ELSEVIER

Solar Energy Materials and Solar Cells 49 (1997) 27–33

Solar Energy Materials and Solar Cells

# Controlled nucleation of thin microcrystalline layers for the recombination junction in a-Si stacked cells

N. Pellaton Vaucher[a,*], B. Rech[b], D. Fischer[a], S. Dubail[a], M. Goetz[a], H. Keppner[a], N. Wyrsch[a], C. Beneking[b], O. Hadjadj[c], V. Shklover[d], A. Shah[a]

[a] *Institut de Microtechnique, Université de Neuchâtel, Breguet 2, 2000 Neuchâtel, Switzerland*
[b] *Institute of Thin Film and Ion Technology, Research Centre Jülich, 52425 Jülich, Germany*
[c] *Laboratoire de Physique des Couches Minces, Ecole Polytechnique, 91128 Palaiseau, France*
[d] *Laboratorium für Kristallographie, ETH Zentrum, 8092 Zürich, Switzerland*

**Abstract**

In high-efficiency a-Si : H based stacked cells, at least one of the two layers that form the internal n/p junction has preferentially to be microcrystalline so as to obtain sufficient recombination at the junction [1–6]. The crucial point is the nucleation of a very thin μc-Si : H layer on an amorphous (i-layer) substrate [2, 4]. In this study, fast nucleation is induced through the treatment of the amorphous substrate by a $CO_2$ plasma. The resulting n-layers with a high crystalline fraction were, however, found to reduce the $V_{oc}$ when incorporated in tandem cells. The reduction of the $V_{oc}$ could be restored only by a precise control of the crystalline fraction of the n-layer. As a technologically more feasible alternative, we propose a new, combined n-layer, consisting of a first amorphous layer for a high $V_{oc}$, and a second microcrystalline layer, induced by $CO_2$ treatment, for a sufficient recombination at the n/p junction. Resulting tandem cells show no $V_{oc}$ losses compared to two standard single cells, and an efficient recombination of the carriers at the internal junction as proved by the low series resistance (15 $\Omega cm^2$) and the high FF ( $\geq$ 75%) of the stacked cells.

*Keywords:* a-Si:H based stacked cells; Combined n-layer; n/p junction; Tandem cells

* Corresponding author.


*PII* S0927-0248(97)00172-4

## 1. Introduction

Tandem structures are essential for high-stabilised-efficiency a-Si : H-based solar cells. In such structures, the recombination junction (n/p junction, also called "tunnel junction") has to be efficient in terms of recombination of carriers and of low absorption.

As suggested by Hou [1], a high-recombination layer must be incorporated into the n/p contact for efficient recombination. Two alternatives must be considered: (1) the insertion of an additional recombination layer at the n/p interface [7, 8], and (2) obtaining recombination through the doped layers themselves. The first alternative has the disadvantage of inducing additional parasitic optical absorption, leading to current losses in the device [9]. The second alternative leads to the application of microcrystalline (μc-Si : H) doped layers [2–6]. The higher doping density as well as the smaller mobility gap in these layers allows for efficient recombination.

In the case of superstrate cells (i.e. glass/TCO/p–i–n–p–i–n type), microcrystalline p-layers are not likely to fulfil such demands because of the necessity to find crystallites directly at the n/p junction (i.e. from the beginning of the p-layer's growth) and the sensitivity of the n/p interface to any surface treatment that may have to be used for initiation of μc-Si layer growth.

In this paper we, therefore, study the growth of microcrystalline n-layers on intrinsic amorphous i-layer and the application of these layers in high-efficiency p–i–n–p–i–n tandem cells.

## 2. Experimental

This study concentrates on n-type layers and on their implication in superstrate-type two-stacked cells. All layers and solar cells were prepared with VHF-GD at 70 MHz, in a UHV single-chamber deposition system equipped with a load-lock.

For film analysis, the n-layers were prepared in the same way as in tandem cells (i.e. on i-layer substrates deposited in the same run as the subsequent n-layer). Conductivities were measured in a co-planar configuration, at room temperature. The crystallite fraction was determined by ellipsometry, performed at Palaiseau. Cross-sectional TEM pictures were obtained at ETH Zürich.

