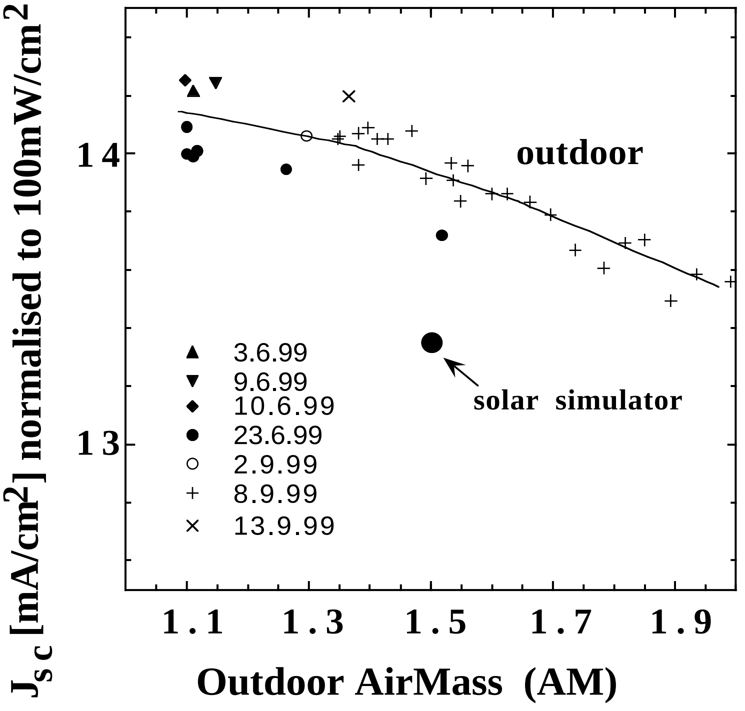

Fig. 22: Short-circuit current measurements of a 1 cm^2 micromorph tandem cell under outdoor and indoor illumination, normalised to 100 mW/cm^2. The light intensity was determined by a calibrated monocrystalline silicon solar cell (from ISE Freiburg). The airmass (AM) value was determined by measuring simply the incident angle of sunlight. Note that due to atmospheric variations (dust, humidity, temperature), various outdoor conditions can always differ slightly from one another, even at the same incident angle of sunlight.

3.6.3 Mini-module fabrication

Based on the development of our laser-scribing facilities, we proceeded to the preparation of our first micromorph mini-modules, applying thereby the monolithic series connection concept (which is already generally well used for amorphous silicon large-area module manufacturing). Microcrystalline and micromorph tandem cells are, however, much thicker than a-Si:H based cells; thus, the question remains if this laser-scribing technique is also well suited for our 2 to 3 µm thick microcrystalline silicon films and can be applied here without damaging the cells. (Note, for example, that the laser scribing technique is not readily applicable to CIGS-based solar cells in the latter case mechanical scribing is essentially used). Our first experiments on the preparation of such mini-modules show that the laser-scribing technique is indeed applicable to micromorph cells and modules; in fact, an upscaling of the micromorph cells from areas of 1 cm^2 to several tens of cm^2 is, in principle, possible, based on the monolithic series-connection technique (see Fig. 21 above). Figure 23 shows our first micromorph mini-module of a total surface area of 23.5 cm^2. It consists of 6 cell segments, each one having an area of 3.8 cm^2. The I-V characteristics result in a total module efficiency of 9.2 %. Further optimisation on the different patterning steps have now to be done, in order to obtain a better technological understanding and, thus, a full process control w.r.t. the laser-scribing process for micromorph cells.

The application of such a monolithic series-connection technique is industrially important, because it allows for further cost reduction of module manufacturing, as compared to crystalline wafer technology; in the latter the cells have to be interconnected (often by hand) by soldering/bonding and by external wiring, to form the full solar module.

