

# High-efficiency p-i-n a-Si:H solar cells with low boron cross-contamination prepared in a large-area single-chamber PECVD reactor

U. Kroll<sup>a,\*</sup>, C. Bucher<sup>a</sup>, S. Benagli<sup>a</sup>, I. Schönbächler<sup>a</sup>, J. Meier<sup>a,1</sup>, A. Shah<sup>a</sup>, J. Ballutaud<sup>b</sup>,  
A. Howling<sup>b</sup>, Ch. Hollenstein<sup>b</sup>, A. Büchel<sup>c</sup>, M. Poppeller<sup>c</sup>

<sup>a</sup>*Institut de Microtechnique, 2000 Neuchatel, Switzerland*

<sup>b</sup>*CRPP/EPF Lausanne, 1015 Lausanne, Switzerland*

<sup>c</sup>*Unaxis Displays, 9496 Balzers, Liechtenstein*

## Abstract

In this work, a new type of short water vapor treatment of the interface between the p- and i-layer is presented. This novel treatment is performed under vacuum below 1 mbar for 5 min and considerably reduces the i-layer boron contamination in amorphous silicon (a-Si:H) p-i-n solar cells prepared in single-chamber reactors. A significant advantage is that the substrate with the p-layer can remain loaded in the reactor during this oxidation treatment. The high effectiveness of this treatment in reducing the boron cross-contamination is directly supported by secondary ion mass spectroscopy measurements, by tracing the boron concentration depth profile across the p-i interface and by quantum efficiency measurements of the deposited cells. By applying this water vapor treatment, 0.3- $\mu\text{m}$ -thick a-Si:H p-i-n solar cells of 1  $\text{cm}^2$  with high initial conversion efficiencies of 10.1% are deposited in a commercial large-area (35  $\times$  45  $\text{cm}^2$ ) single-chamber PECVD KAI<sup>TM</sup> reactor and can clearly compete with cells deposited in multi-chamber systems. Light soaking of these cells for 1200 h at 50 °C leads to stabilized efficiencies of 8.2%. The relative typical efficiency degradation of 20% of such 0.3- $\mu\text{m}$ -thick single-junction cells demonstrates that this treatment does not affect the stability in a negative manner.

*Keywords:* Amorphous silicon; Solar cells; Boron contamination; PECVD; Single-chamber process

## 1. Introduction

Amorphous silicon (a-Si:H) solar cell manufacturers use either single-chamber or multi-chamber reactors to produce commercial modules. Plasma deposition of a-Si:H p-i-n solar cells in a single-chamber reactor leads to considerable simplifications and reduced costs as compared to multi-chamber processes. However, in a single-chamber process, the subsequent deposition of the i-layer on the p-layer can cause boron recycling from the reactor walls. As a result, boron can contaminate the initial i-layer at the critical p-i interface and thereby weaken the strength of the electrical field in the i-layer close to the p-i interface. This provokes a less efficient carrier separation just in this zone and leads to

a reduced collection efficiency in the solar cell and thereby to a deterioration of the cell performance.

At present, most a-Si:H p-i-n solar cell modules are deposited using the multi-chamber reactors wherein boron cross-contamination by recycling is avoided by simply depositing the p-layer and the i-layer in different chambers. However, the higher investment in multi-chamber systems becomes a drawback particularly in the field of solar cells where costs are a major issue. Thus, the ideal solution would be to combine a low-cost single-chamber reactor with a process scheme able to suppress the boron cross-contamination. Previous studies have focused on the use of different treatments like  $\text{NF}_3$  gas flush [1], hydrogen plasmas [2] or  $\text{CO}_2$  plasmas [3,4] with encouraging results, but leave open the question on the light-induced degradation of these solar cells, use expensive gases, have long treatment duration or are incompatible with large-area deposition in industrial reactors.

\*Corresponding author. Tel.: +41-79-44-11-535; fax: +41-32-732-5581.

E-mail address: ulrich.kroll@unaxis.com (U. Kroll).

