

PREPARATION OF UNDOPED AND DOPED MICROCRYSTALLINE SILICON ($\mu\text{c-Si:H}$) BY VHF-GD FOR P-I-N SOLAR CELLS

R. Flückiger, J. Meier, H. Keppner, M. Götz, A. Shah,

Université de Neuchâtel, Institut de Microtechnique, rue A.-L. Breguet 2, CH-2000 Neuchâtel, Switzerland

ABSTRACT

The electronic transport properties of $\mu\text{c-Si:H}$ materials were investigated. The $\mu\text{c-Si:H}$ was deposited by the Very High Frequency - Glow Discharge (VHF-GD) technique at a RF-excitation of 70 MHz. Very thin $\langle\text{p}\rangle$ doped layers (100 - 400 Å) were studied. Conductivities higher than $10^{-3} (\Omega\text{cm})^{-1}$ could be achieved for films thicker than 150 Å. The as-deposited $\mu\text{c-Si:H}$ is a slightly $\langle\text{n}\rangle$ -type material and compensation was obtained by μ -doping with boron. Light-induced degradation of the compensated film showed better stability than for a-Si:H. Entirely $\mu\text{c-Si:H}$ p-i-n solar cells were prepared by incorporating the compensated layer in the structure. The $\mu\text{c-Si:H}$ cells show indeed an increase in the spectral response beyond 750 nm compared to amorphous silicon solar cells. These results indicate that the slightly doped $\mu\text{c-Si:H}$ is a new promising photovoltaically active material, which merits closer investigation.

INTRODUCTION

The growth of microcrystalline silicon ($\mu\text{c-Si:H}$) is empirically realised in a glow-discharge (GD) system by a high dilution of silane in hydrogen (~3 %) at a sufficiently high deposition temperature and a high discharge power. Our earlier studies have shown [1 - 3] that by the VHF-GD technique at 70 MHz the input power for the growth of $\mu\text{c-Si:H}$ can significantly be reduced. Also, the deposition temperature can be kept lower than in the case of conventional 13.56 MHz GD [4]. Thus, "thick" doped layers show excellent conductivities, as high as $130 (\Omega\text{cm})^{-1}$ for n-type and $30 (\Omega\text{cm})^{-1}$ for p-type material [1 - 3]. Supported from plasma diagnostics [5] we believe that the lower ion energies due to a reduced sheath potential and a higher atomic hydrogen flux on the growth surface enhance the surface mobility of the species, which contribute to the favourable growth of $\mu\text{c-Si:H}$ in VHF conditions. The challenge to achieve more stable thin film solar cells encouraged us to investigate the properties of intrinsic $\mu\text{c-Si:H}$ as a potential new solar cell material, since it is known that light-induced degradation in $\mu\text{c-Si:H}$ films is lower than for amorphous silicon [6 - 8]. As previously reported [4], we found in a temperature depen-

dence study, that the undoped $\mu\text{c-Si:H}$ shows $\langle\text{n}\rangle$ -type properties as is also reported by the work of [6, 7]. Now, in the present study we tried to compensate our already optimised undoped material by adding some traces of diborane into the plasma gas. Further, the stability of such films were analysed under strong light illumination.

Before preparing finally p-i-n solar cells, we first developed very thin, appropriate $\langle\text{p}\rangle$ -type $\mu\text{c-Si:H}$ window layers; their detailed study will be given here. In the second part of this work we prepared p-i-n solar cells with entirely microcrystalline $\langle\text{i}\rangle$ and $\langle\text{n}\rangle$ layers in combination with different $\langle\text{p}\rangle$ windows (a-SiC:H, $\mu\text{c-Si:H}$).

EXPERIMENTAL

Films and solar cells were deposited in a single VHF chamber reactor at 70 MHz. The deposition parameters were: $T_{\text{dep}} = 170 - 200$ °C, $p = 0.4 - 0.8$ mbar, power input of $3 - 10$ W, $\text{SiH}_4/\text{total} \sim 1 - 3$ %, deposition rate $0.5 - 1$ Å.

To have the same original state of the chamber at the beginning of each new experiment and after each cell, we always deposited an a-Si:H dummy layer to minimise contamination residues.

a) Films

For the compensation of the $\mu\text{c-Si:H}$ material an additional mixing chamber was installed which allowed "micro-doping". For both the compensation and deposition of thin $\langle\text{p}\rangle$ -type window layers, B_2H_6 was used.

All films were deposited onto Dow Corning 7059 glass and on c-Si wafers for their characterisation. Thin copper grids were also used for the deposition of the thin $\langle\text{p}\rangle$ -type layers. The films were analysed by IR- and UV/visible transmission spectroscopy, dark- and photoconductivity. Further, Raman and X-ray diffraction were investigated to verify the crystallinity. The thickness of the samples for the compensated material was kept constant around $0.33 - 0.44$ μm , contacts used here were 1000 Å thick aluminium in a coplanar configuration. The dark conductivity of the films was measured under vacuum condition after standard annealing at 200 °C.

The thicknesses of the films were determined by a step profiler. Specially for the thin p-doped layers the given values were

averaged over about twenty measurements. To avoid a change in the surface of the thin <p>-doped series, all films were stocked in an argon atmosphere.

