Solar Cells for self-sustainable intelligent packaging

António Vicente,^{*^a} Hugo Águas, ^a Tiago Mateus, ^a Andreia Araújo, ^a Andriy Lyubchyk, ^a Simo Siitonen, ^b Elvira Fortunato, ^a and Rodrigo Martins^{*^a}

^aCENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa and CEMOP/UNINOVA, 2829-516 Caparica, Portugal.

^bStora Enso Oyj, Renewable Packaging, Research Centre Imatra, Tornansaarenraitti 48, 55400 Imatra, Finland.

*amv17109@campus.fct.unl.pt; rm@uninova.pt

1. Experimental details and preliminary results

1.1. Fabrication and characterization of silicon thin films

Three different substrates were used: corning glass, as reference for intrinsic a-Si:H layer, glass coated with 200 nm Al and liquid packaging cardboard (LPC). Silicon active layers (n-, p- and i-type) were deposited at 145 °C in a single chamber radio frequency (27.12 MHz) plasma enhanced chemical vapor deposition (PECVD). Undoped (intrinsic) hydrogenated amorphous silicon (a-Si:H) thin films were deposited with a mixture of silane (SiH₄) and hydrogen (H₂)¹. For the reference glass substrate, the first step was the deposition of the Al back contact (200 nm) evaporated in vacuum (10^{-6} mbar) using an e-beam system. The following step, common to both substrates, was the growth of an AZO (Al₂O₃: 2 wt%, ZnO: 98 wt%) interlayer with ~60 nm (resistivity, ρ , is in the order of ~5x10⁻² Ω .cm) deposited by RF-magnetron sputtering (13.56 MHz), at 155 °C, in order to ensure an efficient degassing prior to the solar cell deposition and prevent possible contaminations of the active layer due to material migration from the substrate. Then, the samples were transferred to the PECVD system where the silicon layers were deposited according to the n-i-p structure. A mixture of SiH₄ and H₂ was used to obtain the intrinsic layer, with addition of trimethylboron (TMB, B(CH₃)₃) and PH₃ to produce p- and n-layers, respectively, under the process conditions depicted in Table S1.

trimethylbo	trimethylboron to silane and R _{PH3} , ratio of fosphine to silane.									
Laver	P (Torr)	$P_{\rm W}$ (mW/cm ²)	D _H (%)	R _{TMB} (%)	R _{PH3} (%)					
Layer		r _w (mw) em)	$H_2/(Total flow)$	TMB/SiH ₄	PH ₃ /SiH ₄					
p-layer	1.0	15	92	0.68	-					
i-layer	0.4	21	80	-	-					
n-laver	0.4	21	79	-	0.26					

Table S1 Deposition conditions of the silicon layers deposited in a single chamber PECVD system. P_{gas} is the deposition pressure; P_{W} , refers to the power density; D_{H} hydrogen dilution; R_{TMB} , ratio of trimethylboron to silane and R_{PH3} , ratio of fosphine to silane.

The corresponding electrical and optical properties of investigated silicon active layers were evaluated by spectroscopic ellipsometry (SE) and conductivity measurements. SE measurements were performed using a Jobin Yvon UVISEL ellipsometer and the data was simulated using a Tauc-Lorentz dispersion model and the Bruggeman effective medium

approximation (BEMA), with 50% TL and 50% voids. From this characterization, four parameters are highlighted, namely the optical gap (*Eg*), the physical density (*A*), the oscillator resonance energy (E_0) and the broadening term of the *Lorentz Oscillator* (*C*).

The electrical properties of the films were studied via temperature dependent dark conductivity, from which the room-temperature conductivity, $\sigma_{d@25^{\circ}C}$, and activation energy, *Ea*, were calculated. The linearity of the *I* (*V*) dependence was confirmed before each conductivity measurement. Low voltages (0.1 – 1 V) were used to reduce high-field effects, such as field-enhanced hopping transport. Coplanar aluminum contacts (200 nm thick, 4 mm long and 1 mm apart) were deposited after the Si active layer by electron beam evaporation. In order to determine the photosensitivity, $\sigma_{ph}/\sigma_{d@25^{\circ}C}$, of the intrinsic layers, the photoconductivity measurements were performed on DLTS from Polaron equipped with a Bio-Rad cryostat ranging from 200 K to 400 K, a vacuum pump and a pico-ammeter from Keithley model 6517. The corresponding performances are depicted in Table S2.