The n/p recombination junction properties are evaluated in complete tandem cells. Cell measurements were performed under a two-source sun simulator (Wacom, "super solar simulator"), at a temperature of 25°C. Currents were evaluated by integration from the spectral response measurement.

## 3. μc-Si : H layers

### *3.1. μc-Si : H growth on a-Si : H substrate*

Deposition of thin μc-Si : H layers has in the past been studied extensively, although often not when deposited on an a-Si : H substrate. The growth of thin μc-Si layers is, however, strongly dependent on the substrate. We effectively observed that a 200 Å thick n-layer deposited under microcrystalline growth conditions on a glass substrate (leading to $\sigma \approx 10$ S/cm) [10] shows no microcrystalline signature when deposited on an a-Si : H layer not exposed to air. This could be explained by a model postulating "epitaxy-like growth" of the amorphous network. To "hide" the amorphous network w.r.t. the growing layer without inserting an extra layer that would disturb the cell behaviour, the a-Si : H i-layer was exposed to a "soft" $CO_2$ plasma (i.e. a short, low power $CO_2$ plasma). Concequently to this pre-treatment of the underlying i-layer, very thin, "truly" microcrystalline layers have been obtained: the conductivity of these films is 2–3 orders of magnitude higher than without the $CO_2$ plasma, reaching values of 1 S/cm for 100–200 Å thick layers, with 70% crystallites volume fraction in the layer (Fig. 1c).

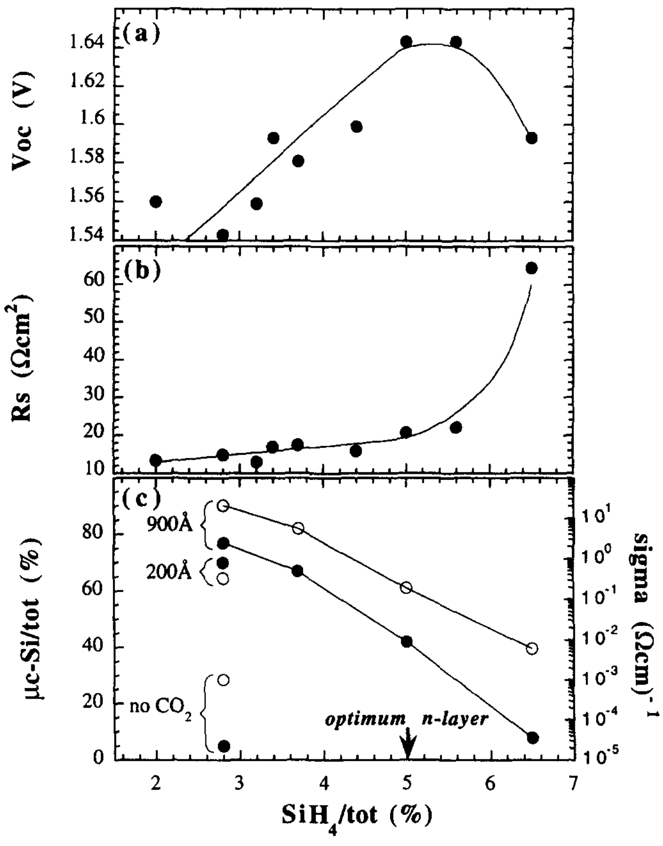


Fig. 1. Influence of the hydrogen dilution during the deposition of the n-layer (after $CO_2$ plasma treatment) on the properties of tandem cells (a, b) and of i(a-Si)/n(µc-Si) samples (c). In part (c), we also present characteristics for n (µc-Si) layers produced without $CO_2$ plasma treatment, as well as characteristics of thinner n-layers. In part (a) the open-circuit voltage $V_{oc}$ of the tandem cells and in part (b) the series resistance $R_s$ of the tandem cells are plotted; in part (c) full dots indicate the crystalline volume fraction (in %) and open dots the dark conductivity (sigma).

