# GROWTH OF THIN <p> μc-Si:H ON INTRINSIC a-Si:H FOR <nip> SOLAR CELLS APPLICATION

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## ABSTRACT

The <p> μc-SiC:H / <i> a-Si:H junction can be considered to be a sub-system of a n/i/p solar cell. Optimised performance of this junction can be assumed to be a key feature for obtaining high efficiency solar cells.

In this paper the authors present results on the conductivity of boron doped microcrystalline hydrogenated silicon (<p> μc-Si:H) thin films deposited on amorphous substrates (e.g. glass or glass/<i> a-Si:H). It is shown that, without any treatment of the substrate or of the underlying surface, the <p> layers showed a strongly reduced conductivity. This indicates either a bad nucleation or a poor microcrystalline behaviour. By using an appropriate surface treatment of the substrate, a gain in photoconductivity of about three orders of magnitude could be obtained ($\sigma > 3$ S/cm at a layer thickness of 400Å). We conclude from this, that for thin <p> type μc-Si:H layers the nucleation conditions are essential for obtaining best electric properties of the film w.r.t. solar cell performance.

Based on these results, interface treatment was successfully implemented in n/i/p solar cells deposited on TCO coated glass and stainless steel. The results of these experiments are also presented.

## INTRODUCTION

Amorphous hydrogenated silicon (a-Si:H) solar cell technology is one of the leading techniques for low-cost and large-area photovoltaic cell manufacturing. In contrast to the well established p/i/n junction deposited on a glass/TCO, the less studied "inverted" structure, i.e. the n/i/p structure, offers the possibility to use substrates such as stainless steel, aluminium or plastic. For obtaining the best performance of n/i/p structures with respect to the <p> type window layer and the a-Si:H junction, the following factors have to be taken into account:

a) the doped layers in the device play a key role in building up a strong internal electric field across the <i> layer,

b) the <p> doped window layer should have high electric conductivity, a wide optical bandgap and a high transmission within the spectral range of the sun,

c) the compatibility in terms of electrical contact with both the <i> layer and the top contact (TCO) is required to guarantee a high fill factor (FF). A good solution consists of using a <p> type μc-SiC:H layer [11]; nevertheless, the microcrystalline character of such a layer strongly depends on its nucleation condition on the substrate [4-8], i.e. on its immediate microcrystalline growth [6-8].

In this paper, we focus our attention, in a first part, on the understanding of $H_2$ and $CO_2$ plasma treatments which allow the growth of a <p> μc-Si:H thin layer (400Å) by the nucleation or oxidation of the <i> layer. In a second part, we show how these plasma treatments can be applied to n/i/p cells deposited on glass/TCO and stainless steel substrates.

## EXPERIMENTAL

All films and solar cells were deposited with the VHF-GD technique at an excitation frequency of 70 MHz in a single chamber deposition system [1]. The two coplanar electrodes have a surface of 133 $cm^2$, the substrate is fixed face down on the upper electrode. The RF is applied on the lower electrode. The gap between the electrodes is fixed at 14 mm during the deposition of the films and solar cells.

The effective temperature of the electrodes is kept between 170˚C and 240˚C (depending on the layer), the walls of the chamber are kept close to ambient temperature.

The gases used for the film and cell deposition were silane ($SiH_4$), diborane ($B_2H_6$), phosphine ($PH_3$), hydrogen ($H_2$) and methane ($CH_4$).

The film thicknesses were measured with a step profiler on steps etched out by a KOH solution and averaged over 5 measurements. The deposition rate was determinated separately for the <i> and <p> layers deposited on glass of type Schott AF45 (4 x 4 $cm^2$).

The plasma treatment was performed using either a $CO_2$ or a $H_2$ plasma. Gas pressure, VHF - power and time of treatment were varied, respectively.

a) <u>Test structure:</u> A cross-section of the test structure used is given in Fig. 1: The thickness of all <i> a-Si:H layers was 1500 Å, and 400 Å for the <p> µc-Si:H layers. All samples were exposed to an annealing step close to the deposition temperature of the <p> layer under $N_2$ atmosphere. The (lateral) conductivity of the p-layer was measured using a four-point probe measurement system. In order to check homogeneity, the measurement was carried out at 9 sites distributed on the surface. Only homogenous layers were taken into consideration for the plots presented here.

When necessary, the conductivity was measured, after the same annealing step, by using two coplanar aluminium ohmic contacts (1000 Å) under $N_2$ atmosphere at a pressure of 10 mbar. As shown in Fig. 1, the test structure was used to study the conductivity of the <p> doped layer in function of the plasma treatment.

For the deposition from undiluted $SiH_4$ of the undoped layer, a pressure of $p = 0.4$ mbar and a power of 4W was applied.

