

INTRINSIC MICROCRYSTALLINE SILICON ($\mu\text{c-Si:H}$) - A PROMISING NEW THIN FILM SOLAR CELL MATERIAL

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ABSTRACT

"Compensated" microcrystalline silicon is obtained by adding 8 - 20 ppm diborane in the plasma gas phase. p-i-n cells with such i-layers have increased infrared sensitivity, when compared to a-Si:H p-i-n cells. The preparation of the world's first "mixed stacked" a-Si:H/ $\mu\text{c-Si:H}$ tandem cell with an initial efficiency of 9.1 % is reported. The $\mu\text{c-Si:H}$ cells showed no degradation of the cell performance under intense light-soaking. Typical properties of the $\mu\text{c-Si:H}$ cell indicate that the electronic transport is dominated by the crystalline phase of the material.

INTRODUCTION

Light-soaking experiments on amorphous (a-Si:H) and microcrystalline silicon ($\mu\text{c-Si:H}$) have generally shown $\mu\text{c-Si:H}$ to be more stable or even completely stable under light-exposure [1-4]. This fact encouraged us to incorporate the intrinsic microcrystalline silicon in a p-i-n solar device [1, 5-7]. According to previous measurements, $\mu\text{c-Si:H}$ turns out to be a defect-rich material with defect densities in the order of 10^{17} to 10^{18} per cm^{-3} [2, 8-10]. The defects are proposed to be located at the grain boundaries or in amorphous zones between the crystallites. The high defect densities were one of the reasons why $\mu\text{c-Si:H}$ did not receive much scientific and technological interest so far. In the present study we show that despite this intrinsic $\mu\text{c-Si:H}$ has the potential to be a very promising thin film solar cell material.

Compared to the conventional 13.56 MHz plasma process, the Very High Frequency (VHF) technique has several advantages for the growth of $\mu\text{c-Si:H}$ [11, 12], as e.g. higher deposition rate and larger grain sizes. Results from plasma diagnostics [13] and impedance analysis [14] suggest that lower ion energies and a higher atomic hydrogen flux to the growth surface lead to a favourable growth of $\mu\text{c-Si:H}$ under VHF conditions.

As-grown undoped intrinsic (i) $\mu\text{c-Si:H}$ is a n-type semiconductor. This is probably due to its high oxygen content and possibly also to internal structural effects. In the first part of the paper we will point out the effect on i $\mu\text{c-Si:H}$ properties of adding small traces of diborane to the plasma phase. The absorption spectra of such "compensated" $\mu\text{c-Si:H}$ will be compared with that of amorphous silicon. In the second part, the effect of "compensated" i-layers on the properties of fully $\mu\text{c-Si:H}$

p-i-n solar cells as well as the world's first a-Si/ $\mu\text{c-Si}$ tandem cell will be presented. The light-induced degradation of $\mu\text{c-Si:H}$ and a-Si:H p-i-n cells under 6 suns illumination will be compared.

EXPERIMENTAL

All films and solar cells were deposited in a single VHF-GD chamber reactor at an excitation frequency of 70 MHz. The properties of p-doped $\mu\text{c-Si:H}$ window layers and the less critical n $\mu\text{c-Si:H}$ back contact for the $\mu\text{c-Si:H}$ p-i-n cell were recently reported elsewhere [1, 15-16]. For the intrinsic $\mu\text{c-Si:H}$ we used the following deposition parameters: $T_{\text{dep}} = 220^\circ\text{C}$, $p = 0.4$ mbar, $P = 7$ W, $\text{SiH}_4/\text{total} \sim 2-3\%$, leading to a deposition rate of around 0.9 \AA/s . To compare film properties directly with the cell devices, the film thickness in the compensation study was done on 1.5 and 1.8 μm films, i.e. relatively thick $\mu\text{c-Si:H}$ films. In a previous temperature study [5], where the deposited $\mu\text{c-Si:H}$ films were thinner (0.4 μm), the above parameters led to a material with a high crystalline fraction of over 90 % (Raman spectroscopy) and a crystallite size of around 220 \AA (Scherrer's equation). To compensate the as-grown n-type character of $\mu\text{c-Si:H}$, diborane (B_2H_6) in the ppm range was added to the silane/hydrogen gas mixture. We call this the "microdoping technique". The films were deposited on Corning glass (7059), the p-i-n cells on SnO_2 - and ZnO-coated glass. For dark conductivity measurements coplanar aluminum electrodes were used. Subgap absorption was measured by PDS (Photothermal Deflection Spectroscopy) and calibrated by transmission/reflection spectroscopy.