### 3.2. μc-Si : H layers in the internal junction of tandem cells

$CO_2$ plasma treatment was applied for the deposition of μc-Si : H n-layers as part of the recombination junction of tandem cells. Although good recombination is obtained as confirmed by the low values of the serial resistance ($\leq 15\,\Omega\,cm^2$), open-circuit voltages of the tandem cells show a loss of as much as 100 mV. We performed the same $CO_2$ pre-treatment on tandem cells with an amorphous internal n-layer (with a recombination layer at the n/p interface to insure reasonable recombination) and no such $V_{oc}$ losses were observed. The $V_{oc}$ losses are therefore not inherent to the $CO_2$ treatment itself, but to the subsequent highly crystalline n-layer.

In order to observe when these $V_{oc}$ losses occur, we scanned the whole range between μc-Si and a-Si of the top n-layer, depositing a set of tandem cells with various hydrogen dilution ratios for this n-layer, after the $CO_2$ plasma. The n-layer was slightly thicker than those used conventionally in tandem cells (350 Å instead of 200 Å), to avoid an influence of a small thickness variation on the $V_{oc}$ and FF. Results are shown in Fig. 1a and Fig. 1b. We can see that the $V_{oc}$ is strongly influenced by the hydrogen dilution ratio; $V_{oc}$ becomes lower for increased $H_2$ dilution.

To understand this phenomenon, the same study of hydrogen dilution was performed on single n-layers deposited on a-Si : H treated by a $CO_2$ plasma. Fig. 1c shows the results of ellipsometry and conductivity measurements: for lower $SiH_4$ content in the gas phase, which corresponds to the decrease of $V_{oc}$ in the tandem cells, the n-layer contains a higher proportion of crystallites (see also Ref. [11]). It comes into evidence that the crystallite ratio has to be carefully controlled to fully realise the efficiency potential of the tandem cell: if it is too high, the band discontinuities at the i/n interface due to the low band gap of the n-layer will be responsible for the $V_{oc}$ losses; on the contrary, when the n-layer becomes amorphous, the recombination of carriers at the n/p junction is not efficient enough and this leads again to $V_{oc}$ and FF losses. The optimum n-layer for tandem cells (5% $SiH_4$/tot, Figs. 1 and 2) is found to

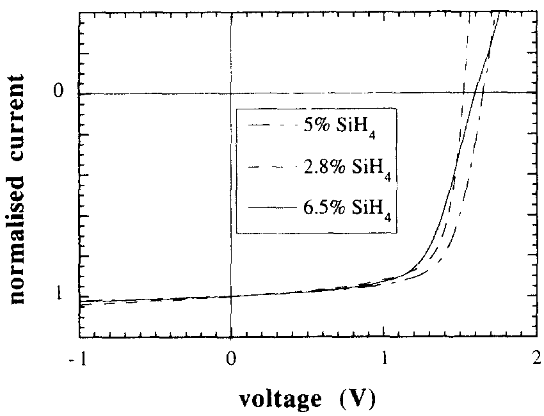


Fig. 2. $I$–$V$ curves of tandem cells with a single n-layer in the n/p recombination junction between the two cells; this single n-layer is deposited under three different hydrogen dilution conditions, but in all three cases after $CO_2$ plasma treatment on the underlying i-layer.

be a layer that is just in the transition region between microcrystalline and amorphous material. To reach this optimum in the critical transition region, however, requires a certain "fine-tuning" of the deposition conditions.

**Remark.** A doping study was performed in the tandem cells with μc-Si : H n-layer deposited from 2.8% $SiH_4$/tot so as to insure that the low $V_{oc}$ is not a consequence of a too low doping level. Results are presented in Fig. 3. Increasing the gas-phase doping ratio pushes down the $V_{oc}$. This behaviour is opposite to the one that we would expect if the activation energy in the n-layer was thereby decreased. The reason why a higher gas-phase doping ratio affects the $V_{oc}$ in such an adverse way has, however, not yet been found.