The <p> µc-Si:H layers were deposited at $T_{dep}$ = 170˚C; power input P = 4W; total gas flow =100 sccm; $SiH_4$/tot = 1%; $B_2H_6/SiH_4$ = 0.4%.

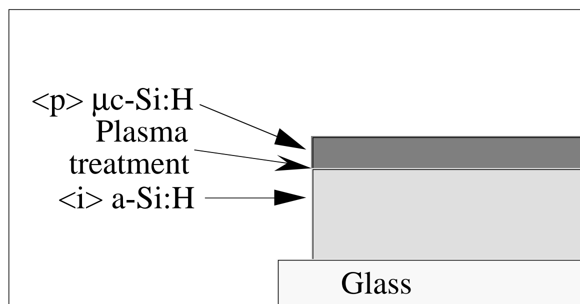


*Fig. 1: Test structure of a <i> a-Si:H / <p> µc-Si:H on glass.*

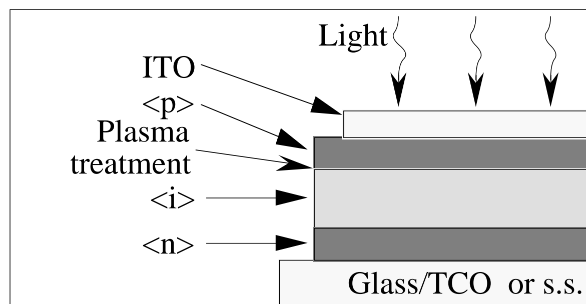


*Fig. 2: Structure of a <n/i/p> cell deposited on glass / TCO or stainless steel.*

b) <u>Cell structure:</u>
The complete n/i/p cells were developed on glass / TCO (Asahi type U) and stainless steel in the same deposition system as mentioned before. The thicknesses of the layers were: <n> µc-Si:H: 250Å; <i> a-Si:H: 4500Å; <p> µc-SiC:H: 250Å.

The only difference between all cell structures measured consisted in a different plasma treatment at the i/p interface. The front contact ITO was sputtered through a mask defining 15 cells of 0.2 $cm^2$.

Like in test structure a) the cells were also annealed at the same temperature in an $N_2$ atmosphere. The cells were characterised by the illuminated j-V curve, thereby a two source solar simulator was used. From the j-V characteristics, the open circuit voltage $V_{oc}$ and the fill factor FF were determined. The short circuit current ($I_{sc}$) was determinated by integration of the spectral response curve [3] of a selected cell.

## RESULTS AND DISCUSSION

Conductivities as high as 3 S/cm could be obtained for a <p> doped µc-Si:H (400Å) layer deposited on glass treated with an Ar – $H_2$ plasma [2]. If no plasma treatment was applied, the deposition of <p> µc-Si:H, on glass or in the test-structure a), yielded very poor lateral conductivities of the doped layer of around $10^{-3}$ – $10^{-4}$ S/cm. This clearly shows – and is already well known [4-8, 10]– that the microcrystalline nature of a <p> doped layer is highly dependant on the treatment of the underlying surface.

With a $H_2$ or a $CO_2$ plasma treatment at the i/p interface, it is possible to obtain high conductivities, however. Figs 3 and 4 show that, for a set of parameters of pressure and power, the conductivity of the <p> layer depends on the exposure time of the substrate to the $H_2$ or $CO_2$ plasma .

For a long $H_2$ plasma treatment (not shown on the graphic), the conductivities are already reduced, furthermore the layer became inhomogeneous. It seems that, on one hand, the surface is saturated by the hydrogen and, on the other hand, the amorphous layer is etched away by the prolonged treatment. A conductivity of 3 S/cm of the <p> doped layer was achieved with a $H_2$ plasma treatment of 3 min., corresponding to the conductivity of the same <p> doped layer deposited directly on treated glass [2]. Thus, for a fixed set of parameters (pressure and power), an optimum in surface treatment can be found.

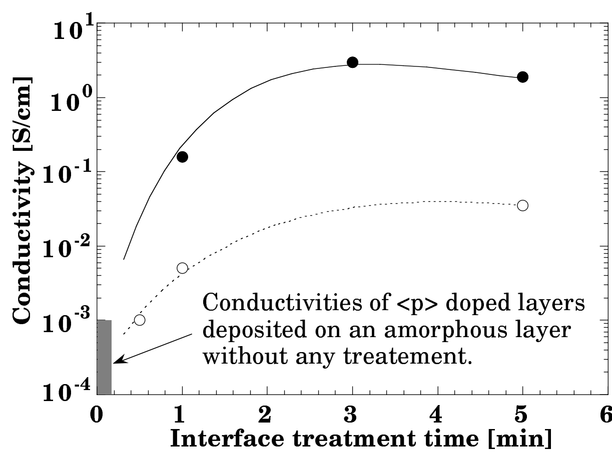


*Fig. 3: Conductivity of 400Å thick <p> doped layers on an amorphous intrinsic layer of 1500 Å in function of the exposure time of the interface by a $H_2$ plasma. Parameters:* 1*: 0.035 mbar, 10W;* m*: 0.1 mbar, 8W. The variable is the duration of the treatment.*