Layer	<i>Ea</i> (eV)	σ _{d@25℃} (S/cm)	<i>Eg</i> (eV)	Α	$E_0(eV)$	С
p-layer	0.41	1.0 x10⁻⁵	1.79	182	3.70	2.50
i-layer	0.97	1.5×10^{-11}	1.73	212	3.67	2.17
n-layer	0.17	1.9 x10 ⁻²	1.69	202	3.67	2.20

Table S2 | Electrical, optical and morphological properties of the silicon active layers.

1.2. Fabrication and characterization of solar cells.

An optimized formulation of silicon active layers were applied for the fabrication of n-i-p amorphous silicon solar cells with the following structure: substrate/Al/a-Si:H/IZO. The Al back contact was deposited by electron beam evaporation, while the IZO (In_2O_3 : 89.3 wt%, ZnO: 10.7 wt%) was produced by RF-magnetron sputtering (resistivity is in the order of $\rho = ~5x10^{-4}$ Ω .cm) at room temperature. The solar cells were characterized by current-voltage (*J–V*) measurements at room temperature under AM1.5 (100 mW/cm²) light conditions in a Spire Sun Simulator 240A.

2. Liquid packaging cardboard surface analysis

The study of the Liquid Packaging Cardboard (LPC) surface is of major relevance in order to determine which strategy should be implemented during the deposition process and to ensure the best quality of the produced solar cells. To assess the LPC substrate's properties several characterization and analysis were performed, as described in the main article. Here more information regarding the optical emission spectroscopy acquired spectra is presented.

2.1. Optical Emission Spectroscopy (OES)

OES was used to study the deposition process and gas decomposition during solar cell production. The simplicity of the setup and non-interference with plasma makes OES a useful tool that can provide valuable information about the film forming precursors and radicals

present in the plasma²⁻⁵. The plasma-emitted light was collected by a photo-collimator placed at a quartz viewport of the reactor (to ensure the recording of total emission of the plasma – from bulk and sheaths) and guided by the optical fiber to an Ocean Optics HR4000 spectrometer with a spectral range of 200 - 1100 nm.

Fig. S1 depict the optical emission spectra generated by excited species in the plasma during the deposition of intrinsic thin film on LPC, corning glass and Al glass coated.



Fig. S1 Comparison of OES spectra obtained during intrinsic layer deposited on LPC, AI coated glass, and corning glass at 145 °C and 200 °C (control samples).

Regarding possible contaminants, namely carbon and oxygen species, from the spectra analysis (Fig. S1) one can see OES is not sensible enough to provide qualitative conclusions. Carbon emission is not observed as its density is below the OES detection limit and Si and H emissions would also hide any emission from such species whose intensity are several orders of magnitude higher. Oxygen related peaks can be detected, but without significant difference between glass with deposited AI and LPC substrate.

3. Design of Experiment and mathematical modeling (DoE)

Combining experimental data with statistical analysis, to optimize the deposition process of amorphous silicon, can be an attractive strategy to achieve high quality thin films in a shorter time frame and with a minimum number of experimental sampling iterations, thus reducing the used resources.

It is well known that given the complexity behind silicon thin films, when optimizing a deposition process by randomly varying factors in a sequence, such as the OVAT system (One Variable At a Time) it can be misleading, since the one dimensional analysis that it allows makes it difficult and time consuming to find the optimal set of conditions. On the other hand, by employing design of experiments (DoE) and statistical analysis one has the opportunity to explore in a multidimensional fashion all the possible effects and interactions between the several deposition parameters and the expected optical, morphological and electrical properties of the films.