<sup>1</sup> Present address Unaxis SPTec, 2000 Neuchatel, Switzerland.

Therefore, we developed in a large-area industrial PECVD KAI™-S reactor of Unaxis, a novel interface treatment between the p- and i-layer deposition, which is fast and bears the potential to obtain high cell performances due to low boron cross-contamination and especially does not aggravate the light-induced degradation.

## 2. Experimental

The radio-frequency (RF) glow discharge deposition system used in this work is an adapted version of the industrial KAI™-S reactor commercialized by Unaxis displays. It is a parallel-plate capacitively coupled reactor of dimensions 47 cm width  $\times$  57 cm length with 2.4 cm distance between RF electrode and ground electrode. The plasma excitation frequency used was 40.68 MHz. For p-type doping, trimethylboron,  $B(CH_3)_3$ , instead of diborane,  $B_2H_6$ , was used as the boron source gas because it has superior thermal stability in the hot reactor and is reported to cause less contamination [5].

The process gases are introduced through a shower-head incorporated within the RF-powered electrode. The deposition temperature of the a-Si:H layers and cells was 200 °C keeping the pressure at 0.3 mbar and applying an RF power level of 60 W. The total feed gas flow was 150 sccm for the intrinsic layer deposition. To diminish powder formation the silane was diluted by hydrogen to a silane concentration of 70% during the i-layer deposition. Under these i-layer preparation conditions, deposition rates of  $3.3 \text{ \AA s}^{-1}$  have been obtained.

In this single-chamber reactor, 0.3- $\mu\text{m}$ -thick p-i-n a-Si:H solar cells were deposited on glass/TCO substrates (Type Asahi U, based on  $\text{SnO}_2\cdot\text{F}$ ). In a second phase to obtain the full potential for high-efficiency a-Si:H solar cells an optimized hydrogen-diluted buffer layer was inserted between the p- and i-layer. It has to be noted that this buffer alone has already an usually beneficial effect on the boron cross-contamination in the i-layer. Sputtered ITO and aluminum are used as a back contact.

Between the p- and i-layer (respectively, buffer layer) deposition the following interface treatments were investigated: gas flushing, long vacuum pumping and water vapor flush performed under vacuum. The water vapor is generated directly from deionized water filled in a separated bottle and connected to the reactor via a valve. By opening the valve, water starts boiling in the bottle due to the low pressure and the water vapor flushes into the reactor. Due to the pumping of the reactor the pressure is kept below 1 mbar. In some cases the water was replaced by alcohol.

The effectiveness of the treatments were evaluated by secondary ion mass spectroscopy (SIMS) tracing the boron concentration depth profile across the p-i interface, deposited in this case on c-Si wafers. Furthermore,

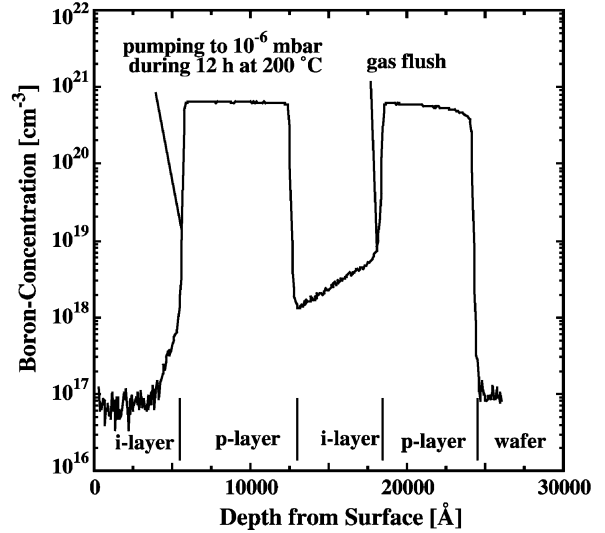


Fig. 1. SIMS profile of boron concentration of a sandwich structure deposited on c-Si wafer using two different treatments between the p- and i-layer deposition.

