

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

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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 $\mu\text{c-Si:H}$ 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 ($15 \Omega\text{cm}^2$) 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

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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 ($\mu\text{c-Si : H}$) 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 $\mu\text{c-Si}$ 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. $\mu\text{c-Si : H}$ layers

3.1. $\mu\text{c-Si : H}$ growth on a-Si : H substrate

Deposition of thin $\mu\text{c-Si : H}$ layers has in the past been studied extensively, although often not when deposited on an a-Si : H substrate. The growth of thin $\mu\text{c-Si}$ 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” CO₂ plasma (i.e. a short, low power CO₂ plasma). Consequently 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 CO₂ plasma, reaching values of 1 S/cm for 100–200 Å thick layers, with 70% crystallites volume fraction in the layer (Fig. 1c).

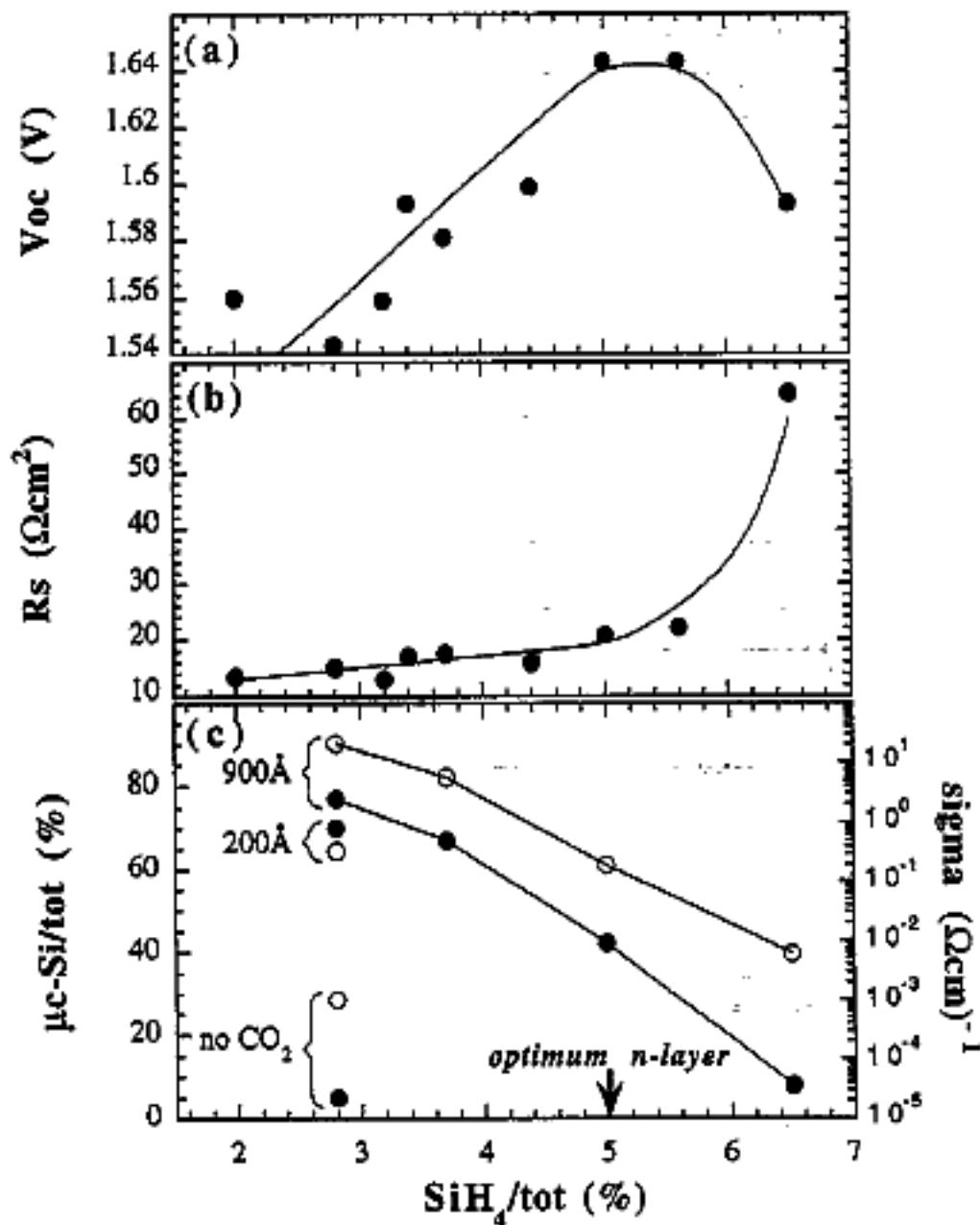


Fig. 1. Influence of the hydrogen dilution during the deposition of the n-layer (after CO₂ plasma treatment) on the properties of tandem cells (a, b) and of i(a-Si)/n($\mu\text{c-Si}$) samples (c). In part (c), we also present characteristics for n ($\mu\text{c-Si}$) layers produced without CO₂ plasma 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 (σ).

3.2. $\mu\text{-Si:H}$ layers in the internal junction of tandem cells

CO_2 plasma treatment was applied for the deposition of $\mu\text{-Si:H}$ 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 ($\leq 15 \Omega \text{ cm}^2$), 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 $\mu\text{-Si}$ 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

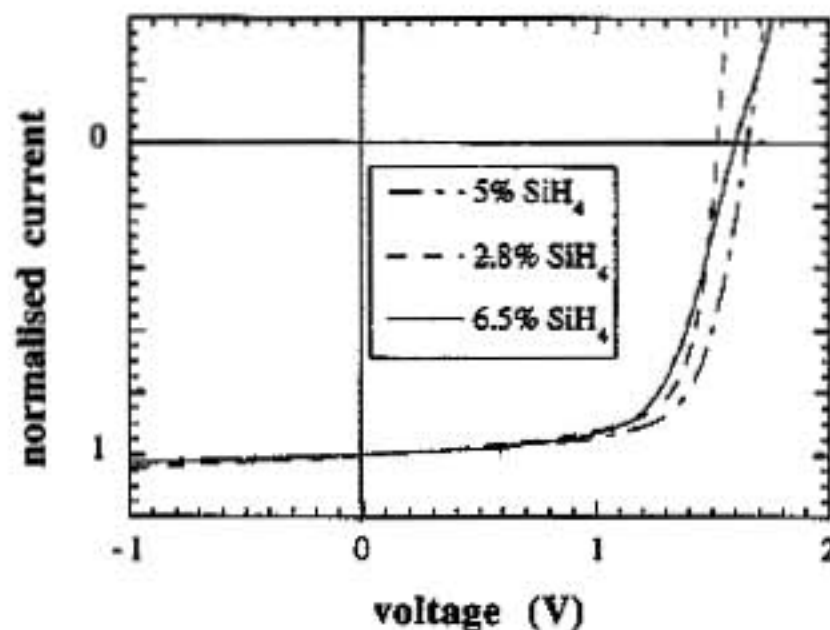


Fig. 2. I - V curves of tandem cells with a single n-layer in the n/p recombination junction between the two cells; this single n-layer is deposited under three different hydrogen dilution conditions, but in all three cases after CO_2 plasma treatment on the underlying i-layer.