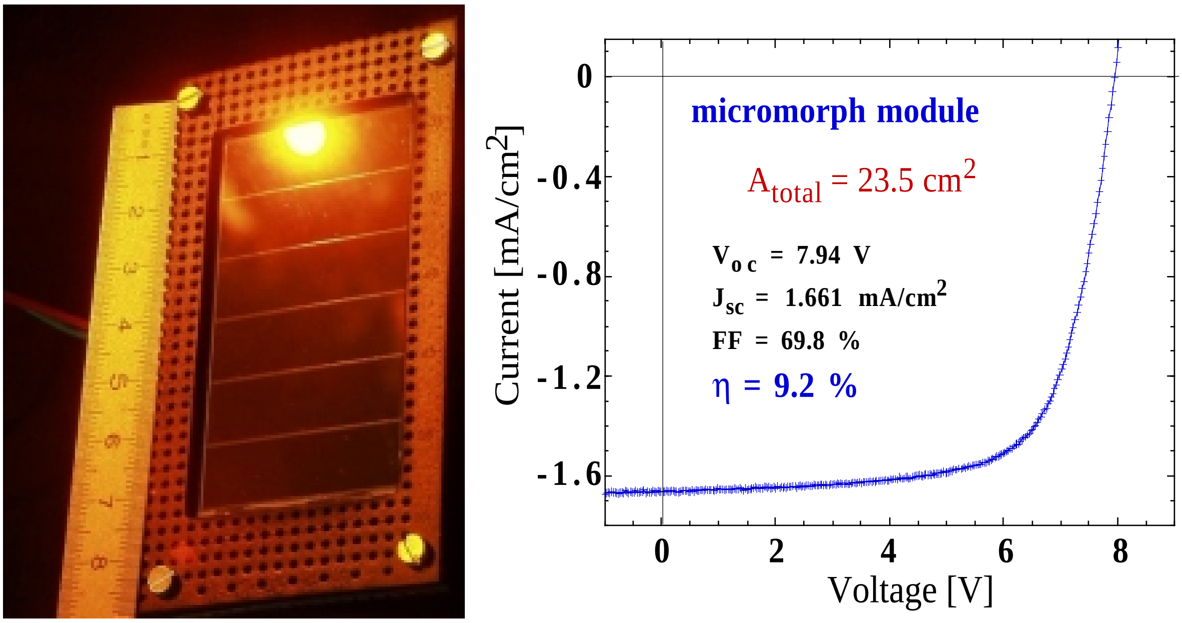

Fig. 23: Demonstration of applicability of monolithic series-connection to the micromorph concept: First IMT micromorph mini-module (23.5 cm^2) with a module efficiency of 9.2 % prepared by applying the laser-scribing technique.

3.7 Technological characterisation and test facilities

3.7.1 Technology infrastructure

Over the past 3 year period the solar cell and thin film technology laboratory of the IMT has undergone very important developments and extensions. Until 1996, exclusively test solar cells of small area (<1cm^2) could be realized on research-type equipment. Under the influence of more application-oriented projects, and by stepwise addition of important new equipment, this has strongly changed, such that by 1999/2000, the IMT thin-film silicon lab owns a comprehensive technological infrastructure allowing us to perform research and development of solar cells from the small test cells up to 30cm x 30cm solar modules.

3.7.1.1 Building transformation/clean room facility

Changes started with important transformations in 1996, after acquisition of the building of Rue Breguet 2 by the Canton of Neuchâtel. At this occasion the original technology lab was profoundly renewed and extended in surface, including a completely new deposition gas installation and air-conditioning system. In addition to the original lab, a new clean room lab was built on the same floor. In this class 10000 lab of 60 m^2 area, wet-benches with laminar flows allow us to work even under class 100 conditions.

Fig. 24: Class 10000 cleanroom of 60 m^2 area on the second floor of the Breguet 2 building. In the wet-bench areas with laminar flow, class 100 conditions can be obtained for critical operations.

3.7.1.2 Small area VHF-plasma deposition reactor upgrade

Following those transformations, with now more space available, extensions and additions started regarding the technology equipment, as described below. As a first step, the first- and second-generation of small-area lab reactors were upgraded and extended, to allow for better microcrystalline silicon and/or amorphous silicon solar cell device fabrication.