The microdoping technique was applied to the growth of the i-layer in the $\mu\text{c-Si:H}$ cell. The back metallisation of the cells was made by an ITO/Ag contact. The tandem cell was realized by the open transfer of the a-Si:H top cell from the a-Si:H reactor to the $\mu\text{c-Si:H}$ reactor. The cells were characterised under AM1.5 illumination at 100 mW/cm^2 in a two-source solar simulator (Wacom WXS-140S-10). The short circuit current densities (J_{SC}) were calibrated by integrating spectral response (SR) data in the range of 350 to 1000 nm times AM1.5 sun spectrum.

Previous degradation experiments with a long-term AM1.5 illumination source (outdoor conditions) so far showed no degradation for the entirely $\mu\text{c-Si:H}$ p-i-n device [7]. In order to apply a harder check for stability a 6 sun sodium lamp was used. Taking into account an absorption coefficient of $1.3 \times 10^4 \text{ cm}^{-1}$ at the peak wavelength (590 nm) and the contribution of the ITO/Ag back reflector, almost uniform absorption can be

assumed. During the degradation experiment, the cells were kept at a constant temperature of $46 \pm 2^\circ\text{C}$ (controlled by an infrared thermometer).

Finally, films and cells were characterised by Scanning Electron Microscopy (SEM).

RESULTS AND DISCUSSION

1. Compensation of $\mu\text{c-Si:H}$

The microdoped films were analysed by dark conductivity measurements: in Fig. 1, dark conductivity σ_{dark} and dark conductivity activation energy E_σ are plotted in function of the $\text{B}_2\text{H}_6/\text{SiH}_4$ flux ratio.

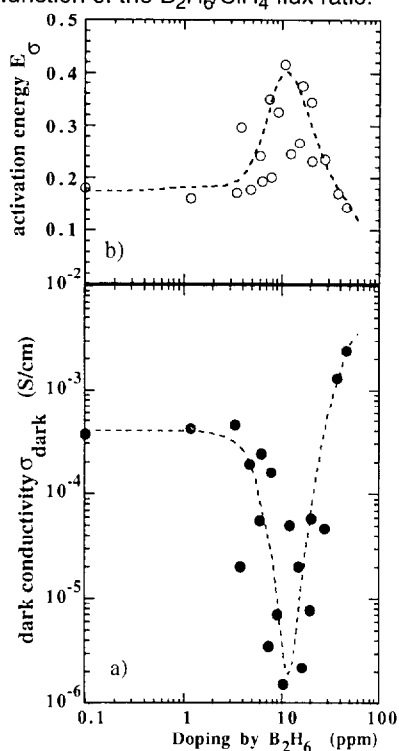


Fig. 1: Room temperature dark conductivity σ_{dark} and dark conductivity activation energy E_σ of $\mu\text{c-Si:H}$ films (thickness: 1.5 - 1.8 μm), in function of the diborane microdoping of the gas phase. The values were obtained by coplanar evaporated Al electrodes. (Dashed lines are merely to guide the eye).

Fig. 1 shows that the electrical properties of the microcrystalline silicon react sensitively on the diborane partial pressure. The σ_{dark} value shows a sharp minimum in the regime of 8 to 20 ppm. The activation energy E_σ peaks in the same range of doping: Here, we find "compensated" $\mu\text{c-Si:H}$ material. One has to notice that all obtained E_σ -values are smaller than half the gap of crystalline silicon. From our experience we observed that the compensation regime is also dependent on the outgassing rate, the dopant desorption of the chamber walls and the type of turbomolecular pump used. Furthermore, a previous study [17] showed that the oxygen content in the films is partially correlated with the deposition rate.