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 $\mu\text{-Si:H}$ 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/ $\mu\text{-Si:H}$ 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 $15 \Omega \text{ cm}^2$ 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 $\mu\text{-Si}$ n-layer with 5% SiH_4/tot . The gain in the total

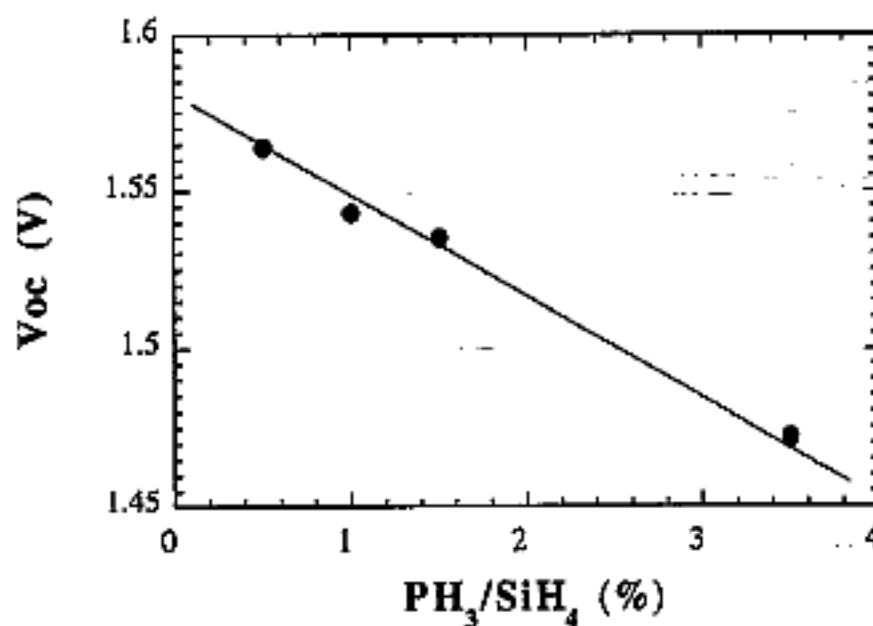


Fig. 3. Open-circuit voltage of a tandem cell as a function of the gas-phase doping ratio of the n-layer in the n/p recombination junction. The hydrogen dilution of the n-layer corresponds to 2.8% $\text{SiH}_4/(\text{SiH}_4 + \text{H}_2)$. CO_2 plasma treatment is applied to the i-layer before deposition 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 $\mu\text{-Si}$ 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).