Given the fact that high quality amorphous thin films can be obtained close to the microcrystalline-silicon phase transition⁶, films obtained in this regime show increased light

stability against light induced degradation, given the increased medium range order and the inclusion of nanosized silicon grains in the amorphous matrix². Taking in consideration the type of films we are interested and from previous knowledge, the regime of interest under investigation, comprises a hydrogen dilution $(D_H(\%)=[H_2/(H_2+SIH_4)]*100)$ between 0 and 90% (onset of crystallinity phase), low power (15 mW/cm² $\leq P_W \leq 53$ mW/cm²) and low pressure (0.2 Torr $\leq P_{gas} \leq 0.4$ Torr). A selected set of samples was prepared, with conditions within the aforementioned limits, which was also used as the input parameters to construct the model for the statistical analysis. The thickness of the layers around 300 nm and the following Table S3 summarizes the set of depositions conditions initially tested (see chapter 1.1).

Table S3 Initial set of deposition conditions for the intrinsic films which will afterwards feed the statistical analysis as input parameters. P_{gas} is the deposition pressure; P_w , refers to the power density, H_2 and SiH₄ gases flows and D_H is hydrogen dilution.

Sample	P _{gas} (Torr)	P _w (mW/cm ²)	H ₂ Flow (sccm)	SIH ₄ Flow (sccm)	D _H (%)
1	0.2	15	0	14	0.0
2	0.2	15	112	14	88.9
3	0.3	21	40	10	80.0
4	0.4	53	80	10	88.9
5	0.4	21	20	10	66.7
6	0.4	15	40	10	80.0

The characterization parameters are the variables that will define the statistical analysis outputs and model responses. The table below (Table S4) summarizes the electrical, optical and morphological properties of the initial set of i-a-Si:H films.

Sample	<i>Ea</i> (eV)	σ _{d@25°C} (S/cm)	<i>Eg</i> (eV)	А	E ₀	С
1	0.84	1.5 x10 ⁻¹⁰	1.68	206.8	3.58	2.14
2	0.81	1.2 x10 ⁻⁹	1.72	212.7	3.60	2.14
3	0.94	3.2 x10 ⁻¹²	1.73	213.8	3.64	2.14
4	0.98	3.8 x10 ⁻¹¹	1.76	210.2	3.70	2.21
5	1.08	1.5×10^{-11}	1.72	212.8	3.67	2.17
6	1.08	2.1 x10 ⁻¹¹	1.72	211.0	3.66	2.15

Table S4 Optical, electrical and morphological properties of the initial set of deposited intrinsic films.

The computational modulation and statistical data analysis were performed using JMP 8.0 (S.A.S. Institute Inc., Cary, NC, USA), a statistical software that provides an interactive statistical graphical interface to display and analyze data.

With the initial pool of intrinsic films a *Stepwise* regression was applied to each one of the six continuous responses (*Eg*, *C*, *E*₀, *A*, *Ea*, $\sigma_{d@25^{\circ}C}$) in order to study all types of possible effects and it is an approach that facilitates searching and selecting among many models, especially when there is little theory to guide the selection of terms for a model. In the particular case of the dark conductivity, it is important to state that the values used in the model are logarithmic, $\log_{10}(\sigma_{d@25^{\circ}C})$, which facilitates the modeling and gives more emphasis to the magnitude order.

The Stepwise model applied to the input parameters (in bold) is composed of a:

- Three-way full factorial P_{gas}, P_W, P_{gas}*P_W, D_H, P_{gas}*D_H, P_W*D_H and P_{gas}*P_W*D_H
- Polynomial (P_{gas}, P_w, D_H) to Degree 2 P_{gas}, P_{gas}*P_{gas}, P_w, P_w*P_w, D_H and D_H*D_H

After identifying the main correlations between the deposition conditions, for each response, these significant effects were applied in a Standard Least Squares fitting method to generate response surfaces maps, an essential visual aid to determine the regimes that give rise to high quality films.

For each response, the regimes with identical output are highlighted with the same color, according to the mathematical prediction. Fig. S2, represents only one of the responses to exemplify the concept. Overlapping all the modeled response surface maps (*Eg*, *C*, *E*₀, *A*, *Ea*, $\sigma_{d@25^{\circ}C}$) one can now optimize the properties of the films by identifying the optimum regime of each response and determine which deposition conditions should be pursued to obtain improved intrinsic films.



Fig. S2 Contour profile plots for the mathematical modeling of the activation energy (*Ea***)**; (a) *Ea* response with the variation of power density (P_w) and pressure (P_{gas}) and hydrogen dilution (D_H) is kept constant, $D_H = 70\%$; (b) evolution of *Ea* response while P_{gas} and D_H change and P_w is kept constant, $P_w = 25 \text{ mW/cm}^2$; (c) *Ea* response while P_w and D_H change and P_{gas} is kept constant, $P_{gas} = 0.30$ Torr. The regimes with identical *Ea* output are highlighted with the same color.