Investigations by SEM indicate a preferential columnar growth of the deposited films (Fig. 2). That means that the electrical properties obtained in Fig. 1 using a copla

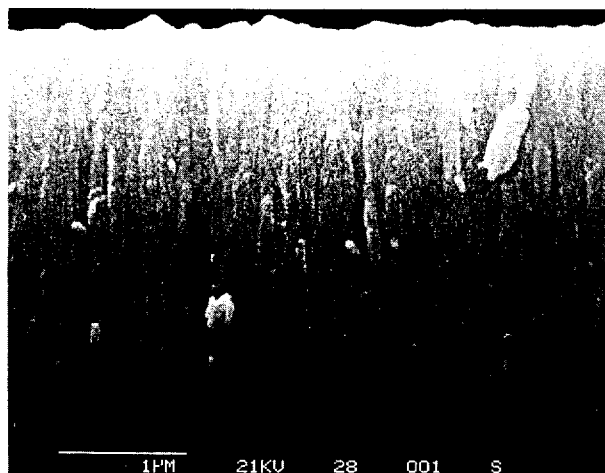


Fig. 2: Cross-section SEM picture of a 2.6 μm thick $\mu\text{c-Si:H}$ film on glass.

planar electrode configuration may differ from those obtained for a sandwich configuration of the film. This fact has to be kept in mind, because the properties relevant to cells are those of vertical transport.

Microcrystalline silicon has a weaker absorption for the short wavelengths; however, in the near-infrared an enhanced absorption can be observed. Fig. 3 shows the absorption spectra of a "compensated" film measured by PDS. A similar absorption behaviour was found by different groups [18, 8]. However, our material seems to have a significant **lower subgap absorption** than that of so far published $\mu\text{c-Si:H}$ data: Our subgap absorption reaches the level of good quality a-Si:H material in the annealed state.

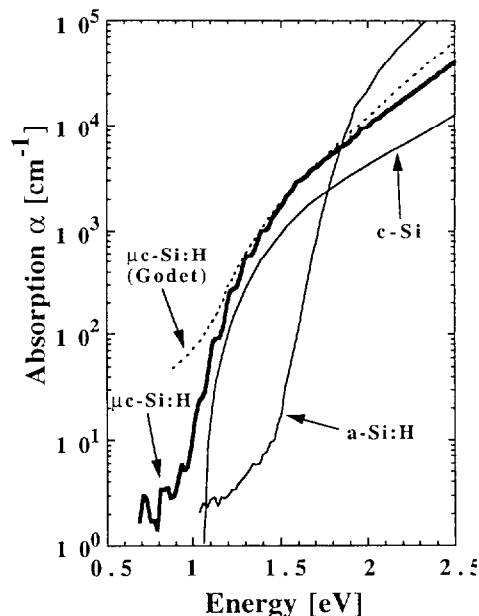


Fig. 3: Absorption spectra of a 1.8 μm thick compensated $\mu\text{c-Si:H}$ film measured by PDS and transmission/reflection spectroscopy. For comparison the spectra of another work [18], of amorphous and crystalline silicon are added.

Somehow, $\mu\text{c-Si:H}$ combines both properties: in the high absorption range it seems to be dominated by the amorphous phase, and in the infrared range by the crystalline phase.

2. Fully $\mu\text{c-Si:H}$ p-i-n solar cells

Microdoping of the i-layer has a very pronounced effect on the cells and on their spectral response (Fig. 4). All three samples presented have the same p-, n-layers, and the same i-layer except for microdoping. Fig. 4 confirms the enhanced infrared absorption of the $\mu\text{c-Si:H}$ cell compared to a-Si:H: however the i layer thickness has to be increased to obtain sufficient J_{sc} .

The highest cell efficiency obtained so far for the entirely $\mu\text{c-Si:H}$ p-i-n solar cell is 4.6 % ($V_{oc} = 375$ mV, FF = 60 %, $J_{sc} = 20.5$ mA/cm², active area 5 mm², i-layer ~1.6 μm). By further increase of the i-layer thickness (1.8 - 2 μm) short circuit current densities of up to 24.4 mA/cm² were obtained. This is significantly above the highest values obtained for amorphous silicon. Further potential for increasing the efficiency lies in an optimization of the p-i interface for achieving higher V_{oc} -values. In a previous study [1] we have shown that V_{oc} -values of 600 mV can be obtained using very thin a-Si:H buffer layers.