the boron contamination in the i-layer close to the p-layer is indirectly detected by performing voltage-dependent quantum efficiency measurements as well as monitoring the global cell performance, especially the cell fill factor. The  $I$ - $V$  characteristics are measured under AM 1.5 illumination using a Wacom WXS 140S-10 sun simulator. The cells were light-soaked for over 1200 h under the light of a high-pressure sulfur lamp at 50 °C. The spectrum of this microwave powered sulfur lamp is close to the AM 1.5 spectrum and is adjusted to  $100 \text{ mW cm}^{-2}$ .

## 3. Results and discussion

### 3.1. Preliminary experiments without buffer layer

Fig. 1 shows the SIMS analysis of the boron content present in a sandwich structure. This structure was fabricated by alternating the p-layer to i-layer depositions. Between the p- and i-layer a silane-hydrogen gas flushing for 30 min or a long pumping period of 12 h to high vacuum at 200 °C substrate temperature is performed. It can be clearly seen that by using gas flushing, the p-layer boron concentration of approximately  $10^{21} \text{ cm}^{-3}$  falls sharply, directly after the p-layer, by two orders of magnitude down to  $10^{19} \text{ cm}^{-3}$  and then tails strongly into the subsequent i-layer deposition of approximately 5000 Å. The p-i-n cells prepared under these conditions show a quite low fill factor below 60% and a globally weak but strongly bias-voltage-dependent quantum efficiency (QE) in the blue light region (e.g. at the wavelength of 400 nm the QE is 20% at 0 V and 55% at  $-3 \text{ V}$  reverse bias voltage). This indicates the presence of a strong boron cross-contamination from the

p-layer into the i-layer and, therefore, a p/i interface that is not well defined, i.e. not abrupt enough.

In contrast, after a long pumping period to high vacuum at 200 °C, the boron tailing into the i-layer deposition is considerably reduced and the base level boron contamination of  $10^{17} \text{ cm}^{-3}$  in the i-layer is reached. By replacing the gas flushing by this 12-h vacuum pumping between the p- and i-layer deposition, a considerable improvement of the cell performances could be obtained for identical p-i-n cells. The fill factor increases to over 70% and QE values in the blue light region show a bias-voltage dependence that is reduced and is now comparable to cells deposited in multi-chamber systems. Therefore, in agreement with the SIMS measurements, we conclude that the absence of a high boron cross-contamination in the i-layer after the p-layer deposition leads to a better electrical field distribution within the i-layer and, hence, an enhanced current collection in the cell. The two treatments suggest that the boron is not simply present in a gaseous state that can be flushed out easily by gas purging but might be physisorbed on the internal reactor surfaces, chamber walls, pump ducts, etc. and desorbs very slowly. A more or less complete desorption occurs after the long pumping time of 12 h. Further experiments confirm that a reduction of the pumping time gradually leads to reduced cell performances, especially with respect to the fill factor.

### 3.2. Cells with buffer layer between p- and i-layer

Therefore, in the next phase, a cell deposition sequence has been developed wherein a carefully optimized thin buffer layer has been inserted to lessen, on the one hand, the boron contamination in the i-layer by trapping most of the boron contamination in this thin interlayer [6] and, on the other hand, to match the band gap difference between p-silicon carbide layer and i-layer. Applying this optimized buffer layer and using a readapted process for the doped layer preparation, cell performances, as shown in Fig. 2, could be obtained after the reduction of the vacuum pumping time to 30 min.

Reasonably high fill factors of, respectively, 67.7 and 69.6% are obtained. In cell b, only the i-layer is deposited at 27.12 MHz to investigate the influence of the plasma excitation frequency and hence, the increased ion-bombardment energy [7] on the boron cross-contamination. Since even slightly higher fill factors are obtained at 27.12 MHz than that at 40.68 MHz, boron liberation by active sputtering out of the p/buffer-layer, which could in turn lead to a subsequent boron contamination of the gas phase during the initial i-layer deposition, seems not to be occurring.