The activation energy (*Ea*) corresponds to an energy barrier separating the metastable from the initial stable state⁷. From Fig. S2, *Ea* follows an expected trend for films produced at low pressure and power. The increase in pressure is directly correlated with higher *Ea* values, as the atomic hydrogen concentration decreases which leads to amorphization⁸. The increase

of hydrogen dilution (Fig. S2b) can somewhat oppose this tendency by increasing atomic hydrogen concentration; likewise a higher power density counteracts the scavenging of hydrogen atoms by SiH₄ by increasing the depletion of the same⁹. In conclusion, and given our interest in intrinsic films with properties typical of the boundary a-/ μ -Si:H, the preferable *Ea* should be below 1 eV and above 0.85 eV.

Subsequent to the determination of the desired properties for all the six responses (*Eg*, *C*, *E*₀, *A*, *Ea*, $\sigma_{d@25^{\circ}C}$), the following response surface maps of Fig. S3 depict the overlapping of these individual responses, by excluding the regimes that do not fit our requirements in grey. In other words, the area outside the white zone corresponds to the exclusion regimes for each parameter where the model predicts properties which are not relevant for high quality intrinsic thin films in the boundary a-/µ-Si:H.



Fig. S3 Contour profile plots for the mathematical modeling of the best combination of intrinsic film properties. For each morphological, optical and electrical response predicted, the area outside the white zone excludes the low quality films according to the input parameters, P_w, P_{gas} and D_H. Thus the white area highlights the estimated optimum intrinsic thin films deposition conditions. The evolution of the exclusion and optimum regimes is given by varying two deposition parameters and keeping the third fixed: (**a**) P_w & P_{gas}, D_H = 70%; (**b**) P_{gas} & D_H, P_w = 25 mW/cm²; (**c**) P_w & D_H, P_{gas} = 0.30 Torr.

The overlapping creates regimes of different grey intensities. The darker, the less relevant (more film properties are excluding that regime), hence $D_{H} < 50\%$, 0.30 > P_{gas} (Torr) < 0.4 and

 $20 > P_w (mW/cm^2) < 25$, take us away from the high quality transition regime of amorphous to microcrystalline. Given all the film properties, it is the broadening term of the *Lorentz Oscillator* (*C*) that imposes more limitations to the relevant regime but, at the same time, it is important to keep this value as close to 2.10 as possible, though films with fine properties can be found outside this boundary.

To attest the model precision, a new set of intrinsic films were prepared taking in consideration the regime of deposition conditions predicted by the model for high quality films (Table S5).

Sample	P _{gas} (Torr)	P _w (mW/cm ²)	H ₂ Flow (sccm)	SIH ₄ Flow (sccm)	D _H (%)
8	0.40	21	31	10	75.6
9	0.40	21	40	10	80.0
10	0.40	36	80	10	88.9

Table S5 New set of intrinsic films deposited to verify the model predictability accuracy.

The next table presents the predicted film properties and compares it with the actual experimental values (Table S6). The calculated error is the percentile difference between the experimental and the predicted value, where % $Error = \frac{|predicted-experimental|}{predicted} \times 100\%$.

Table S6 Comparison of optical, electrical and morphological properties between predicted and experimental data. The photosensitivity was only calculated experimentally, given by $\sigma_{ph}/\sigma_{d@25^{\circ}C}$, where σ_{ph} is the photoconductivity.