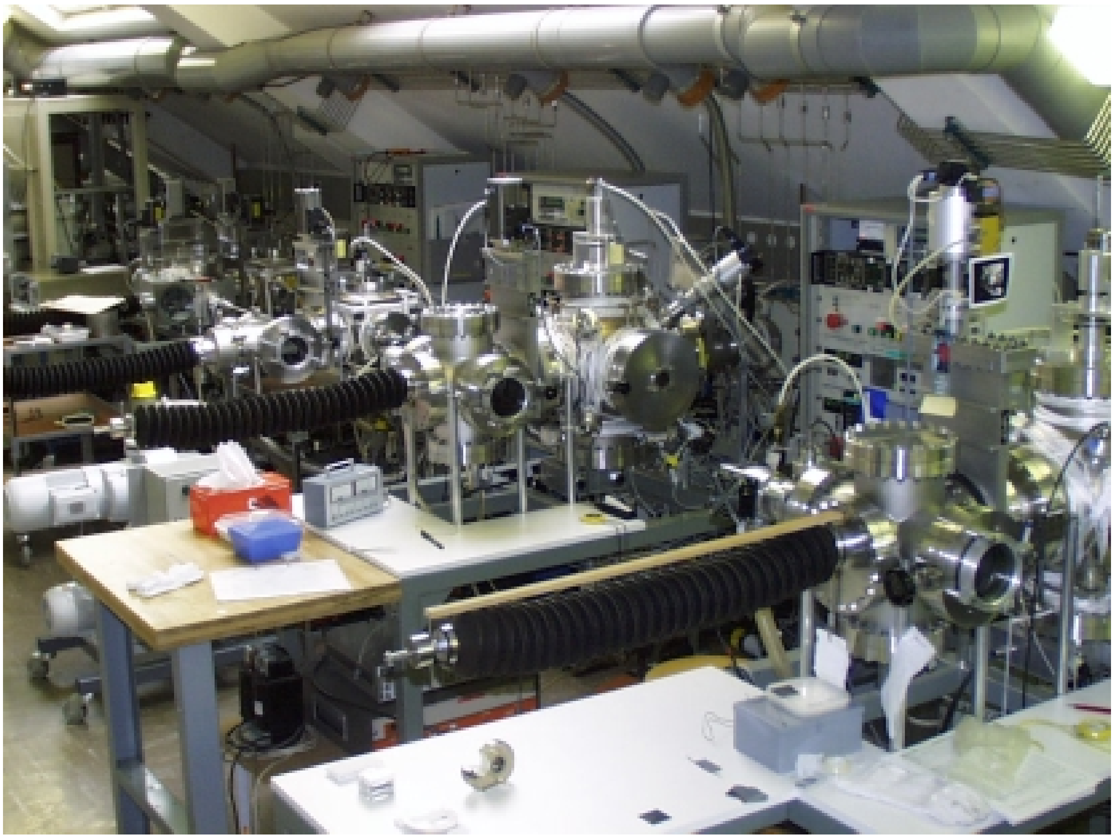

Fig. 25: Partial view of the general technology lab after transformation, with small-area (8cm x 8cm) plasma deposition reactors B, A, E, and F, equipped with new VHF-electrodes, load-locks and reactor B with an additional second chamber.

3.7.1.4 Large area deposition equipment

Thanks to different research projects (EUREKA, CTI) as well as thanks to exceptional Cantonal equipment subsidies, different facilities for larger area deposition could be added to the lab over the last three year period. This equipment includes, in particular, two 30cm x 30cm VHF-plasma deposition reactors for the deposition of amorphous and microcrystalline silicon. Here, second hand conventional RF reactors were equipped with VHF-Electrodes, the latter being designed and built at the IMT. One of these reactors is further fully-computer controlled, allowing for the automatic deposition of single-junction, tandem, and triple-junction solar cells.

Fig. 26: Computer controlled automatic 30cm x 30cm VHF-plasma deposition reactor for fabrication of amorphous silicon solar cells.

Additional large-area deposition equipment includes a 3 source magnetron sputtering system for 30cm x 30cm area, bought by a special equipment credit of the Canton of Neuchâtel. This system is currently equipped for deposition of Aluminum and ITO, i.e. for the realization of solar cell front and back contacts.

Further, in the new clean room lab, substrate cleaning installations have been designed and installed to accommodate substrate sizes of up to 30cm x 30cm. Together with the laser scribing facility (see below), the IMT owns in principle now all necessary infrastructure to develop and fabricate, completely in-house, full 30cm x 30cm thin-film silicon solar cells and solar modules.

3.7.1.5 Solar cell and solar module structuring and series connection

Over the last 3 years, solar cell and module structuring and series connection have become important in IMT’s research and development projects. Today, IMT owns 2 laser scribing systems, as well as tampography and sreenprinting equipment for masking and scribing of silicon and contact layers.

Fig. 27: Laser scribing system for structuring and series connection of thin film solar cells, including pulsed YAG laser and computer controlled 30cm x 30cm xy-table. This equipment has been donated to IMT by an industrial partner. It was upgraded in-house to comply with the special needs of IMT's device technology.

Tab. IX: Overview of the technological infrastructure in March 2000.

Type	**Brand**	**Remarks**
General technology lab	-	100 m^2
Clean room lab	-	Class 10000, 60 m^2
Gas supply installation	SL-Gas	SiH_4, H_2, B_2H_6, PH_4, CH_4, SF_6, Ar, N_2
Small area VHF system A	IMT-built	8cmx8cm, load-lock
Small area VHF system B	IMT-built	2 chambers of 8 cm x 8cm, load-lock
Small area VHF system C	IMT-built	2 chambers of 8 cm x 8cm, load-lock
Small area VHF system D	IMT-built	8cmx8cm
Small area VHF system E	IMT-built	8cmx8cm, load-lock
Small area VHF system F	IMT-built	8cmx8cm, load-lock
Large area VHF system S	IMT-built	30cmx30cm double sided, computer controlled
Large area VHF system X	IMT-built	30 cm x 40cm
Box coater	Leybold L560	Evaporation and e-beam, ITO sputter unit
Evaporator small	Balzers	5cm x 5cm
Magnetron sputtering small	Leybold	3 x 3 inch cathodes, ZnO, Ag, Cr
Magnetron sputtering large	MRC 603	3 cathodes (Al, ITO, ZnO), 30cmx30cm, load-lock
LP CVD ZnO	IMT built	15cm x 15cm
Plasma etcher	IPL	5 inch diam.
Tampography	Tecoprint TC60	
Screen-Printer	Schmid-Machines	30cm x 30cm
Laser scribing 1	IMT-built	Laser YAG 532 nm, 20 Hz, 30cm x 30cm
Laser scribing 2	Bosch	Laser YAG 1064 nm, 40 kHz, 30cm x 30cm