The photoconductivity of three typical films of the compensation study series were characterised during long-term illumination under an intensive high pressure sodium lamp (1.5×10^{18} photons/cm²s). With the wavelength of this light source of 590 nm and the absorption coefficient of about 1×10^4 cm⁻¹ of the μ c-Si:H we get a relatively uniform illumination through the entire film (transmission ~ 70 %). The temperature during the light exposure was 40 °C and was measured by an infrared thermometer.

b) Solar cells

The p-i-n solar cells were deposited onto ZnO and SnO₂ coated glass substrates. Thus, the newly developed μ c-Si:H window layer has been applied in the cells and was compared with a <p>-type a-SiC:H window layer. The latter we commonly use in our standard a-Si:H solar cells was not especially optimised for the μ c-Si:H reactor. As active layer we introduced our compensated material of first 0.3 μ m thickness (finally 1.1 μ m), followed by a thin <n>-doped microcrystalline silicon layer (between 100 and 400 Å). This <n> μ c-Si:H is well established in our a-Si:H p-i-n solar cells [9]. As back contacts we used either aluminium, titanium-silver (TiAg) or the transparent indium-tin-oxide (ITO).

In order to avoid the evident large peripheral effect as reported [4], the cell surface has been defined using masks.

The cells were characterised under AM1.5 illumination at 100 mW/cm² by a two-source solar simulator (Wacom WXS-140S-10) and in the dark. The external quantum efficiency was measured in the range of 350 to 1000 nm. Light Beam Induced Current (LBIC) measurements were carried out to monitor the peripheral effect of the cells and to check the back contact.

To improve the performance of the devices we systematically annealed the cells.

RESULTS AND DISCUSSION

a) Thin <p>-doped μ c-Si:H films (window layers)

For solar cells applications the most important features for a high quality <p>-type window layer are: its transparency, its conductivity and its overall ability of being an efficient emitter. The properties of the emitter can be verified by measuring the activation energy.

As already reported, doping efficiency for μ c-Si:H is much higher than for a-Si:H. Thus, for thick <p> layers (0.3 μ m) activation energies of 20 meV and conductivities of 30 (Ω cm)⁻¹ can be obtained. This very low value of E_{act} and the high conductivities encouraged us to investigate the properties of very thin <p> layers. The influence of the film thickness on the conductivity σ_d and the activation energy E_{act} is summarised in fig. 1.

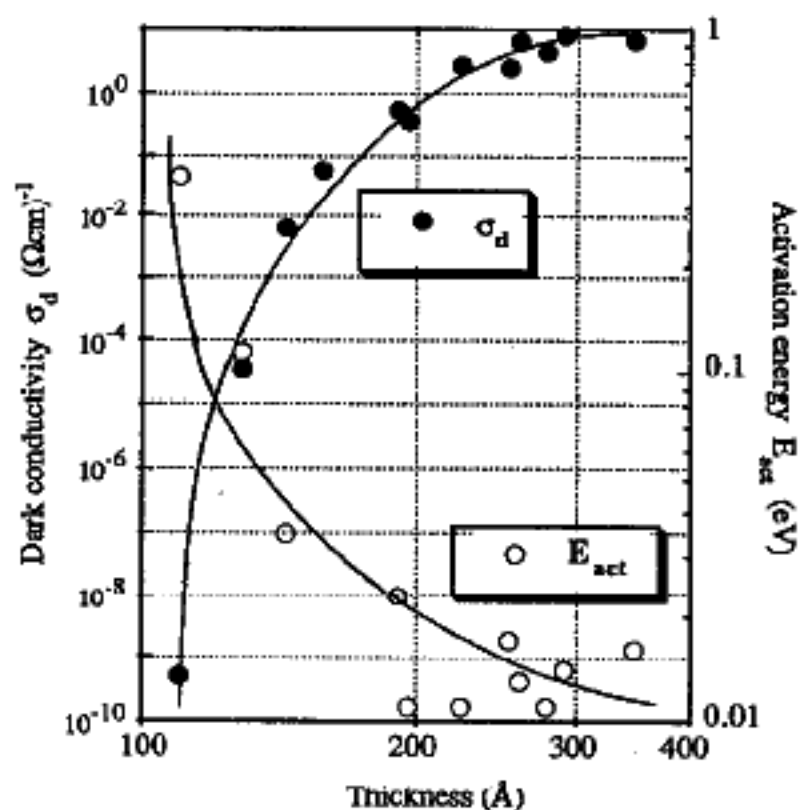


Fig. 1: Dark conductivity and activation energy as a function of <p> μ c-Si:H film thickness (diborane-doped).