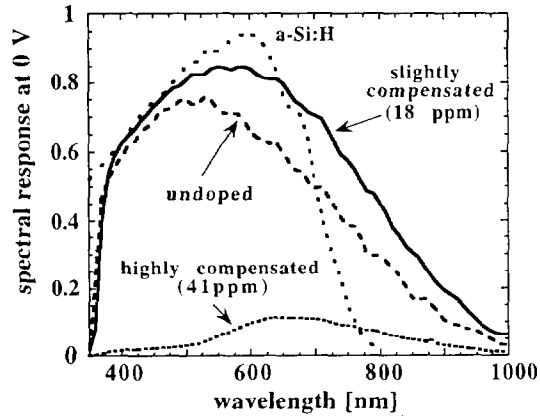


Fig. 4: Influence of microdoping on the spectral response of entirely $\mu\text{c-Si:H}$ p-i-n cells (1.6 μm thickness). For comparison, an a-Si:H cell is also plotted.

3. "Mixed stacked" cells (a-Si:H/ $\mu\text{c-Si:H}$)

The extended spectral response to wavelengths above 800 nm makes $\mu\text{c-Si:H}$ an attractive material for a bottom cell in tandem structures. For the first time, we present a mixed stacked a-Si:H/ $\mu\text{c-Si:H}$ cell. At optimized current matching of the top a-Si:H cell (thickness 0.26 μm) to the $\mu\text{c-Si:H}$ bottom cell (see Fig. 5), a current density of 11.5 mA/cm² for AM1.5 conditions was obtained (top 11.6 mA/cm²). The I-V characteristics of this new tandem cell proves (Fig. 6) that the whole **growth process of the $\mu\text{c-Si:H}$ p-i-n cell is fully compatible** with the amorphous p-i-n cell preparation. The results show that the substitution of conventional a-Si:H or costly a-Ge:H by the $\mu\text{c-Si:H}$ bottom cell opens new ways to increase the efficiency of silicon thin film solar cell.

The morphological cross-section of our new a-Si:H/ $\mu\text{c-Si:H}$ tandem cell is documented by the SEM picture of Fig. 7. The different layers, as the first thinner amorphous top cell on the SnO_2 and the more "rocky" $\mu\text{c-Si:H}$ bottom cell on the top, are clearly visible.

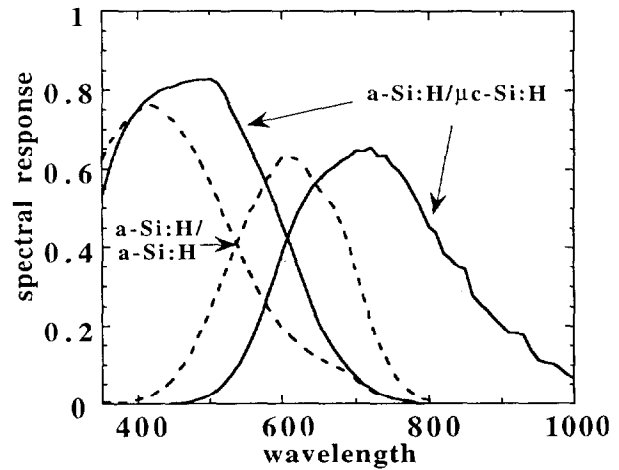


Fig. 5: Spectral response of the a-Si:H/ $\mu\text{c-Si:H}$ tandem solar cell in comparison with a standard a-Si:H/a-Si:H tandem cell. The J_{sc} values for AM1.5 conditions are 11.5 mA/cm² for the $\mu\text{c-Si:H}$ bottom and 11.6 mA/cm² for the a-Si:H top cell (active area 8.7 mm²).