3.7.2 Characterisation infrastructure

During the last 3 year period, our characterization infrastructure has been consolidated, in order to respond to the present needs of our cell development and project activities. This improvement of our facilities concerned mainly the fields of surface characterization (surface morphology) for µc-Si:H and TCO layers, of sub-bandgap absorption for a-Si:H and µc-Si:H layers, as well as of improved cell characterization in terms of reproducibility and accuracy.

3.7.2.1 Surface and layer characterisation

In order to improve µc-Si:H material analysis as well as analysis of ZnO layers, an atomic force microscope (AFM) VISTA 100 from Burleigh was acquired. This microscope was chosen because of its capability of imaging large samples, its ease of use and availability of various scanner ranges.

Fig. 28: AFM VISTA 100 on its optical table.

Sub-bandgap absorption (which is used to determine the defect density of the layers) is usually determined either by photothermal deflection spectroscopy (PDS) or constant photocurrent measurement (CPM). The latter only measures relative absorption and must therefore be calibrated by means of another technique. A recent development called absolute–CPM (A-CPM) relies on a simultaneous measurement of the optical transmission. Such a technique has been implemented on our previous PDS setup for combined measurement of both PDS and CPM on the same optical bench.

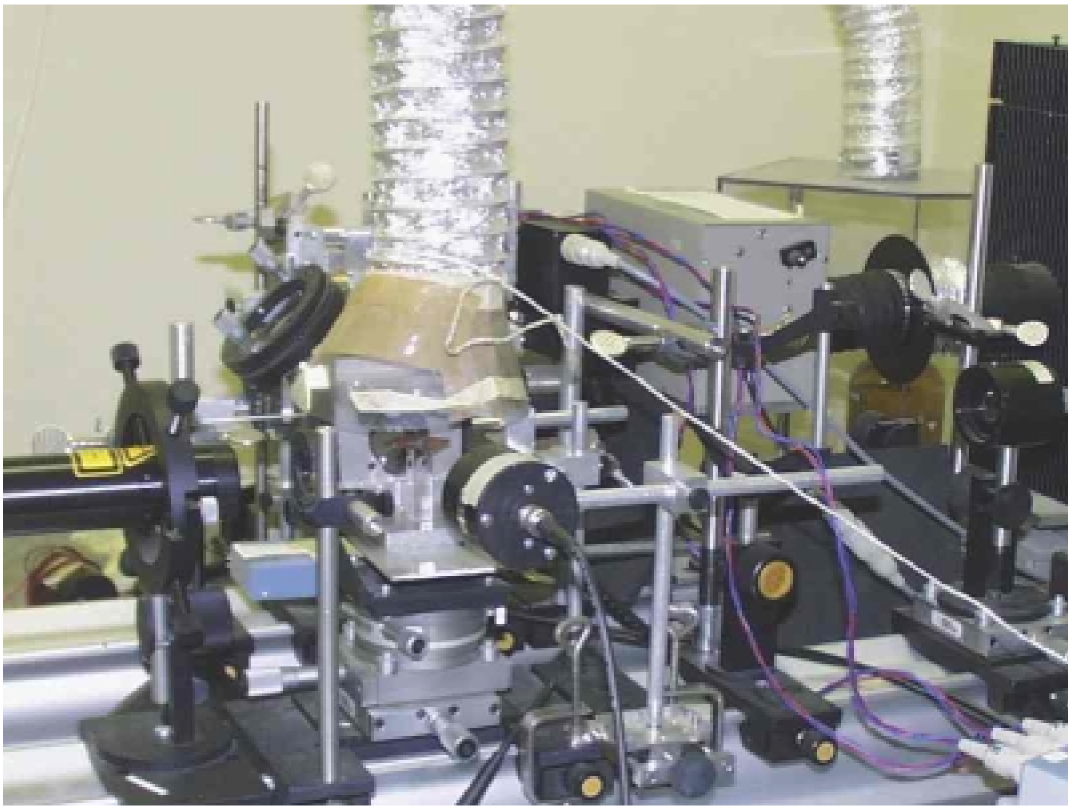

Fig. 29: PDS and CPM setup sharing the same light source (halogen lamp and monochromator).