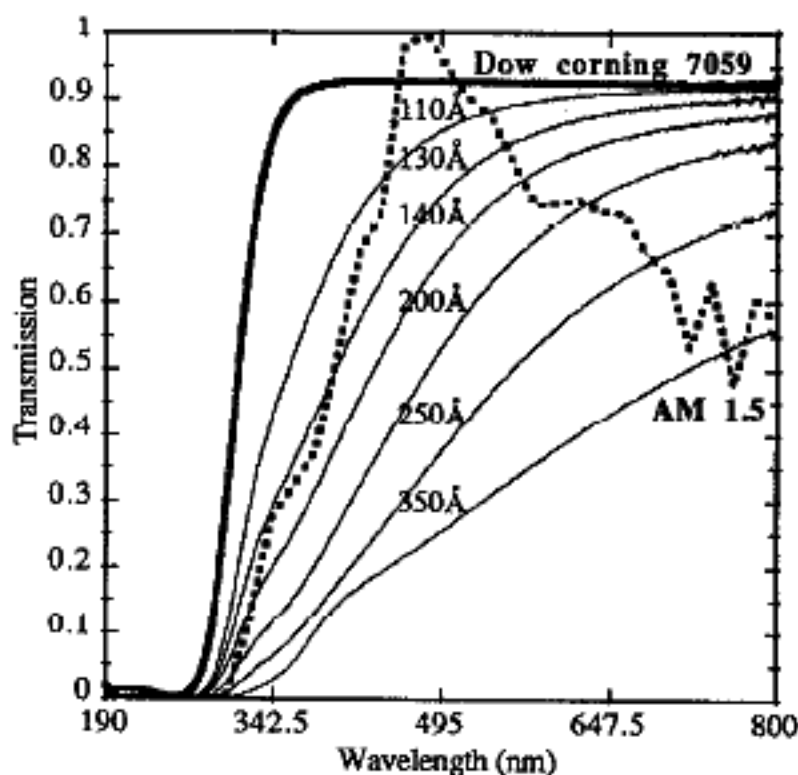


Fig. 2: Spectral transmission of the thickness series of <p> μ c-Si:H films, deposited onto glass substrates (Dow Corning 7059).

σ_d remains still at really high values of 1 to 10 (Ω cm)⁻¹ down to thicknesses of about 200 Å, while beyond this value the conductivity begins to fall and E_{act} to increase. The conductivity reaches, even for thinner films (~ 150 Å), remarkably high values of $> 10^{-2}$ (Ω cm)⁻¹ which are well above those of doped a-SiC:H ($\sim 10^{-6}$ (Ω cm)⁻¹). These high conductivities are a reliable monitor for microcrystallinity.

The measurements were carried out using Al contacts (1000 Å) with a 1 mm gap. The thinner the investigated films are, the more important influence of e.g. nucleation on size effects will become. A reliable and correct characterisation of such thin films is therefore very difficult and strongly substrate-dependent. Possibly, conductivity and activation energy of the films would be seen not to change as strongly, if the films could be characterised by a sandwich configuration.

The solar cell device will probably show the thickness influence more evidently, but in this case the roughness of the TCO, too, will significantly influence growth and properties of the thin $\langle p \rangle$ $\mu\text{c-Si:H}$ window layer.

These thin window layers were further characterised by spectral transmission. Fig. 2 shows the transmission curves obtained from the layers of the thickness series, deposited onto glass; the transmission of the substrate is also plotted; for comparison, the sunlight spectrum is also given.

Films between 110 and 140 Å show a remarkable transparency in the important visible range of the sun light.

An extensive study of these thin $\langle p \rangle$ doped films (optimisation and characterisation) will be published later.

b) Compensated $\mu\text{c-Si:H}$ (potentially active layer)

To compensate the $\langle n \rangle$ -type character of undoped $\mu\text{c-Si:H}$ material, small amounts of diborane (B_2H_6) were systematically added to the gas mixture. Fig. 3 shows the response of these experiments on the dark conductivity and the activation energy in function of very light doping ("micro-doping").

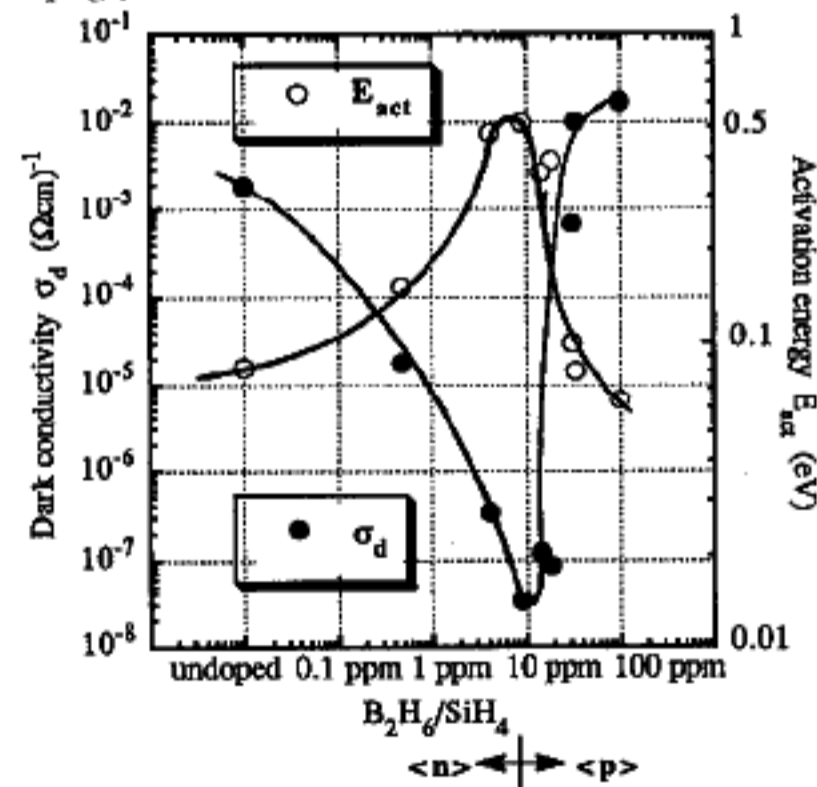


Fig. 3: Variation of dark conductivity and activation energy as a function of "micro-doping" with B_2H_6 .