A reduction of the pumping time below 30 min quickly leads to lower cell performances to levels that

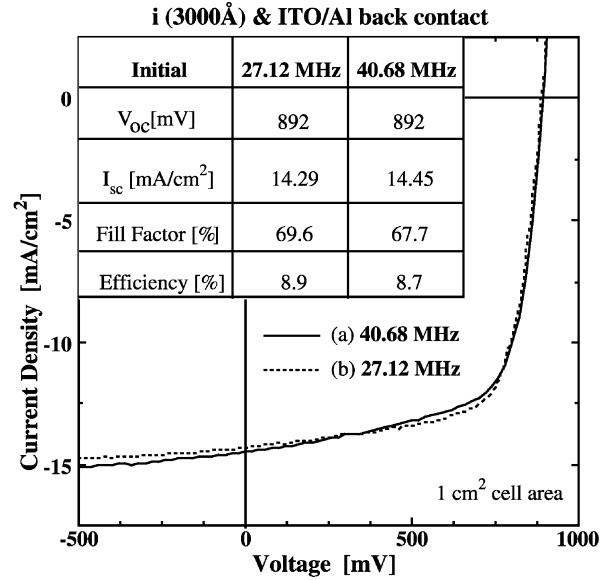


Fig. 2. Initial  $I$ - $V$  curves of buffer optimized p-b-i-n a-Si:H cells using 30-min pumping before the i-layer deposition. In cell b, the i-layer has been exceptionally deposited at 27.12 MHz.

are no longer acceptable. Therefore, instead of removing the boron out of the reactor and pump ducts by not very effective gas flushing or time-consuming vacuum pumping, the authors developed a novel treatment that transforms the physisorbed boron on all internal surfaces into a stable chemical compound unable to desorb. Inspired by the success of oxidizing  $\text{CO}_2$  plasma treatments [3,4] applied for, respectively, boron removal and oxidation, our treatment follows a similar approach using also oxidizing agents like water or alcohol vapors. These vapors are directly evaporated in the reactor at a reduced pressure of below 1 mbar. However, in contrast to the  $\text{CO}_2$  plasma treatment, our new vapor oxidation process step bears the advantage that a plasma is not required and acts, therefore, on all internal surfaces (also those not exposed to the plasma) and, moreover, the substrate with the p-layer can remain loaded during the treatment. Surprisingly, an oxidation by directly using oxygen gas does not work.

Fig. 3 shows the  $I$ - $V$  characteristic of cells obtained by the water vapor oxidation treatments in comparison to the 30-min pumping time alone. Compared to the vacuum pumping process the application of the water vapor oxidation treatment increases the efficiency remarkably by almost 1.5% resulting in an absolute initial conversion efficiency of 10.13%, whereas in parallel the process time is considerably reduced by 20 min. It has to be added that the net deposition of the p-, b-, i- and n-layer requires an accumulated time of 17 min resulting, finally, in a total process time of approximately 30 min for the complete cell fabrication using our oxidation treatment. As can be seen in the