3.7.2.2 Cell characterisation

In order to improve the reliability of our I(V) characterization, spectral response (SR) of the cells, a new calibration standard was adopted. This consists, of photodiodes calibrated by the Fraunhofer Institute (in Freiburg, Germany) which are, in their turn, used to calibrate the SR setups and to check our solar simulator intensity. A portable optical spectrometer (Ocean Optics) was also bought for checking the spectral variation of our solar simulator light sources.

Under low light illumination levels, solar cells performances are in general limited by the parallel resistance (shunt resistance R_{sh}). An analysis of the dependence of R_{sh} on the light intensity (with the help of variable intensity measurement – VIM technique) can be used to determine the effective $\mu^0\tau^0$ quality parameter of the i-layer within the full cell. A system has therefore been set-up to perform such VIM characterizations.

Uniformity of the solar cells (over the cell area) can be checked with light-beam induced current (LBIC). In order to overcome the limited scan area of our first set-up, a second set-up was built on one of our laser scribing system. Such a combined system could possibly be used to detect and “kill” solar cell pin-hole or shunt defects.

Tab. X: Overview of the now available characterisation systems at IMT. Field indication refers to cells (C), layers (L) or other (O).

Systems	Field	Analysed properties	Brand	Remarks
Steady-State-Photocarrier-Grating (SSPG)	L	Ambipolar diffusion length $\mu^0\tau^0$ product	IMT-built	HeNe laser, low light intensity
SSPG	L	Ambipolar diffusion length $\mu^0\tau^0$ product	IMT-built	Kr laser, 500 mW
Time-Of-Flight (TOF)	L	Carrier $\mu\tau$ product, drift mobilities	IMT-built	pumped Dye Laser (400-700 nm), 30-400 K
Dark-/Photo-conductivity	L	Conductivity, activation energy	IMT-built	300-600 K
Photothermal Deflection Spectroscopy (PDS)/Absolute Constant Photocurrent Measurement (A-CPM)	L	Sub bandgap optical Absorption, defect density	IMT-built	500-1800 nm
Diffusion length setup	L	Diffusion length	IMT-built	
UV/VIS/IR spectrometer Lambda 900	L	Optical absorption, energy gap	Perkin-Elmer	
FTIR Spectrometer 1720x	L	Optical absorption, hydrogen bonding/content	Perkin-Elmer	
Optical Spectrometer	O	Light spectra	Ocean Optics	250-1000 nm
Profiler Alpha-step 200	L/C	Thickness profiles	Tencor	
AFM/STM microscope VISTA 100	L/C	Surface morphology	Burleigh	7 and 180 mm scanners, 15x15 cm samples
Optical microscope	L/C	Surface morphology	Leitz	
Degradation setup (laser)	L		IMT-built	Pulsed dye laser (700 nm) and CW HeNe
Degradation setup (PLD)	C/L		IMT-built	Fluorescent tubes (broad band) and filtered white-light
Solar simulator	C	I(V) characteristics	Wacom	2 light sources
Variable Intensity Measurement (VIM)	C	Shunt resistance, material quality ($\mu^0\tau^0$ product)	IMT-built	
Spectral response (SR)	C	Collection efficiency	IMT-built	300-1000 nm
Spectral response (SR)	C	Collection efficiency	IMT-built	400-1100 nm
Light-Beam Induced Current (LBIC)	C	Current collection map	IMT-built	15x15 mm scan
LBIC	C	Current collection map	IMT-built	30x30 cm scans

Other common university facilities:

A new common microscopy laboratory with SEM, TEM and optical microscopes has been setup at the University of Neuchâtel, in collaboration with the CSEM S.A.. A further SEM microscope (type E-SEM) is now available.

4. Conclusions and perspectives

IMT Neuchâtel will, as long as it is reasonably financed by the Swiss Federal Government, continue on the way to develop a "next-generation" PV module technology based on thin-film silicon, a technology that can be industrially implemented in Europe and possibly even in Switzerland.

IMT Neuchâtel is, however, thereby, facing very stiff international competition, as one surely has to expect in such a key technological field as photovoltaic (PV) cell/module design and fabrication. It is to be expected that the competition will become even broader and more dynamic, as the whole PV sector gains even more momentum during the years to come.

As of today (2000), several major PV research groups in Japan, Germany and in the U.S.A. have already started intensive research and development work on:

- plasma-assisted deposition of hydrogenated microcrystalline silicon (µc-Si:H) (pioneered by IMT in the early 1990's)
- VHF (very high frequency) operation of plasma-assisted deposition for both amorphous and microcrystalline silicon (patented by IMT in 1986)
- the "micromorph" concept, i.e. the amorphous / microcrystalline silicon tandem cell concept (introduced by IMT in 1994).