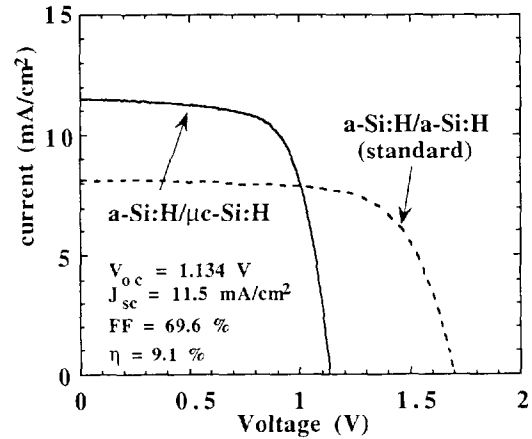


Fig. 6: I-V characteristics under AM1.5 conditions of the a-Si:H/ $\mu\text{c-Si:H}$ tandem cell, in comparison with a conventional a-Si:H/a-Si:H tandem cell.

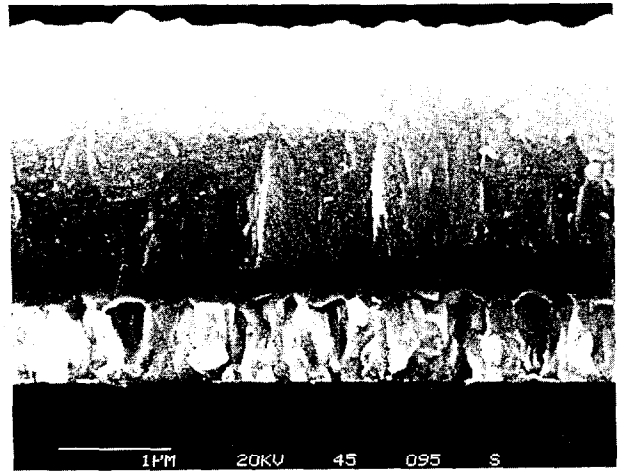


Fig. 7: SEM cross-section micrograph of the a-Si:H/ $\mu\text{c-Si:H}$ tandem cell deposited on SnO_2 -coated glass.

3. Degradation experiments

As already presented [7], the individual $\mu\text{c-Si:H}$ p-i-n cells showed no degradation effect after more than 640 hours of light exposure at AM1.5. In the experiment the 4.6% efficient cell was exposed to the high-intensity sodium lamp. In parallel, an amorphous p-i-n cell of 10% initial efficiency was also exposed. The amorphous cell had a thickness of 0.6 μm , whereas the $\mu\text{c-Si:H}$ 1.6 μm . The result is summarized in Fig. 8, where the kinetics of the degradations are shown: The intense illumination has a strong effect on the amorphous cell which decays already after one day of light exposure to less than 40% of its initial efficiency. Efficiency values given in Fig. 8 are based on an evaluation of standard I-V (simulator) measurements (AM1.5 conditions) before and after the 280 h of intense light exposure.

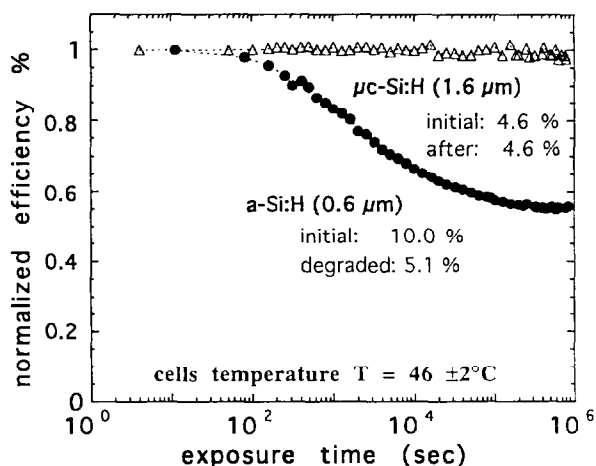


Fig. 8: Degradation kinetics of the normalized efficiencies of a $\mu\text{c-Si:H}$ and an a-Si:H p-i-n solar cell under intensive light illumination (sodium lamp of ~ 6 suns). The cells were precisely characterized before and after 280 h of intense light soaking under AM1.5 conditions (numerical values).

The experiment presented in Fig. 8 confirms previous results from film studies: microcrystalline silicon is more stable than amorphous silicon. The degradation might be masked by the fact that up to now only an efficiency of 4.6% efficiency could be obtained, on the other hand the $\mu\text{c-Si:H}$ cell is much thicker than the amorphous one and should be more affected by light soaking.