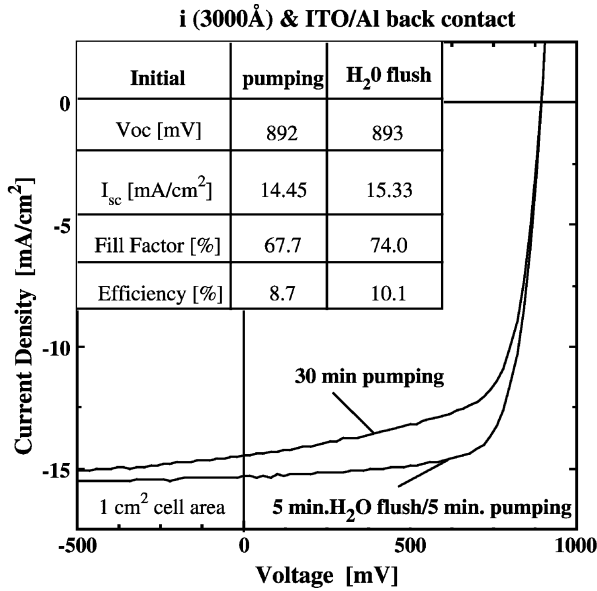


Fig. 3. Effect of water vapor flush on the  $I$ - $V$  characteristics of buffer optimized p-buffer-i-n a-Si:H cells using 5-min water vapor treatment followed by 5-min pumping and 30-min pumping alone before the i-layer deposition.

inserted table in Fig. 3 the increased cell performance is mainly due to the higher fill factor and higher short circuit current.

In Fig. 4 the quantum efficiencies of the cells prepared with both treatments are shown. Indeed, as compared to the pumping alone the QE in the blue region is enhanced

and, moreover, now shows only a small bias-voltage dependence when the oxidation treatment (Fig. 4a) is applied. The weak voltage dependence of the QE in the blue light region represents a good carrier collection in the i-layer close to the p-layer and, therefore, suggests a low boron contamination.

The boron concentration depth profiles detected by SIMS after no treatment and applying the water vapor oxidation are represented in Fig. 5. A drop of the boron concentration in the initial i-layer by more than half an order of magnitude as compared to the untreated interface is observed. This proves directly the effectiveness of the oxidation treatment on the boron cross-contamination. We suppose that boric acid  $B(OH)_3$  and/or boron oxide anchored to silicon (Si-B-O) is formed, which either become unable to desorb or is transformed into an electrically inactive dopant.

Since the oxidation treatment by water vapor increases the oxygen content in our amorphous i-layers to concentrations of approximately  $5-8 \times 10^{19} \text{ cm}^{-3}$ , unfavorable effects on the cell stability cannot be excluded. Therefore, light-soaking experiments of the cells presented in Fig. 3 were performed (Fig. 6).

The efficiency of the cell prepared by the water vapor treatment degrades from initially 10.1% to a stabilized efficiency of 8.2% after prolonged light soaking for 1200 h. This stabilized efficiency still lies approximately 1% above the performance of the degraded cell prepared without the oxidation treatment. Relative cell efficiency degradation of approximately 20% is found in both cases and do not exceed typical values of other single-