## 4. New combined n-layer for tandem cells

To avoid the fine-tuning for the deposition of the n-layer in the critical deposition range near the a-Si : H/μc-Si : H transition (as described in Section 3), we have implemented an alternative scheme: a new, combined n-layer was used, consisting of a first amorphous n-layer that assures a high $V_{oc}$, followed by an n-layer with a high crystalline fraction (using the controlled nucleation by $CO_2$ plasma treatment), assuring a good conductivity of the junction. Cross-sectional TEM pictures performed on this type of n-layers put in evidence the existence of crystallites extending through the whole thickness of the "really thin" (less than 100 Å thick) top part of the n-layer after the $CO_2$ plasma (Fig. 4). By employing this double n-layer, a series resistance as low as 15 $\Omega$ cm$^2$ is obtained in a double-stacked a-Si : H/a-Si : H tandem cell, with $V_{oc}$ values that are coherent with the $V_{oc}$ values of the two component cells.

Considering now the current in the tandem cells, this new double n-layer is found to be favourable compared to the μc-Si n-layer with 5% $SiH_4$/tot. The gain in the total

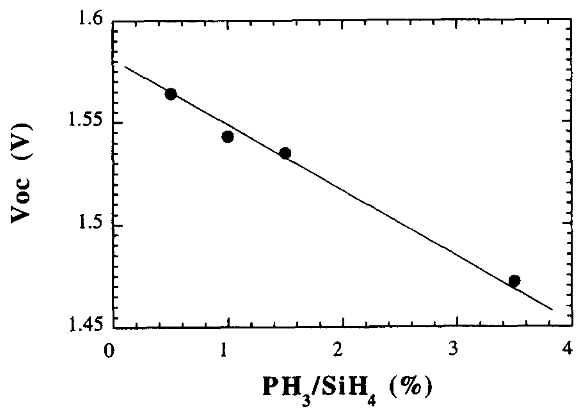


Fig. 3. Open-circuit voltage of a tandem cell as a function of the gas-phase doping ratio of the n-layer in the n/p recombination junction. The hydrogen dilution of the n-layer corresponds to 2.8% $SiH_4/(SiH_4 + H_2)$. $CO_2$ plasma treatment is applied to the i-layer before deposition of the n-layer.

current is of about 0.3 $mA/cm^2$. The reason probably originates in the optical absorption that may be high in the critical 450–600 nm wavelength range for the μc-Si n-layer with an important amorphous phase.

Tandem cells with efficiencies of about 10% are obtained using this double n-layer, even without i-layer engineering such as buffer layers or $H_2$-dilution (Fig. 5).

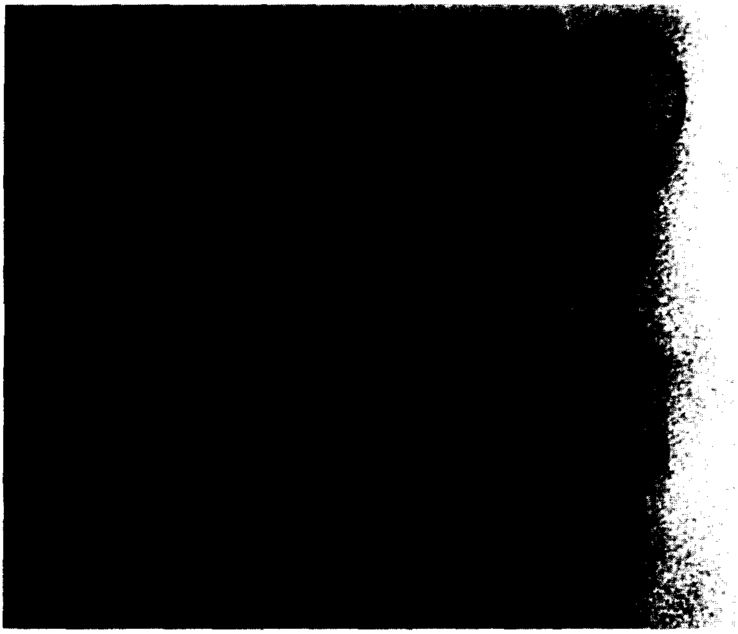

Fig. 4. Cross-TEM picture of the new combined n-layer deposited on an intrinsic a-Si : H layer. Crystallites can be seen extending through the whole thickness of the very thin top layer (after the $CO_2$ plasma).