The most important research groups that have already been able to publish, during 1998 and 1999, significant results in the fields just mentioned are:

- the industrial research labs of Kaneka Corp. and Canon Corp. in Japan
- the Japanese Government Research lab ETL (Electrotechnical Laboratory) in Tsukuba near Tokyo
- the two closely-linked U.S. solar cell firms and their R&D labs in Detroit: ECD Inc. and Unisolar (USSC) Inc.
- the Forschungsanstalt Jülich in Germany.

Japanese groups and Unisolar Inc. are closely and repeatedly following on IMT's developments. Canon even considers our "micromorph tandem "concept to be "the solution for the next generation of photovoltaic modules". As a consequence, Canon has abandoned its long-lasting Si-Ge amorphous alloy development research program, in favour of microcrystalline silicon. All these groups have, in general, been able to invest considerably more rapidly than we have (especially on the equipment side) into micromorph tandem cell research and they have, thus, been more or less able to "catch up with us", as far as overall results are concerned.

One should note that some of these groups have the possibility to deposit much more intensively than IMT (as a comparison, IMT has, with its present equipment, the possibility to deposit around 10 to 12 p-i-n type cells a week, whereas Kaneka has the potential of 15 cells per day; regarding Canon it is said that they have already deposited between 1000 and 2000 µc-Si:H cells in 1998)). This type of situation will continue in the future and will even be more intensified, since there is a widely-based and strong Japanese funding for research labs as well as industries working in photovoltaics (The micromorph tandem cell developed by Kaneka became the sign-board of NEDO at the PVSEC-11 in Japan). IMT, thus, feels like "David competing with Goliath".

Nevertheless, we at IMT are most confident about the future because we possess certain "trump cards" that have remained sofar completely in our hands, e.g.: full mastering of the VHF plasma deposition process (together with CRPP/EPFL); possibility to obtain good cells at relatively very low temperatures, enabling, thus, the use of flexible polymides as substrates; excellent characterisation facilities for layers and cells, backed-up by in-depth physical understanding of the relevant effects and limitations.

IMT has established a close collaboration (especially for the more mature amorphous silicon technology) with several industrial firms in Switzerland and in neighbouring European countries; we also have intensive exchanges in this sector with R&D labs in the whole world.

For obvious reasons, no details about our future plans can be given here. However, it can be clearly stated, that provided adequate financing continues, an overall goal of 9 % stabilized efficiency for large-area PV modules in mass production, based on the micromorph tandem concept should be attained within the next few years; this will be possible for industrially relevant deposition conditions (microcrystalline intrinsic layer not thicker than 2 µm and deposited at least at 10 Å/sec). One should also note that our "micromorph" tandem concept will probably be much more robust w.r.t. industrial production yield, temperature coefficient (w.r.t. application of PV modules in high-temperature environmental conditions) and spectral variations of incoming sunlight, than other low-cost thin-film PV module technologies (such as CIGS and CdTe) that have been recently suggested and that are now intensively investigated, especially in European solar cell research labs.

5. Collaboration with other research groups and with industries

5.1 Collaboration within Switzerland

Since 1988 there exists a formalized and intensive collaboration between IMT and CRPP (Centre de recherches de la physique des plasmas), Lausanne, concerning VHF plasma measurements and large-area amorphous silicon deposition with VHF plasmas.

IMT Neuchâtel collaborates with the CSEM (Centre Swiss de Recherche en électronique et Microtechnique) Neuchâtel.

IMT Neuchâtel has collaborated with the Institut de Chimie and the Institute de Biologie (Zoologie animale) of the University of Neuchâtel to have access to an SEM microscope and with the Institute de Géologie to obtain X-Ray analysis and Atomic Force Microscopy of its layers.

A collaboration was built up with Prof. L. Zuppiroli of the Physics Department of EPFL Lausanne for the analysis and for non-photovoltaic applications of ZnO layers.

IMT Neuchâtel had a R&D collaboration on solar cells for energy applications, with Alusuisse Management & Technology Neuhausen, and with Ernst Schweizer AG, Hedingen. The latter collaboration formed part of a PSEL-funded research project. A follow-up project submitted to the PSEL in 1998-99 has unfortunately been rejected.

Within an existing EUREKA project, financed in Switzerland by the CTI (Commission pour la Technologie et l'Innovation) of the Swiss Federal Government, IMT is preparing the industrial fabrication of low-cost amorphous silicon cells by VHF glow discharge; this is intended for application in watches and other small electronic appliances. The Swiss partners here are Asulab S.A. (SMH group), Valgay S.A., and Valtronics S.A. The exact nature of the work done here is confidential.