Sample	Source	<i>Ea</i> (eV)	σ _{d@25℃} (S/cm)	$\sigma_{ph}/\sigma_{d@25^{\circ}C}$	<i>Eg</i> (eV)	A	E ₀	С
	Experimental	0.95	2.9 x10 ⁻¹²	2.3×10^7	1.72	215.1	3.65	2.21
8	Predicted	1.08	1.8 x10 ⁻¹¹	-	1.72	213.3	3.58	2.16
	% Error	12.0%	7.3%*	-	0.0%	0.8%	2.0%	2.3%
	Experimental	0.97	1.5 x10 ⁻¹¹	1.3 x10 ⁷	1.73	212.2	3.67	2.17
9	Predicted	1.06	1.1 x10 ⁻¹¹	-	1.72	213.6	3.58	2.16
	% Error	8.5%	1.2%*	-	0.6%	0.7%	2.5%	0.5%
	Experimental	0.98	4.5 x10 ⁻¹²	1.5 x10 ⁵	1.75	216.0	3.66	2.15
10	Predicted	1.02	1.5 x10 ⁻¹¹	-	1.74	216.0	3.62	2.18
	% Error	3.9%	4.9%*	-	0.6%	0.0%	1.1%	1.4%

*The dark conductivity output given by the model is the logarithmic value $-\log_{10}(\sigma_{d@25^{\circ}C})$, hence the calculated error also uses the logarithmic values to give a linear error.

From the analysis of Table S6, one can distinguish that errors for the electrical properties are higher. This happens due to the difficulties associated with these measurements, which have lower accuracy and higher systematic and/or random errors. Nevertheless, the majority of the samples have errors below 5% for the electrical properties, while ellipsometry data shows remarkable agreement with the predicted values (%Error < 2.5%), hence the empirical modeling in this study shows reasonably good prediction ability in terms of the overall i-layer performance. Therefore, this study allows the development of a powerful and feasible tool to predict the performance of a PECVD thin film deposition process on the basis of the deposition conditions. Moreover, re-feeding the mathematical model with the new experimental data will increase the model accuracy, better define the response regimes and improve prediction.

However, the films deposited up to this point are of high quality and suitable for use in solar cells.

From the intrinsic layer samples pool, i-layer 9 was selected as the one with the best overall properties, to be applied in solar cells. Although the electrical properties are slightly inferior to those with lower D_H ($D_H < 80\%$), the measured photosensitivity ($\sigma_{ph}/\sigma_{d@25^{\circ}C}$, where σ_{ph} refers to the photoconductivity) is still in the range of 10^7 and the higher hydrogenation will on the other hand improve stability and reduce light degradation¹⁰, as it is closer to the transition phase. Regarding p-layer and n-layer, they were optimized previously and the deposition conditions, also in the low-pressure and power regime, are shown in Table S1.

Afterwards, the thickness of each layer was optimized to achieve the highest solar cell efficiency, following a similar mathematical statistic approach. In this particular study, since there is no previous knowledge of what if the optimum combination of layers thicknesses, 8 solar cells were deposited according to an orthogonal 2^k factorial screening design, where k is the number of factors which in this case equals to 3 (n-, i-, p-layer thickness), restricted to two levels. Screening factorial design allows the reduction of the initial pool of experiments by restricting the number of levels and performs only a fraction of the full factorial design.

Three different thicknesses for each layer were tested, hence defining a regime of interest where it is expected to achieve the optimal combination of thicknesses. Table S7 resumes the conditions and properties of the deposited cells (input parameters) used for the following mathematical modeling to find the best thickness combination. The error associated with the actual thickness of the deposited layer is not taken into consideration for model simplification. Since the thickness growth is controlled just by the residence time and given its low deposition rate, the uncertainty is low and the error constant.

Solar Cell	n-layer	i-layer	p-layer	η	FF	V _{oc}	J _{sc}	R _s	R _{sh}
	(nm)	(nm)	(nm)	(%)	(%)	(V)	(mA/cm ²)	(Ω.cm)	(Ω.cm)
1	36	325	15	3.22	54.2	0.82	7.25	35	754
2	33	325	12	3.05	59.6	0.72	7.13	21	783
3	33	325	15	4.23	58.2	0.84	8.65	24	1154
4	33	325	19	3.50	54.9	0.82	7.77	30	662
5	33	300	19	3.88	58.9	0.83	7.94	32	2290
6	33	350	15	3.67	54.6	0.81	8.30	29	644
7	30	300	15	4.04	55.6	0.81	8.97	25	668
8	30	325	19	3.78	61.7	0.84	7.29	25	1321

Table S7 Characterization properties of the initial set of deposited solar cells. These parameters are applied as the statistical analysis output responses, with exception to the shunt resistance (R_{Sh}) which does not show significant correlation with the layer thickness.