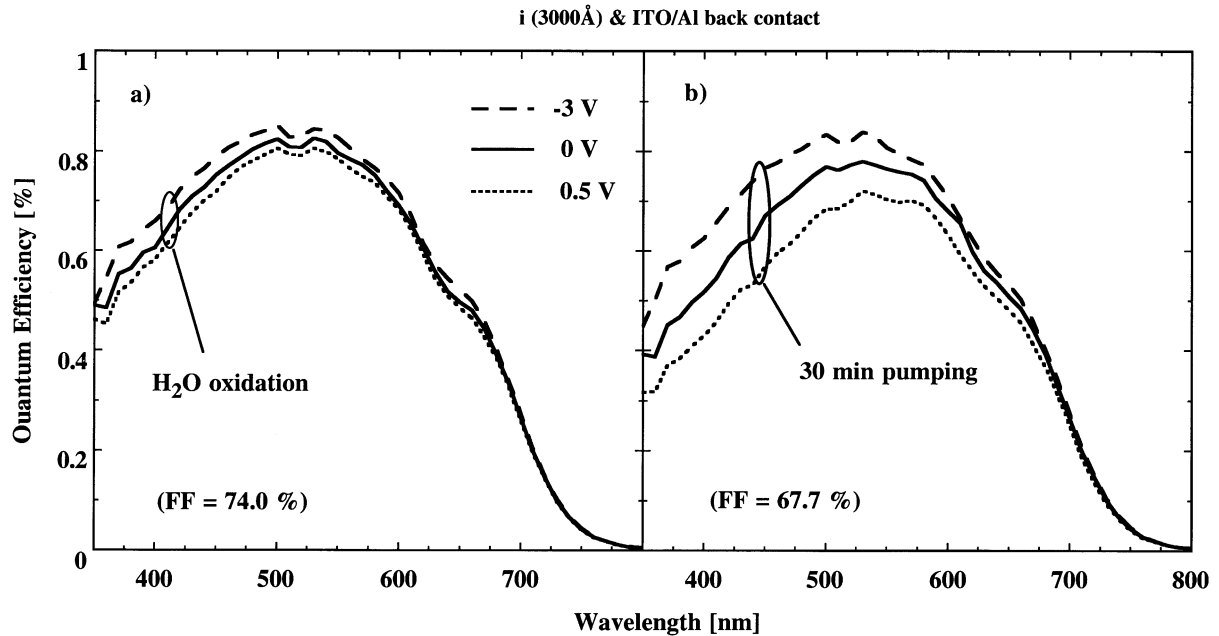


Fig. 4. Impact of water vapor flush on the bias-voltage-dependent quantum efficiencies of the cells from Fig. 3. (a) Using the water vapor treatment and (b) pumping before the i-layer deposition.

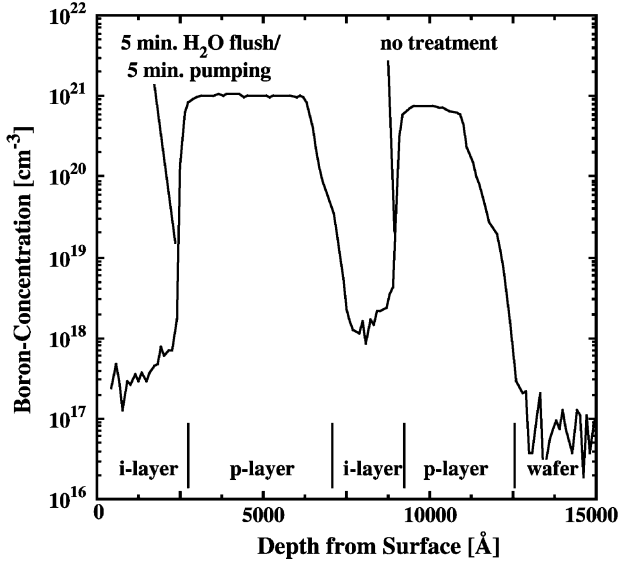


Fig. 5. Boron concentration depth profile measured by SIMS of a sandwich structure using water vapor oxidation treatments and no treatment.

junction cells having i-layer thickness of 3000 Å and deposited in multi-chamber reactors [8].

#### 4. Summary and conclusions

A new type of short treatment of the interface between the p- and i-layer has been introduced. This special oxidation treatment, consisting of an exposure of the reactor walls, pump ducts and cell p-layer itself by water

vapor under vacuum at a pressure below 1 mbar, considerably reduces the i-layer boron cross-contamination. A significant advantage is that the substrate can remain loaded in the reactor at the deposition temperature during this 5-min treatment plus 5-min pumping time. The high effectiveness of this treatment in reducing the boron cross-contamination has been proven by spectral response measurements of the deposited cells and directly by SIMS measurements, by tracing the boron concentration depth profile across the p-i interface. By applying this treatment, 0.3- $\mu\text{m}$ -thick a-Si:H p-i-n solar cells with high initial conversion efficiencies of 10.1% have been deposited in a commercial large-area ( $35 \times 45 \text{ cm}^2$ ) single-chamber PECVD KAI™ reactor. A considerable gain in cell performances, mainly, in fill factor, QE and final efficiency are achieved, as compared to identically deposited cells using the time-consuming 30-min pumping procedure after the p-layer. Using this short 10-min oxidation treatment the total fabrication time for a complete p-i-n cell having an i-layer thickness of 3000 Å could be reduced to half an hour. Besides the performance and time gain we additionally found that the oxidation treatment improves the process robustness with respect to boron cross-contamination. This means that even less optimized p-layers and buffer layers lead to low cross-contaminated cells and, finally, allow the preparation of high performance cells. Light-soaking experiments of such cells do not show any aggravated degradation due to this treatment and stabilized cell efficiencies in the light-soaked state of 8.2% for 3000-Å-thick p-i-n cells are obtained.