It is clearly shown that the Fermi level position reacts sensitively to the diborane partial pressure. Micro-doping shifts

the dark conductivity over a wide range from $2 \times 10^{-3} (\Omega\text{cm})^{-1}$ for the undoped material to $3 \times 10^{-8} (\Omega\text{cm})^{-1}$ at the compensation point. In the same way the activation energy increases from 80 meV to the maximum value of 517 meV. Further doping leads to a sharp increase of σ_d to $\langle p \rangle$ -type material with again smaller values for E_{act} . The very sharp compensation point is obtained at a concentration of about 10 ppm B_2H_6 in SiH_4 .

The activation energy was determined by a temperature ramp of the dark conductivity from 200 °C down to room temperature (RT). The Arrhenius plot of σ_d shows for the higher temperatures a steeper decrease than for temperatures below 100 °C. We plotted therefore the lower values of E_{act} which correspond to the drawn RT conductivity points in fig. 3.

The achieved compensation of the material at ~ 10 ppm is in well agreement with the work reported in [6, 7] using a remote PECVD system. The maximum of the photoconductive gain of 6×10^3 at 100 mW/cm² for the compensated $\mu\text{c-Si:H}$ is a little higher than the one observed in [6, 7]. In contrast to [6, 7] where an activation energy of 0.7 eV is reported we observe a smaller value of only 0.517 eV for the compensated material.

Degradation of the compensated layers

The stability behaviour of the $\mu\text{c-Si:H}$ under light exposure was performed on three different films in fig. 3. During the light-soaking the photocurrent of all three samples was simultaneously monitored: the intensity of the sodium lamp used (500 mW/cm², $\sim 1.5 \times 10^{18}$ photons/cm²s) was controlled by a photodiode in parallel. Fig. 4 shows the photoconductivity versus light exposure time. The behaviour of the three samples

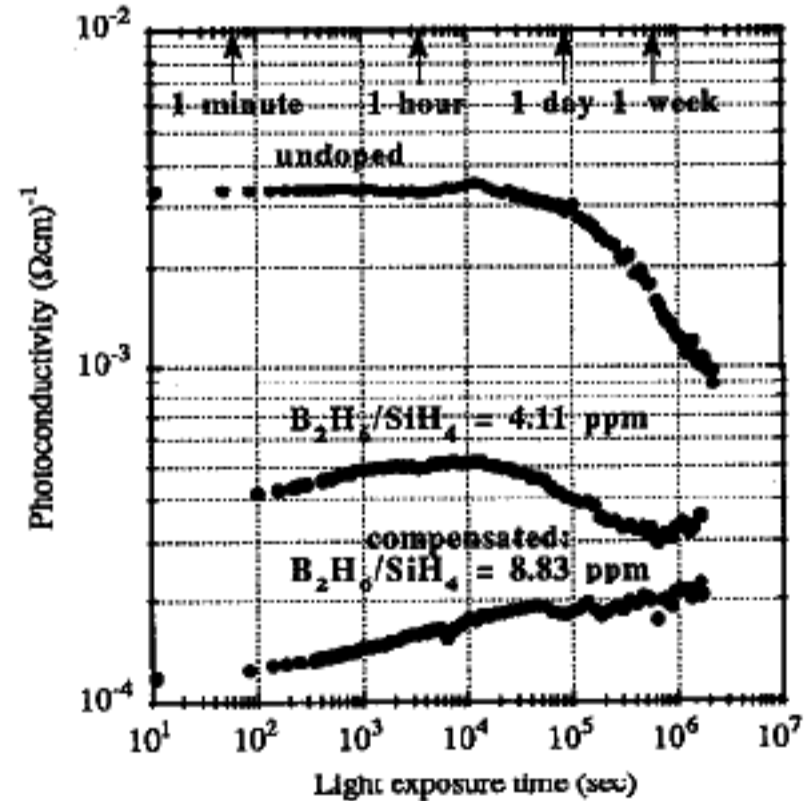


Fig. 4: Simultaneous long-time light exposure of three different $\mu\text{c-Si:H}$ films. The light source was a sodium lamp ($\lambda = 590$ nm) of 500 mW/cm². The films were kept at 40 °C.

is very surprising. While the σ_{ph} of the undoped material slowly decreases by long-term illumination, in the compensated sample (8.83 ppm) in contrast σ_{ph} seems to increase slightly with time. The undercompensated probe (4.1 ppm, slightly $\langle n \rangle$ -type) shows a small fluctuation but remains more or less constant over the observed time period. These degradation experiments, which were carried out under a strong light source, are very encouraging: the new photovoltaic material has now to be explored by light-soaking of the whole solar cell device, where all possible effects of degradation (field, interface effects) are taken into account.

c) p-i-n solar cells

In a previous paper we have already reported about the strong peripheral effect. By a simple p-i-n deposition through a metal mask a better definition of the active cell area could be obtained. All solar cell data presented in this paper are based on this technique (see fig. 5). The areas of the mask holes were 8.55 to 80.12 mm².