Following the same protocol, as for intrinsic layer optimization, the regimes of interest for each individual response were superimposed on a single graphic to correlate two of the input layer thickness and fixing the remaining one (Fig. S4). The area outside the white zone corresponds to the exclusion regimes for each parameter where the model predicts solar cells with lower output conversion.



Fig. S4 Contour profile plots for the mathematical modeling of the best combination of layer thickness. For each solar cell characterization parameter the area outside the white zone excludes the low yield according to the thickness of the p, n and intrinsic layers. Hence, the regime in white highlights the estimated optimum combination. The evolution of the exclusion and optimum regimes is given by varying two layer thicknesses and keeping the third fixed: (a) n-layer & i-layer, p-layer = 15 nm. (b) p-layer & i-layer, n-layer = 30 nm. (c) p-layer & n-layer, i-layer = 325 nm.

From the response surface maps (Fig. S4), one can distinguish how differently the responses react not only according to the thickness but also with the layer combination considered, as it was expected since each layer poses distinct constrains and influences differently the solar cells characteristic outputs¹¹.

For the considered range of thicknesses, J_{sc} is the most limiting factor for both doped layers, where the increase in the doped layer thickness decreases considerably the current density. This is directly related with the increase of the series resistance. In the case of the player, higher thickness prevents light trapping in the intrinsic layer¹².

On the other hand, the decrease of p-layer thickness also reduces the V_{oc} and efficiency, since for a very thin p-layer the interface TCO/p can influence the electrical field homogeneity through the junction.

Regarding the intrinsic layer, the greater the thickness, the higher the current density (the collection width increases¹³) but at the same time the more instable is the film, as the electric

field in the center regime of the layer weakens, which can also be correlated with the increase of defects and lower carrier collection¹⁴.

Given the analysis conducted to the simulation output, the combination of layers thickness which led to the best solar cell and were used in the article is the following: p-layer = 15 nm, i-layer = 325 nm and n-layer = 30 nm.

4. Influence on the solar cell properties of performing hydrogen plasma treatment on the substrate

The following study assesses the influence of the initial hydrogen plasma (before the deposition of the active solar cell layers) on the properties of previously optimized solar cells. Between the TCO interlayer deposition and the solar cell fabrication, the substrate is exposed to air for several minutes while moving from one reactor to another. In order to assure a substrate free of contamination, moisture and reactive dangling bonds, hydrogen plasma treatment is performed on the substrate prior to the silicon active layer deposition, by comparing different hydrogen plasma treatment ($P_{gas} = 500 \text{ mTorr}$, $P_w = 43 \text{ mW/cm}^2$, H_2 Flow = 200 sccm) times (3 and 6 min). Fig. S5 presents the *J-V* curves achieved and compares LPC with a reference solar cell deposited on glass.



Fig. S5 J-V curves for the solar cells (SC) deposited on glass and LPC subject to different initial H₂ plasma cleaning time.

A typical glass substrate prepared for nip solar cells (coated with aluminum and a thin interlayer of AZO) is not affected by this initial hydrogen plasma In particular, the presence of a transparent conductive oxide (TCO) such as AZO has not only the advantage of being stable in H-plasma environment¹⁵⁻¹⁷, but can also see its electrical, morphological and optical properties improved¹⁸⁻²⁰. However, according to Carlsson *et al*²¹, the exposure of a cellulose substrate to hydrogen plasma for a period above 4 min leads to a dramatic change of the surface composition. The hydrogen plasma treatment reduces the hydroxyl groups on the cellulose and creates low molecular weight materials. Although this cellulose based substrate has a thin foil of laminated aluminum, plasma can reach the uncovered cellulose edges or even the back. Hence, it is important to understand if a prolonged exposure to hydrogen plasma has any detrimental influence on the solar cell properties. Table S8 summarizes the effect of H₂ plasma

on the solar cell properties when deposited on LPC and compares it with a similar solar cell deposited on glass.

Table S8 Solar cell properties for different exposure hydrogen plasma times, prior to the deposition of the silicon layers.