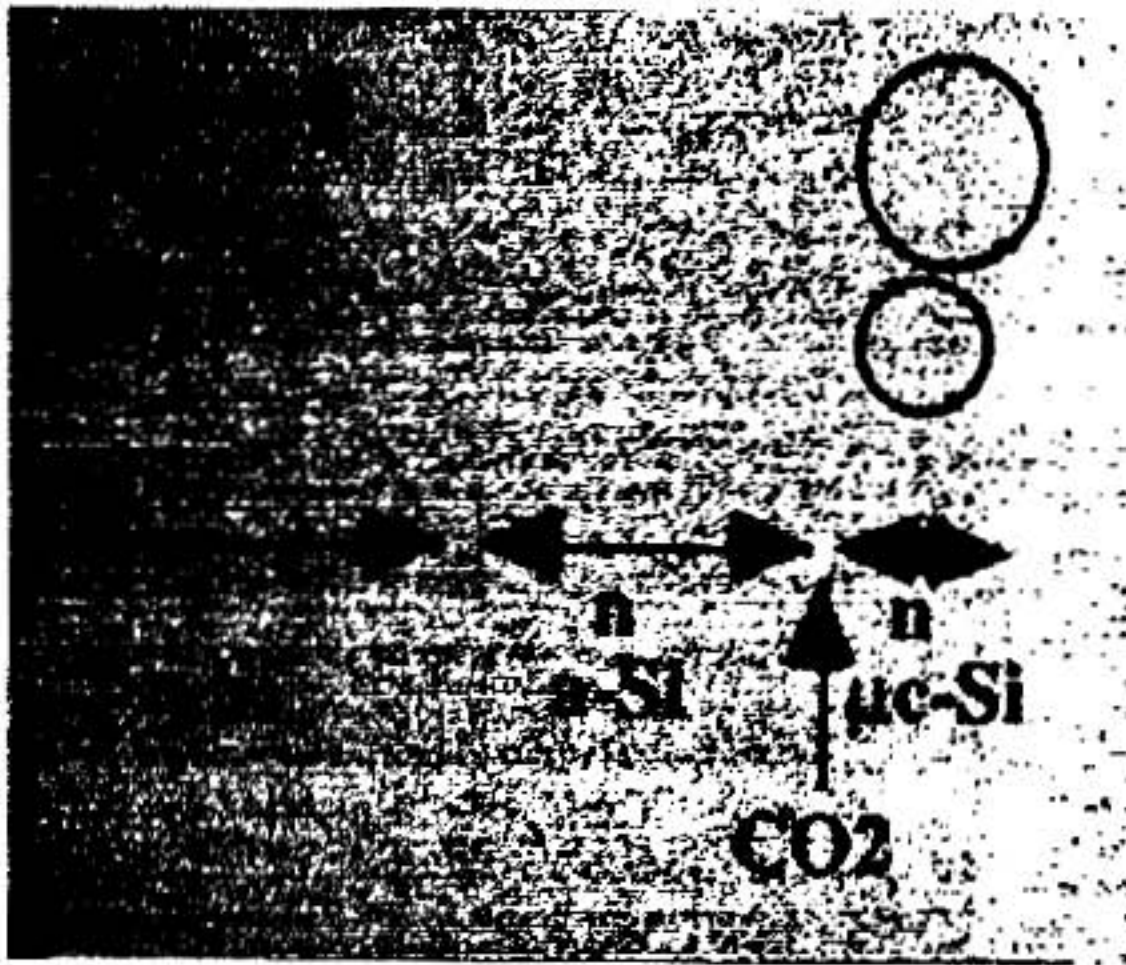


Fig. 4. Cross-TEM picture of the new combined n-layer deposited on an intrinsic a-Si : H layer. Crystallites can be seen extending through the whole thickness of the very thin top layer (after the CO_2 plasma).

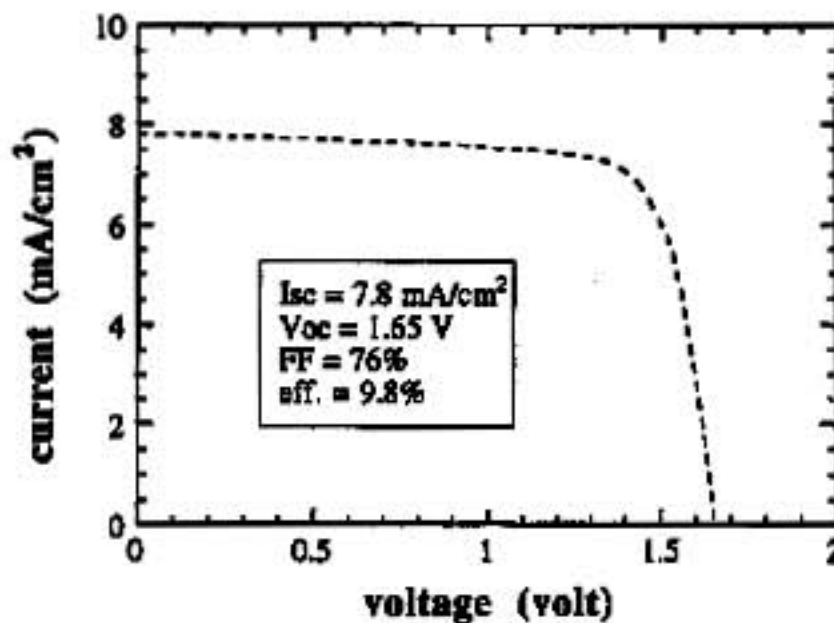


Fig. 5. I - V curve of an a-Si/a-Si tandem cell incorporating the new double n-layer in the n/p recombination junction.

5. Summary

With a CO₂ plasma, we could control the nucleation of thin microcrystalline layers grown on an a-Si:H substrate. These μ c-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 μ c-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

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