Voltage-dependent SR measurements have recently [7] indicated that the carrier transport in complete $\mu\text{c-Si:H}$ p-i-n cells is different from that of a-Si:H cells and might be partly supported by diffusion, in addition to drift transport; systematic studies have yet to be conducted.

CONCLUSIONS

Compensated microcrystalline silicon has the potential to become a promising new material for thin film solar cells. The high infrared absorption and the surprising stability favours the material as a bottom cell in $\text{a-Si:H}/\mu\text{c-Si:H}$ tandems or even in triple cell structures. The first $\text{a-Si:H}/\mu\text{c-Si:H}$ mixed stacked cell with an initial efficiency of 9.1% and an enhanced short circuit current density of 11.5 mA/cm^2 was realized by our group. The results

have shown that the growth of entirely microcrystalline cells is fully compatible with the growth of amorphous silicon, when using the VHF-GD technique at 70 MHz.

The electronic transport in $\mu\text{c-Si:H}$ films turns out to be describable by the model used for polycrystalline silicon: This means that the crystallites determine the transport properties. Because of their higher infrared sensitivity, their improved stability against light-soaking, because of the fact that activation energies are smaller than the half gap of crystalline silicon, and because of the partly diffusion-like characteristics, we suggest that electronic transport of our $\mu\text{c-Si:H}$ cells is dominated by the crystalline phase of the material. The role of the grain boundaries where the high defect densities are supposed to be located is still unclear and not understood. However, it seems that the overall cell behaviour is not affected by these high defect densities.

The limits of this new solar cell material, w.r.t. the V_{oc} , J_{sc} and FF are open and requires for further investigation. For future applications two problems have to be solved: a further increase in efficiency and a higher deposition rate.

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REFERENCES

- [1] R. Flückiger, J. Meier, H. Keppner, M. Götz, and A. Shah, *Proc. 23rd IEEE PVSC*, 1993, p. 839.
- [2] H. Liu et al., *Solid State Comm.*, **58**(9), 1986, p. 601.
- [3] M.J. Williams et al., *AIP Conf. Proc.*, **234**, 1991, 211.
- [4] R. Flückiger, J. Meier, M. Götz and A. Shah, to be published in *J. Appl. Phys.*, Jan. 1995.
- [5] R. Flückiger et al., *Proc. 11th EC PVSEC*, 1992, 617.
- [6] J. Meier, R. Flückiger, H. Keppner, M. Götz, A. Shah, *Proc. 12th EC PVSEC*, p. 1237.
- [7] J. Meier, R. Flückiger, H. Keppner, A. Shah, *Appl. Phys. Lett.*, **65**, 1994, p. 860.
- [8] H.N. Liu, Y.L. He, F. Wang, and S. Grebner, *J. Non-Cryst. Solids*, **164-166**, 1993, p. 1005.
- [9] P.G. LeComber, G. Willeke, and W.E. Spear, *J. Non-Cryst. Solids*, **59/60**, 1983, p. 795.
- [10] F. Finger et al., *Phil. Mag. Lett.*, **70**, 1994, p. 247.
- [11] R. Flückiger et al., *Proc. MRS*, Boston 1994, in press.
- [12] F. Finger, P. Hapke, M. Luysberg, R. Carius, H. Wagner, *Appl. Phys. Lett.*, **65**(20), 1994, p. 2588.
- [13] A.A. Howling, J.-L. Dorier, Ch. Hollenstein, U. Kroll, F. Finger, *J. Vac. Sci. Technol.*, **A10** (1992), p. 1080.
- [14] U. Kroll et al., *Proc. MRS*, **336**, 1994, in press.
- [15] R. Flückiger et al., *Proc. MRS*, **336**, 1994, in press.
- [16] D. Fischer, H. Keppner, F. Finger, K. Prasad, A. Shah, *Proc. 10th EC PVSEC*, 1991, p. 201.
- [17] U. Kroll, J. Meier, H. Keppner, A. Shah, to be published.
- [18] C. Godet, Ph.D. thesis, Univ. Paris-Sud, Centre D'Orsay (1987).