Plasma time (substrate)	η (%)	FF (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	R _s (Ω.cm)	R _{sh} (Ω.cm)
3 min (LPC)	4.08	53.7	0.84	9.05	31	831
6 min (LPC)	3.35	48.8	0.83	8.28	45	988
6 min (Glass)	4.33	53.3	0.85	9.55	21	446

As expected, the LPC substrate subjected to the longest hydrogen plasma treatment shows the lowest efficiency. Carlsson *et al*²¹ shows that carbon singly bonded to oxygen decreases sharply and reaches the lowest value around 6 min of hydrogen plasma treatment; while at the same time the unoxidized carbon ratio fairly increases, which can imply an extended dehydroxylation of the cellulose molecules.

The prolonged H₂ plasma releases carbon above a threshold, which clearly decreases the solar cell properties, by activating and partly depositing it on the interlayer; Thereby hindering the collection of charges on the back contact which leads to a lower current density.

5. Quadrupole Mass Spectroscopy (QMS)

Quadrupole Mass Spectroscopy (QMS) is a useful tool to analyze plasma deposition processes which provides complete information about the gas phase chemical composition. Real-time process data were collected using a mass spectroscopy system connected to the PECVD system, throughout several steps of the solar cell fabrication. The mass spectrometer (EXtorr, model XT100M) was mounted parallel to the process chamber exhaust line and exhaust gases were collected through a 10 μ m sampling orifice located 500 cm away from the outer edge of the RF electrode, for a detection mass range up to 100 amu.

The PECVD production process comprises several steps and diverse molecules/contaminants, due to the exotic substrate here in study, can be present and contribute differently to the involving atmosphere. Here, it is presented in more detail all the identified peaks partial pressures, which corresponds to more than 98% of the exhaust gas composition (Fig. S6). The remaining 2% are the sum of the relative pressures bellow 10⁻¹⁰ mbar. QMS data was collected for depositions on LPC on several stages, namely, immediately after loading the substrate in the PECVD (0' Load), after 12h of vacuum pumping and baking at 145 °C (12h Load), at the end of the initial 3' H2 cleaning plasma (3' H2 plasma), before starting the deposition of the p-layer and with stabilized pressure (Before p-layer) and at the end of the p-layer deposition (End p-layer).



Fig. S6 Partial pressure histograms of the identified amu signals for different stages of the silicon active layers deposition; (a) H_x peaks (1-3 amu)²²⁻²⁵; (b) 12-15 amu signals²²⁻²⁶; (c) H_xO (x = 0 – 3) peaks (16-19 amu)^{22, 25}; (d) 28-33 amu signals, comprising SiH_x (x = 0 – 3) molecules, hydrocarbyl groups and molecules N₂, CO, O₂^{22-25, 27-30}; (e) organic molecules and Si-R species (39-45 amu)^{22, 23, 25}.

Before the deposition of the p-aSi:H layer, the evolution of the amu signals follows the expected signal trend. Regarding the organic compounds with higher amu values (Fig. S6e) their signal is partially masked due to the presence of the deposition gases, silane and methane; nonetheless the contribution of molecules in this range is below 1% of the total pressure. The signal variation before and at the end of p-layer deposition does not show the presence of new peaks and only a small decrease of the overall partial pressure, except for hydrogen where it increases, indicating silane and methane consumption and hydrogen production during plasma deposition²⁴. The decrease of the amu signals is not as dramatic as

that observed during H_2 plasma treatment, since the applied power for the deposition of the player (15 mW/cm²) is much lower than the H_2 plasma treatment power (42 mW/cm²), which leads to a lower gas dissociation and film incorporation, and a very small variation of the measured partial pressure peaks signal.