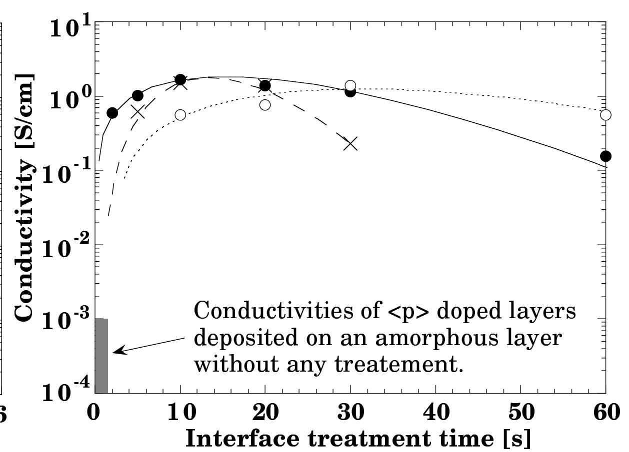


*Fig. 4: Conductivity of 400Å thick <p> doped layers on an amorphous intrinsic layer of 1500 Å in function of the exposure time of the interface by a $CO_2$ plasma. Parameters:* 1*: 0.1 mbar, 3W;* m*: 0.2 mbar, 2W;* 5*: 0.03 mbar, 2W. The variable is the duration of the treatment.*

Using a $CO_2$ plasma, it was found that the conductivity of the <p> doped layer changes drastically within the first 15 sec. The maximum-value strongly depends on the pressure and power. For too high power and/or too long exposure time, the $CO_2$ plasma forms species (similar as water vapour) that increase strongly the base pressure of the vacuum system and that are difficult to be removed by downpumping. Apart from that, it seems that there is an oxidation on the top of the amorphous surface (formation of a-SiO:H) [9] which favours the

nucleation of the microcrystalline growth of the <p> layer. Using the $CO_2$ plasma treatment, conductivities in excess of 1 S/cm were achieved.

Assuming that, in a first step, the optimum growth condition w.r.t. $H_2$ or $CO_2$ plasma treatment are the same for the <p> doped µc-SiC:H layers incorporated in the cells as for the unalloyed individual µc-Si:H layers mentioned before, we applied these treatments in n/i/p cells. In the cells, thinner <p> layers were incorporated; hence, it can be assumed, that the influence of the nucleation properties of the plasma-treated substrate (or, of the underlying <i> layer) should be even more pronounced.

Table 1 summarises the characteristics of these cells deposited on glass/TCO.

| a-Si:H / <p>µc-SiC:H interface treatment: | $V_{oc}$ [mV] | $j_{sc}$ [mA/cm$^2$] | FF [%] | Eff [%] |
|---|---|---|---|---|
| a: none | 667 | 15.95 | 53.4 | 5.7 |
| b: $H_2$ plasma | 823 | 15.7 | 59.1 | 7.6 |
| c: $CO_2$ plasma | 831 | 15.8 | 63.4 | 8.3 |

*Table 1: Characteristics of n/i/p cells deposited on glass/TCO. The different layers have the same parameters of deposition, the only difference is the treatment of the interface i/p.*

Fig. 5 shows the j-V curves of cells deposited on glass/TCO. The $H_2$ and $CO_2$ plasma treatments correspond to the optimum of the curves 1 Fig. 3 and 5 Fig. 4, respectively. As expected, there is a spectacular increase of the $V_{oc}$ value between the cells *a* (without treatment) and *b* and *c* (with treatment), which is due to a better microcrystallinity of the p-doped layer. The increase in the fill factor is probably due to a better contact of the <p>/ITO interface (tunnel junction ?) as deduced from the evaluation of the series resistance.

In a second step, by further adjustment of the p-layer (<p> µc-SiC:H; 250 Å) deposition sequence and the plasma treatment condition, a further increase of the $V_{oc}$ of over 40 mV could be achieved for both $H_2$ and $CO_2$ plasma treatment (Fig. 6).