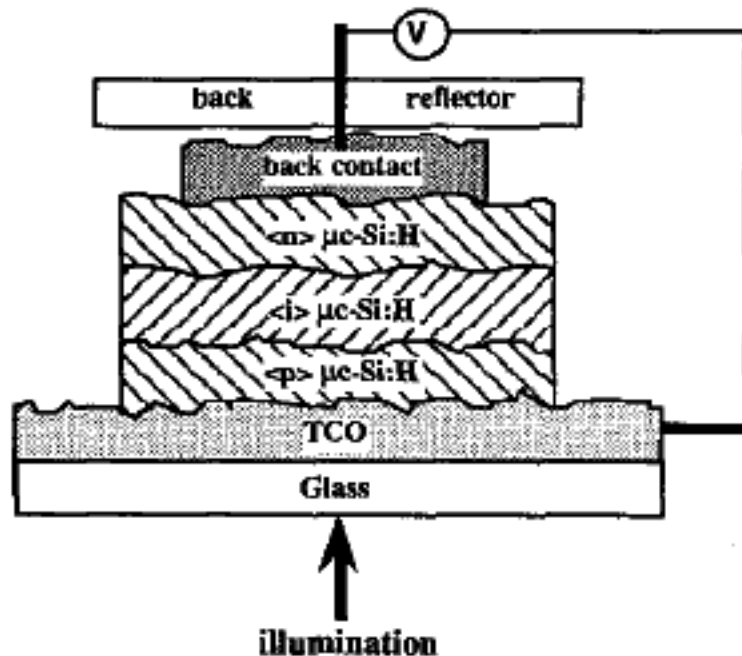


Fig. 5: Structure of the $\mu\text{c-Si:H}$ p-i-n solar cell with a back reflector.

For our present study, two types of p-i-n solar cell structures were investigated:

1. $\langle p \rangle \mu\text{c-Si:H} / \langle i \rangle \mu\text{c-Si:H} / \langle n \rangle \mu\text{c-Si:H}$
2. $\langle p \rangle \text{a-SiC:H} / \langle i \rangle \mu\text{c-Si:H} / \langle n \rangle \mu\text{c-Si:H}$

In both cells compensated $\langle i \rangle \mu\text{c-Si:H}$ layers were used, in case 1 (see fig. 5) the previously developed $\langle p \rangle \mu\text{c-Si:H}$ window layer was used. In case 2, for reference, a $\langle p \rangle \text{a-SiC:H}$ window layer was prepared.

For comparing the quality of both $\langle p \rangle$ windows we kept the compensated $\langle i \rangle$ layer (~ 10 ppm) constant at a thickness of 0.3 μm . As is well known from the experience with a-Si:H the $\langle n \rangle \mu\text{c-Si:H}$ back contact is not so critical for device performance. The thickness of the $\langle n \rangle$ layer was varied between 100 and 400 \AA .

For cell structure 2, a typical illuminated I-V characteristic is shown in fig. 6: all of these cells show high open circuit voltages (up to 778 mV, which is quite surprisingly high compared to the values reported earlier [4]).

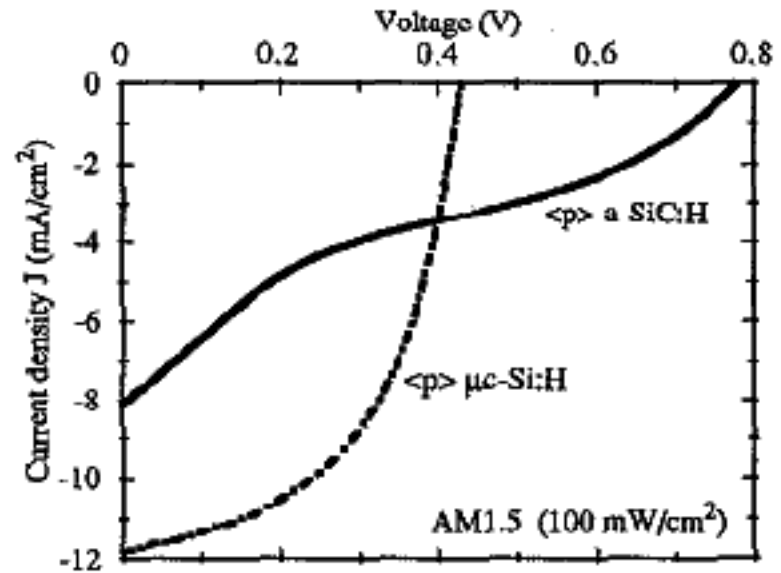


Fig. 6: I-V characteristics of cells with a $\langle p \rangle \mu\text{c-Si:H}$ and a $\langle p \rangle \text{a-SiC:H}$ window layer.