The achieved high initial and degraded single-junction a-Si:H cell efficiencies of, respectively, 10.1 and 8.2% demonstrate, in combination with the new water vapor oxidation treatment, the high potential of the single-chamber process compared to multi-chamber processes leading to considerable simplifications, process robustness and reduced costs. It should be noted that the above indicated cell efficiencies are obtained by using an ITO/Al cell back contact.

We believe that the highly reactive O-H group of water and alcohol selectively forms with physisorbed or chemisorbed boron products like boron oxide or boric acid on surfaces. These stable products either do not easily desorb in the gas phase during the subsequent i-layer deposition or are electrically inactive for doping.

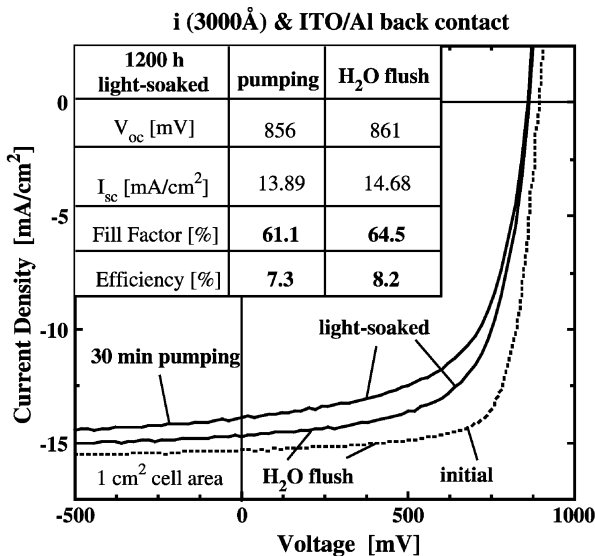


Fig. 6.  $I$ - $V$  characteristics of cells of Fig. 3 in degraded state after 1200-h light-soaking at 50 °C under AM 1.5 illumination. For comparison the initial performance of the cell prepared by water vapor oxidation is added and represented as a dotted line.

#### Acknowledgments

We would like to thank F. Jomard from L.P.S.C. in C.N.R.S. Meudon, France, for performing the SIMS measurements. This work was supported by the Swiss Commission for Technology and Innovation (CTI) under Research Grant #4559.1 and 5994.2.

## References

- [1] A. Catalano, G. Wood, Proc. Mat. Res. Soc. Symp. 118 (1988) 581.
- [2] Y.S. Tsuo, Y. Xu, R.S. Crandall, H.S. Ullal, K. Emery, Proc. Mat. Res. Soc. Symp. 149 (1989) 471.
- [3] J. Bauer, H. Calwer, P. Marklstorfer, P. Milla, F.W. Schulze, K.-D. Ufert, J. Non-Cryst. Solids 164–166 (1993) 685.
- [4] M. Kubon, N. Schulz, M. Kohler, C. Beneking, H. Wagner, Proceeding of 12th European Photovoltaic Solar Energy Conference (1994) p. 1268.
- [5] A. Lloret, Z.Y. Wu, M.L. Thèye, I.El. Zawawi, J.M. Siéfert, B. Equer, Appl. Phys. A 55 (1992) 573.
- [6] B. Rech, Ph.D. thesis, Forschungszentrum Jülich (1997) ISSN 0944-2952.
- [7] A. Howling, J.-L. Drier, Ch. Hollenstein, U. Kroll, F. Finger, J. Vac. Sci. Technol. A 10 (1992) 1080.
- [8] R. Platz, Ph. D. thesis, Université de Neuchâtel (1999) ISBN 3-930803-61-5.