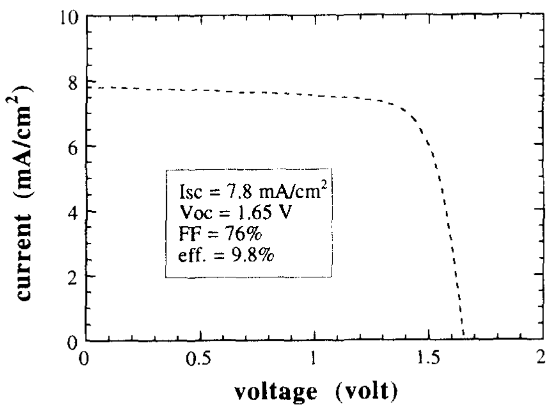


Fig. 5. I–V curve of an a-Si/a-Si tandem cell incorporating the new double n-layer in the n/p recombination junction.

## 5. Summary

With a $CO_2$ plasma, we could control the nucleation of thin microcrystalline layers grown on an a-Si : H substrate. These μc-Si layers with a high crystalline content cannot be used in the recombination junction of tandem cells, because of their low band gap which is responsible for a loss in $V_{oc}$. To recover the complete voltage of the tandem cell, the amorphous phase of the n-layer has to be precisely increased to reach the transition phase between μc-Si and a-Si. This fine tuning can be avoided by the use of a new, combined n-layer: an n-layer that is amorphous near the i/n interface so as to sustain the $V_{oc}$ in the top cell, and microcrystalline with a high crystallite content near the n/p interface to insure sufficient recombination at the junction.

## Acknowledgements

This work was supported by the Swiss Federal Department of Energy BEW/OFEN, grant EF-REN (93)032, by the Swiss Federal Office of Science and Education (OFES), grant 993.0184, within the EU project HELIOS, and by the BMBF (German Federal Ministry of Education and Research).

## References

[1] J.Y. Hou, J.K. Arch, S.J. Fonash, Proc. 22nd IEEE Photovoltaic Specialist Conf., 1991, p. 1260.
[2] L. Yang, L. Chen, S. Wiedeman, A. Catalano, MRS Symp. Proc., vol. 283, 1993, p. 463.
[3] T. Yoshida, K. Maruyama, O. Nabeta, Y. Ichikawa, H. Sakai, Y. Uchida, Proc. 19th IEEE Photovoltaic Specialist Conf., 1987, p. 1095.
[4] M. Kolter, C. Beneking, D. Pavlov, T. Eickhoff, P. Hapke, S. Frohnhoff, H. Münder, H. Wagner, Proc. 23rd IEEE Photovoltaic Specialist Conf., 1993, p. 1031.
[5] P. Lechner, H. Schade, B. Scheppat, A. Bubenzer, Proc. 11th EC PVSEC, 1992, p. 568.
[6] F. Nakabeppu, T. Ishimura, K. Kumagai, K. Fukui, MRS Symp. Proc., vol. 164, 1990, p. 389.
[7] D.S. Shen, R.E.I. Schropp, H. Chatham, R.E. Hollingsworth, J. Xi, P.K. Bhat, Proc. 21st IEEE Photovoltaic Specialist Conf., 1990, p. 1471.
[8] H. Yamagishi, K. Asaoka, W.A. Nevin, T. Fujihara, H. Nishio, T. Endoh, K. Tsuge, Y. Tawada, Proc. 4th PVSEC, 1989, p. 415.
[9] S. Wiedeman, J. Morris, L. Yang, Proc. 21st IEEE Photovoltaic Specialist Conf., 1990, p. 1529.
[10] K. Prasad, U. Kroll, F. Finger, A. Shah, J.-L. Dorier, A. Howling, J. Baumann, M. Schubert, MRS Symp. Proc., vol. 219, 1991, p. 469.
[11] K. Prasad, F. Finger, H. Curtins, A. Shah, J. Baumann, MRS Symp. Proc., vol. 164, 1990, p. 27.