A further investigation of the $\langle p \rangle \text{a-SiC:H}$ window by a variation of the thickness and by adding thin a-Si:H buffers between the $\langle p \rangle$ and $\langle i \rangle$ layers did not solve the problem of the low fill factor so far obtained here (see fig. 6). We suppose that the bend in the active I-V curve is probably caused by a band spike at the p-i interface due to higher gap of the a-SiC:H. Conductivity measurements of $\langle p \rangle \text{a-SiC:H}$ films gave activation energies of about 0.6 eV, which is indeed too high if one takes into account a band gap between 1.1 and 1.4 eV for the $\mu\text{c-Si:H}$. Further work and optimisation of the p-i interface with a-SiC:H should be done to clarify this problem. The high V_{oc} obtained here constitutes a strong motivation to continue with the $\langle p \rangle \text{a-SiC:H}$ window together with intrinsic $\mu\text{c-Si:H}$ base material.

Entirely p-i-n $\mu\text{c-Si:H}$ cells showed from the beginning lower open circuit voltages but better fill factors and higher short circuit currents than cells with $\langle p \rangle \text{a-SiC:H}$ windows (see fig. 6).

An attempt with an ultra-thin a-Si:H buffer layer between the $\langle p \rangle$ and $\langle i \rangle$ layer of about 20 \AA shows, however, that the V_{oc} could thereby be enhanced up to 608 mV. The characteristic in fig. 7 suggests a high series resistance in the cell, which may originate from a too thick a-Si:H buffer. It is well known, for example from MIS device studies, that by optimising the thickness and the quality of the thin buffer layer, one is also able to improve the FF of such a cell, while keeping the high V_{oc} and the J_{sc} .

The preparation of the ultra-thin a-Si:H is very critical because it takes only a few seconds in our fast a-Si:H deposition process compared to the two hours of deposition for a 0.3 μm $\mu\text{c-Si:H}$ cell. By using a more defined a-Si:H layer an enhanced performance seems to be feasible.

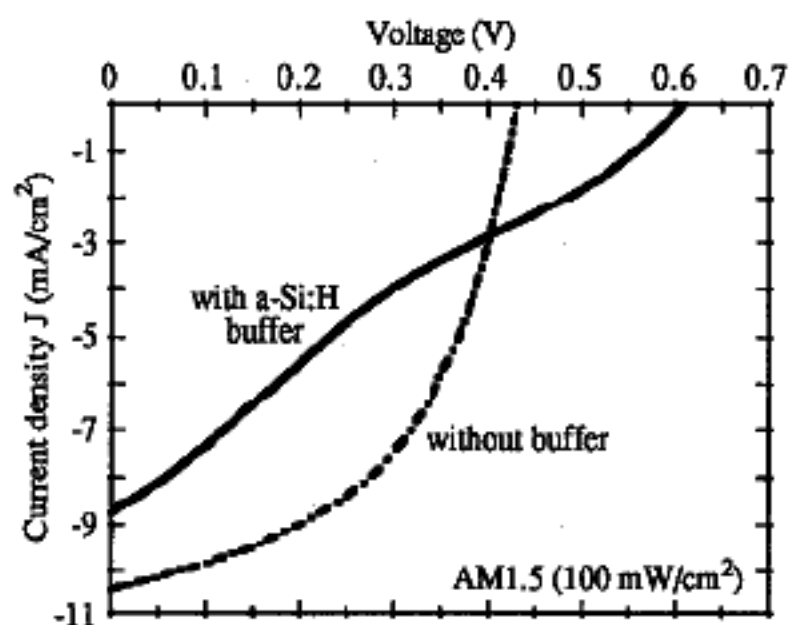


Fig. 7: I-V characteristics of $\mu\text{c-Si:H}$ p-i-n solar cells with and without a thin a-Si:H buffer layer.

The voltage-dependent spectral response measurements showed that the collection efficiency of the $\mu\text{c-Si:H}$ cell under J_{sc} conditions is already close to saturation. Therefore, the thickness of the compensated $\langle i \rangle$ layer was enhanced from 0.3 up to 1.11 μm . The results of these cells are represented in figs. 8 and 9.

As one could assume, the solar cell performance indeed improved with increased $\langle i \rangle$ layer thickness. Specially, the short circuit current increases, whereas the V_{oc} and the FF remained unchanged. Thus, an efficiency of 3.8 % could be measured for the best cells, when putting a white reflector behind the non-metallised gap, as shown in fig. 5, between the external active area radius and the outer border of the metalization. This shows that the IR back reflection properties of the used back contacts were far from being optimised. Hence, a real potential for increasing the cell efficiency is given.