In 1999 the CRPP and IMT have submitted a CTI project where Balzers Processing Systems (BPS) is the industrial partner. This project has started in April 2000.

5.2 Collaboration within Europe

Within our JOULE project "NEST" we had a collaboration with Jülich, Prague and Paris and, to a lesser extent, with Patras. The technical collaboration with the Research Center Jülich (D), i.e. which is one of the main solar cell research groups in Germany, is particularly intensive and extends to virtually all aspects of "micromorph" solar cells. Thanks to our very fruitful collaboration with Dr. I. Kocka and Dr. M. Vanecek of the Institute of Physics in Prague, we are able to obtain access to optical and electrooptical measurement techniques for thin films as well as to gain physical insight into the optical and electronic properties of our layers. Finally, Dr. P. Roca of Ecole Polytechnique Palaiseau has been helpful in the surface analysis of our amorphous and microcrystalline layers.

Apart form the Joule project partners, IMT Neuchâtel has a long-standing and intensive scientific collaboration with the Department of Physics of the University of Konstanz, specially with the solar cell research group of Prof. E. Bucher. In 1997 Dr. J. Pohl of this group carried out a large part of the X-Ray diffractometry for our layers.

Furthermore, IMT has built up a collaboration with the research group of Prof. J. Andreu at the University of Barcelona, regarding solar cell device analysis and measurements. Informal but intensive collaboration extends also to the German company of Phototronics GmbH, Putzbrunn (Dr. H. Schade) and to Siemens Solar AG. (Dr. K.D. Ufert).

On the other hand, as already mentioned, IMT participates in an EUREKA project; within this project, a French firm, Solems S.A., Palaiseau, Paris, is concerned with full-scale industrial solar cell fabrication for watches and small electronic units. This collaboration, that benefits all our solar cell activities, covers topics that are at present confidential.

5.3 Collaboration with USA, Japan and Australia

USA: We may mention here informal but fruitful exchanges with Prof. C. Wronski (Penn State University), Prof. S. Wagner (Princeton University)- where one of our Ph.D. students worked for a full year- and with Dr. S. Guha of UNISOLAR Inc., Detroit.

Collaboration with Japan (Dr. A. Matsuda of Electrotechnical Laboratory (ETL) and Prof. I. Shimizu of Tokyo Institute of Technology) is presently being built up. Our laboratory has been selected as one of 6 laboratories in the whole world, to receive a research contract from the Japanese NEDO (New Energy Development Organization, an agency of MITI).

At present, a new line of collaboration with the University of New South Wales (UNSW) in Sydney/Australia (Prof. A. Aberle) is starting.

Tab. XI: Overview of national and international groups within the collaboration of the IMT.

National:

EPF Lausanne (Dr. Ch. Hollenstein, Dr. A.A. Howling, L. Sansonnens, C. Courteille) :	High-rate deposition of microcrystalline silicon, large area deposition, VHF plasma diagnostics
PSI-Z (Dr. P. Seitz) :	Photoelectrical sensors
ENECOLO (D. Ruoss), E. Schweizer AG (A. Haller), IOA (T. Sidler) and LESO at EPFL (P. Affolter), :	Hybrid solar collectors
Promont-Soleil (Dr. R. Minder and Dr. W. Durisch (PSI))) :	Characterisation of test cells

International:

ETL/Japan (Prof. A. Matsuda) :	improved stability for amorphous silicon fims and n-i-p solar cells
Forschungsanstalt Jülich (Dr. B. Rech and collaborators) :	Micromorph cells, RF deposition
Academy of Sciences Prag (Dr. M. Vanecek) :	Optical characterisation, light-trapping
Fraunhofer Institut Freiburg (Dr. S. Kunzelmann, R. Adelhelm):	Calibration of solar simulator and reference cells, verification of solar cells
Princeton University (Prof. S. Wagner) :	DC deposition and comparison with VHF-GD
Universität Konstanz (J. Pohl) :	X-ray Diffraction
Phototronics-Solartechnik GmbH (Dr. H. Schade) :	Laserscribing, Mikromorph Studie
Siemens-Solar GmbH (Dr. K. Ufert) :	light-trapping
ASULAB S.A. (Dr. E. Saurer) and SOLEMS S.A. (Dr. J. Meot):	large area deposition of amorphous silicon by VHF-GD for rapid batch produc tion of solar cells (EUREKA project)
ESA/ESTEC (Dr. P. deMaagt) and EPFL (Prof. J. Mosig) :	Solant (solar cells on antennas) project