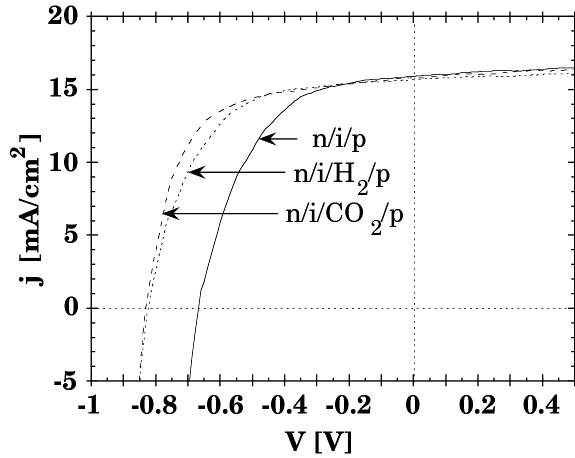


*Fig. 5: j-V curves of n/i/p cells deposited on glass/TCO. The <p> µc-Si:H layers have been optimized as individual layers only. The only difference is the plasma treatment at the interface.*

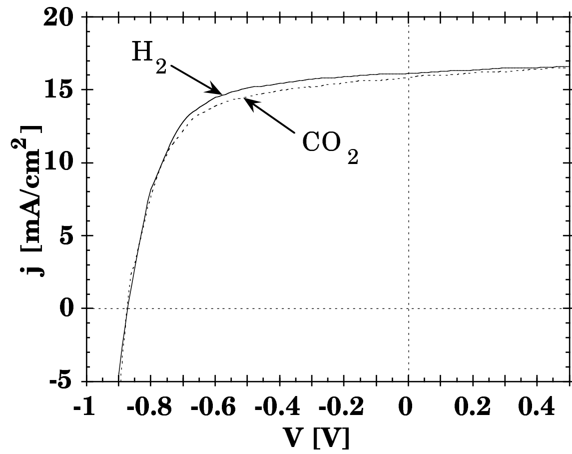


*Fig. 6: j-V curves of n/i/p cells deposited on glass/TCO. The <p> µc-SiC:H layer is further optimised in the cell, w.r.t. the plasma treatment.*

Table 2 summarises the characteristics of these cells:

| <p>μc-SiC:H optimised w.r.t. plasma treatment. | $V_{oc}$ [mV] | $j_{sc}$ [mA/cm$^2$] | FF [%] | Eff [%] |
|---|---|---|---|---|
| d: $H_2$ plasma | 869 | 16.2 | 64.1 | 9.0 |
| e: $CO_2$ plasma | 874 | 15.9 | 63 | 8.7 |

*Table 2: Characteristics of the n/i/p cells deposited on glass/TCO. The cells* d *and* e *are, respectively, the same as the cells* b *and* c *(Table 1), but with improved deposition conditions for the <p> μc-SiC:H.*

Table 3 resumes the characteristic of cells deposited on stainless steel.

| $H_2$ plasma treatment: | $V_{oc}$ [mV] | $j_{sc}$ [mA/cm$^2$] | FF [%] | Eff [%] |
|---|---|---|---|---|
| f: no | 687 | 14.1 | 55.0 | 5.3 |
| g: yes | 890 | 13.3 | 59.7 | 7.2 |

*Table 3: Characteristics of the n/i/p cells deposited directly on stainless steel with the $H_2$ plasma treatment mentioned; the cells* f *and* g *are, respectively, the same as the cells* a *and* d *deposited on glass/TCO. The difference in efficiency is probaly due to the lack of pronounced light trapping in the case of stainless steel substrate.*

For the ideal growth condition of <p> doped μc-Si:H films on amorphous substrates a plasma treatment prior to <p>-layer deposition was found to have a beneficial impact. For the example of optimised hydrogen plasma exposure the best overall cell performance could be achieved. In a previous publication [12], similar results were published regarding an effect called "chemical annealing". In this case exposure to atomic hydrogen (or to a hydrogen plasma) resulted in a post-recrystallization of the already grown amorphous layers. However a relatively complicated procedure was used. Surprisingly, $CO_2$ exposure (no hydrogen involved) shows similar results. We assume, because of this, that plasma exposure generally leads to more favourable nucleation conditions for doped μc-Si:H, somewhat independently of the gas and the substrate / underlying layer involved.

## CONCLUSIONS

Starting from the deposition parameters of good-quality, thick good microcrystalline <p> doped layers deposited on glass (glass/<p> μc-Si:H) with a conductivity of 3 S/cm, we have demonstrated that the microcrystalline structure is completely lost if such layers are deposited as thin layer directly on an underlying amorphous layer (glass/a-Si:H/<p> "μc"-Si:H) without any plasma treatment at the <i/p> interface. By using, first, a $H_2$ or a $CO_2$ plasma treatment, high conductivities of the <p> doped layers can again be found. The introduction of such a plasma treatment was successfully implemented in solar cells with an inverted structure (<n/i/p>) deposited on glass/TCO and stainless steel. A significant improvement of the FF (53.4 –> 64.1%), $V_{oc}$ (667 –> 874mV) and efficiency (5.4 –> 9.0%) could thereby be achieved.

## ACKNOWLEDGMENTS

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