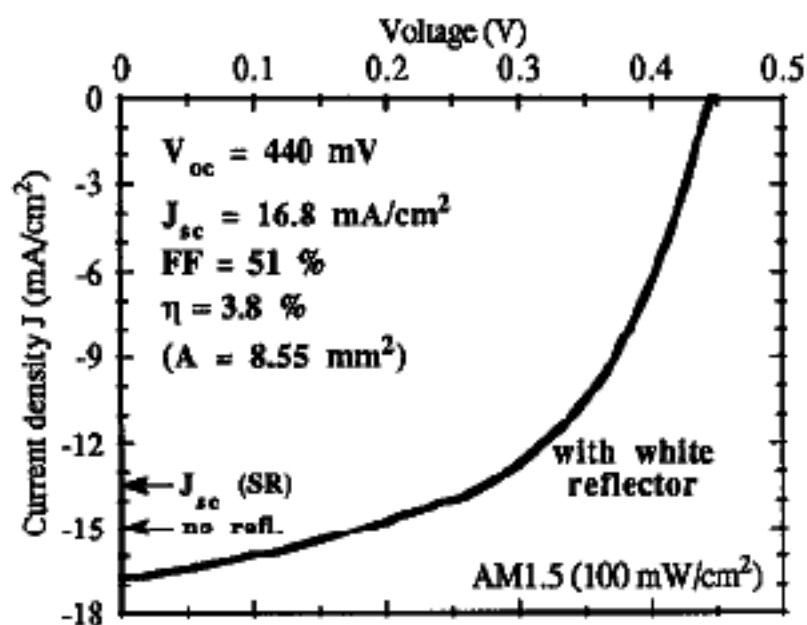


Fig. 8: I-V characteristics: best result of a thick p-i-n entirely $\mu\text{c-Si:H}$ solar cell on ZnO coated glass with external reflector.

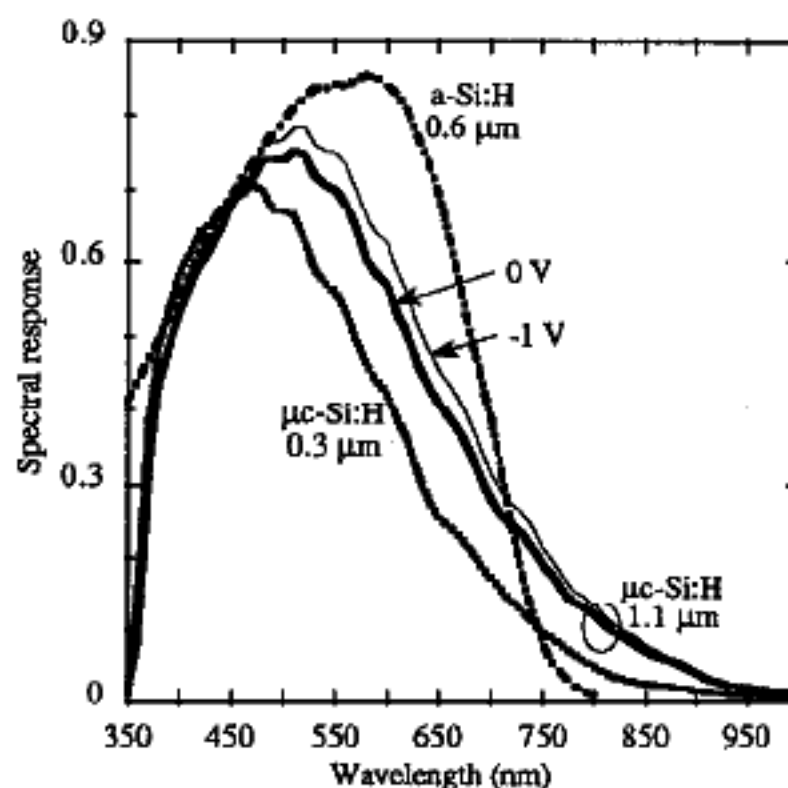


Fig. 9: Spectral response measurements of $\mu\text{c-Si:H}$ p-i-n cells on the metallic back contact (no reflector) with different $\langle i \rangle$ layer thicknesses, in comparison with an a-Si:H standard solar cell.

The spectral response measurements in fig. 9 prove the microcrystalline properties of our base material: due to the reduced "band gap" there is indeed a quantum efficiency in the near infrared where the sensitivity of the a-Si:H is already close to zero. An interesting point of our $\mu\text{c-Si:H}$ cell is even the small signal at longer wavelengths (1000 nm: >1 %), since the "gap" of $\mu\text{c-Si:H}$ was until now generally thought to be around 1.4 eV (\approx 880 nm) [6, 7], somewhere between the gap of crystalline and amorphous silicon. The reverse biasing of the thick cells in the spectral response measurements showed again a rather good collection under J_{sc} -conditions, for carriers being absorbed near the back contact (see fig. 9). The assumption of a strong electrical field in the $\langle i \rangle$ layer is also supported by the dark I-V characteristics where a quality factor of 2 could be found, which can be linked to a space-charge limited recombination current.

Comparing both TCO substrates used, V_{oc} and spectral response (except at very short wavelengths) of the entirely $\mu\text{c-Si:H}$ cells on ZnO and SnO₂ were quite similar. This indicates in contrast to previous work [10], that the growth of the $\mu\text{c-Si:H}$ does not reduce necessarily the quality of the SnO₂ (transparency and conductivity), which is known not to be resistant to atomic hydrogen. The only explanation for the good interface obtained is the sufficiently high growth rate of 1 Å/s, which seems to be high enough so as to cover the sensitive SnO₂ within a short time.

From figs. 8 and 9 one can infer that the efficiency of the entirely $\mu\text{c-Si:H}$ solar cell may possibly be further increased by growing thicker $\langle i \rangle$ layers. It would be interesting to find the thickness where the collection of "deep" photogenerated carriers becomes limited. As already mentioned, an optimised

a-Si:H buffer enables us to improve the open circuit voltage and thus the efficiency. These results show that compensated $\mu\text{-Si:H}$ may really be an excellent photovoltaic material and is worth a more intensive study in future.