6. List of symbols

a-Si:H	: hydrogenated amorphous silicon
μc-Si:H	: hydrogenated microcrystalline silicon
V_{oc}	: Open circuit voltage [V]
J_{sc}	: short-circuit current density [mA/cm^2]
FF	: Fill factor
η	: Solar cell efficiency [%]
VHF	: Very High Frequency
GD	: Glow discharge
CVD	: Chemical vapour deposition
LP-CVD	: Low pressure chemical vapour deposition
HW	: Hot wire
σ_{photo}	: photoconductivity [Ω^{-1}cm^{-1}]
L_{amb}	: ambipolar diffusion length [cm]
SSPG	: steady-state photocarrier grating
$\mu\tau$-product	: mobility × lifetime product [cm^2/V]
$\mu^0\tau^0$-product	: normalised mobility × lifetime product [cm^2/V]
E_{gap}	: Energy bandgap of a semiconductor [eV]
E_F	: Fermi level
PDS	: Photothermal Deflection Spectroscopy
CPM	: Constant Photocurrent Method
TOF	: Time of Flight
VIM	: Variable Intensity Measurement
R_{SC}	: short circuit resistance [Ω]
R_S	: series resistance [Ω]
R_P	: parallel resistance (shunts) [Ω]
$V_{Collection}$	: collection voltage [V]
d	: intrinsic layer thickness [μm]
T_s	: substrate temperature [°C]
TEM	: Transmission Electron Microscopy
AFM	: Atomic Force Microscopy
SEM	: Scanning Electron Microscopy
AES	: Auger Electron Spectroscopy
TC	: relative temperature coefficient

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7. Appendix

Comparison of goals promised and results obtained

a) Microcrystalline silicon layers

	promised	obtained
Sub-bandgap absorption α(0.8 eV)	≤ 5 cm^{-1}	0.7 cm^{-1}
E_{02}	≤ 1.15 eV	1.12 eV
absorption in the visible α(2.5eV)	≥ 3xα(c-Si)	3xα(c-Si)
deposition rate	≥ 10 Å/s	10 Å/s @ η = 6.9% 16 Å/s layers
oxygen content [O]	< 2x10^{-18} cm^{-3}	low enough (no more measured)
normalised mobilityxlifetime product $\mu^0\tau^0$	≥ 3x10^{-7} cm^{2}Vs^{-1}	2x10^{-7} cm^{2}Vs^{-1} (coplanar, ⊥ : probably more)

b) Microcrystalline p-i-n solar cells

Open circuit voltage V_{OC}	≥ 500 mV	560 mV @ FF = 66 % 530 mV @ FF = 70 %
Fill factor	≥ 70 %	71 %
Short-circuit current J_{SC}	≥ 25 mA/cm^2	26 mA/cm^2 @3.5 µm i-layer
Efficiency η	> 9 %	8.5%

c) Hydrogen dilution of amorphous films and cells

oxygen content [O] of diluted layers	< 1x10^{-18} cm^{-3}	low enough (no more measured)
Defect density N_{def} of diluted layers in degraded state	≤$^{1}/_{2}N_{def}$(standard)	o.k.
New criterion (NEDO-Project): Relevant parameter is absorption α(647nm) times normalised mobility times lifetime $\alpha\mu^0\tau^0$ in degraded state	≥ 2$\alpha\mu^0\tau^0$(normal)	obtained with dilution: $\alpha\mu^0\tau^0$(350°C) = 2x10^{-3} undiluted: $\alpha\mu^0\tau^0$(220°C) = 1x10^{-3}
Open circuit voltage of p-i-n cells	V_{oc} > 1V	900 mV (higher could be achieved with higher E_{gap} & lower J_{SC} - not relevant for micromorph tandem)
Layers and cells in the transition region	N_{def}= 3 cm^{-1} & E_{gap} = 1.4-1.5 eV	layers with N_{def}≈ 3-4 cm^{-1}, E_{gap} unclear, no cells

d) ZnO layers by CVD

Transmission	> 85 %	> 80 %
Sheet resistance	2 Ω/	5 Ω/
haze factor	> 35 %	24 %
deposition rate	> 5 Å/s	> 20 Å/s

e) Tunnel Junction

Series resistance	12.2 Ω	15 Ω
Improvement of contact interface layer	promised	obtained by CO_2 treatment
Enhancement of J_{SC}	promised	losses reduced <0.5mA/cm^2

f) Micromorph cells

Stabilized micromorph tandem cells	η = 12 %	indoor: 11.0 ± 0.6 % outdoor: 11.6 ± 0.8 % (A = 0.25 cm^2) in pin configuration
not projected but achieved during this period is an "in-house-made" micromorph mini-module (on glass) by applying the laser-scribing technique for the monolithic series connection		module aperture η = 9.2 % Area = 23.6 cm^2 (6 segments each of 3.8 cm^2)