Before degradation experiments will be started on solar cells, higher initial efficiencies have to be obtained. This is important in order to conclude whether there is a net gain in stable efficiencies, as compared to a standard a-Si:H p-i-n cell, or not.

CONCLUSIONS

Starting from previously obtained results where the VHF-GD process showed to be a very suitable technique for preparing doped highly-conductive $\mu\text{-Si:H}$ layers, a downscaling of the film thickness could be successfully performed. Thus, thin $\langle p \rangle$ -type doped $\mu\text{-Si:H}$ layers can now be prepared and could become excellent window layers for solar cell applications. The VHF-GD process can produce undoped $\mu\text{-Si:H}$ layers that are an active photovoltaic material, although having low activation energies (due to extrinsic impurities, etc.). Therefore a "micro-doping" technique was introduced for the $\langle i \rangle$ layer, in order to shift the Fermi level towards midgap, thus obtaining compensation of the initially $\langle n \rangle$ -type material. Light-soaking experiments with an intensive high pressure sodium lamp have shown a better stability in the photoconductivity of the new, compensated $\mu\text{-Si:H}$ films; however, more detailed studies with other techniques have to be applied before claiming a better stability for these films and for the whole solar cells.

Using such compensated material for solar cell applications, the extension of the built-in field into the cell could be improved compared to our previously published results (better field uniformity). Thus, the cells showed an increase in the infrared collection for wavelengths above 800 nm, which could never be observed in standard amorphous p-i-n solar cells. This fact proves again the microcrystallinity of the $\langle i \rangle$ layer.

The results presented have shown a solar cell efficiency of 3.8 %, that could be further improved following two ways: first, by optimising the p-i interface with an a-Si:H buffer layer in order to increase the open circuit voltage, and secondly, by increasing the $\langle i \rangle$ layer thickness in order to obtain higher short circuit currents. A further potential for increasing the quantum efficiency lies in the optimisation of the back contact reflector for the infrared light.

If the better stability of the all $\mu\text{-Si:H}$ solar cells can be proven, microcrystalline silicon could become a new encouraging thin film base material, that could contribute to a solution to the photovoltaic problem provided the efficiency can be increased close to 10 %.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. H. A. Aulich of Siemens Solar for having provided the ZnO coated glass. We want also to thank Dr. Ch. Fortmann and U. Kroll for helpful discussions

and S. Dubail for substrate preparation. This work was supported by Swiss Federal Research Grant EF-REN (90)045.

REFERENCES

- [1] K. Prasad, "Microcrystalline silicon prepared with very high frequency glow discharge process", thesis 1991, Institute of Microtechnology, University of Neuchâtel.
- [2] K. Prasad, F. Finger, H. Curtins, A. Shah, J. Baumann, "Preparation and characterisation of highly conductive phosphorus doped $\mu\text{-Si:H}$ films deposited using the VHF-GD technique", *Mat. Res. Soc. Symp.*, **164**, 1989, p. 27.
- [3] K. Prasad, U. Kroll, F. Finger, A. Shah, J.-L. Dorier, A. Howling, J. Baumann, M. Schubert, "Highly conductive microcrystalline silicon layers for tunnel junctions in stacked amorphous silicon based solar cells", *Mat. Res. Soc. Symp.*, **219**, 1991, p. 469.
- [4] R. Flückiger, J. Meier, H. Keppner, U. Kroll, A. Shah, O. Greim, M. Morris, J. Pohl, P. Hapke, R. Carius, "Microcrystalline silicon prepared with the VHF-GD technique for p-i-n solar cell applications", *11th EC PVSEC*, 1992, pp. 617 - 620.
- [5] A.A. Howling, J.-L. Dorier, Ch. Hollenstein, U. Kroll, F. Finger, "Frequency effects in silane plasmas for PECVD", *J. Vac. Sc. Technol.*, **A10**, 1992, p. 1080.
- [6] C. Wang, G. Lucovsky, "Intrinsic microcrystalline silicon deposited by remote PECVD: a new thin-film photovoltaic material", *21st IEEE PVSC 1990*, pp. 1614 - 1618.
- [7] M.J. Williams, C. Wang, G. Lucovsky, "A comparative study of the light-induced defects in intrinsic amorphous and microcrystalline silicon deposited by remote plasma enhanced chemical vapour deposition", *Proc. Intern. Meeting on the Stability of a-Si:H*, Golden (1991).
- [8] H. Liu, M. Xu, "The Staebler-Wronski effect in microcrystalline silicon films", *Solid State Comm.*, **58(9)**, 1986, pp. 601 - 603.
- [9] D. Fischer et al., "VHF plasma deposition for low-cost a-Si:H solar cells", *10th EC PVSEC*, Lisbon 1991, p. 201.
- [10] C. Carvalho, E. Fortunato, M. Vieira, R. Martins, B. Fernandes, L. Guimaraes, "Role of hydrogen plasma on the structural and electro-optical properties of transparent conductive oxides", *6th PVSEC*, New Dehli 1992, pp. 667 - 671.