References

- 1. Martins, R., *et al.* Nanostructured silicon and its application to solar cells, position sensors and thin film transistors. *Philosophical Magazine*, **89**(28-30), 2699-2721, 2009.
- 2. Muthmann, S. & Gordijn, A. Amorphous silicon solar cells deposited with non-constant silane concentration. *Solar Energy Materials and Solar Cells*, **95**(2), 573-578, 2011.
- 3. Rath, J. K., Brinza, M., Liu, Y., Borreman, A. & Schropp, R. E. I. Fabrication of thin film silicon solar cells on plastic substrate by very high frequency PECVD. *Solar Energy Materials and Solar Cells*, **94**(9), 1534-1541, 2010.
- 4. Shui-Yang, L., Yu-Cheng, C., Yun-Shao, C., Yin-Yu, C. & Shuo-Jen, L. Deposition and Characterization of High-Efficiency Silicon Thin-Film Solar Cells by HF-PECVD and OES Technology. *Electron Devices, IEEE Transactions on*, **59**(5), 1245-1254, 2012.
- 5. Strahm, B., Feltrin, A., Bartlome, R. & Ballif, C. Optical emission spectroscopy to diagnose powder formation in SiH4-H2 discharges. 74090E-74090E, 2009.
- 6. Collins, R. W., *et al.* Evolution of microstructure and phase in amorphous, protocrystalline, and microcrystalline silicon studied by real time spectroscopic ellipsometry. *Solar Energy Materials and Solar Cells*, **78**(1–4), 143-180, 2003.
- 7. Stutzmann, M., Jackson, W. B. & Tsai, C. C. Light-induced metastable defects in hydrogenated amorphous silicon: A systematic study. *Phys Rev B*, **32**(1), 23-47, 1985.
- 8. Mai, Y., *et al.* Microcrystalline silicon solar cells deposited at high rates. *Journal of Applied Physics*, **97**(11), -, 2005.
- Matsuda, A. Thin-film silicon Growth process and solar cell application. Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers, 43(12), 7909-7920, 2004.
- 10. Guha, S., Yang, J., Banerjee, A., Yan, B. & Lord, K. High quality amorphous silicon materials and cells grown with hydrogen dilution. *Solar Energy Materials and Solar Cells*, **78**(1–4), 329-347, 2003.

- 11. Raniero, L., *et al.* Influence of the layer thickness and hydrogen dilution on electrical properties of large area amorphous silicon p-i-n solar cell. *Solar Energy Materials and Solar Cells*, **87**(1-4), 349-355, 2005.
- 12. Takahashi, K. & Konagai, M. *Amorphous silicon solar cells*. John Wiley & Sons Canada, Limited, 1986.
- 13. Bivour, M., *et al.* n-type silicon solar cells with amorphous/crystalline silicon heterojunction rear emitter. Photovoltaic Specialists Conference (PVSC), 2010 35th IEEE; 2010 20-25 June 2010; 2010. p. 001304-001308.
- 14. Kabir, M. I., *et al.* Amorphous Silicon Single-Junction Thin-Film Solar Cell Exceeding 10% Efficiency by Design Optimization. *International Journal of Photoenergy*, 2012.
- 15. Kang, J., Kim, H. W. & Lee, C. Electrical Resistivity and Transmittance Properties of Aland Ga-codoped ZnO Thin Films. *Journal of the Korean Physical Society*, **56**(2), 576-579, 2010.
- 16. van Deelen, J., *et al.* Transparent conducting materials: overview and recent results. 2012; 2012. p. 84700P-84700P-84708.
- 17. Minami, T. Present status of transparent conducting oxide thin-film development for Indium-Tin-Oxide (ITO) substitutes. *Thin Solid Films*, **516**(17), 5822-5828, 2008.
- 18. Wang, F.-H., Chang, H.-P., Tseng, C.-C., Huang, C.-C. & Liu, H.-W. Influence of hydrogen plasma treatment on Al-doped ZnO thin films for amorphous silicon thin film solar cells. *Current Applied Physics*, **11**(1), S12-S16, 2011.
- 19. Chang, H. P., Wang, F. H., Wu, J. Y., Kung, C. Y. & Liu, H. W. Enhanced conductivity of aluminum doped ZnO films by hydrogen plasma treatment. *Thin Solid Films*, **518**(24), 7445-7449, 2010.
- 20. Wang, F. H., Chang, H. P., Tseng, C. C. & Huang, C. C. Effects of H-2 plasma treatment on properties of ZnO:Al thin films prepared by RF magnetron sputtering. *Surface & Coatings Technology*, **205**(23-24), 5269-5277, 2011.
- 21. Carlsson, C. M. G. & Strom, G. REDUCTION AND OXIDATION OF CELLULOSE SURFACES BY MEANS OF COLD-PLASMA. *Langmuir*, **7**(11), 2492-2497, 1991.
- 22. NIST Standard Reference Data. [cited]Available from: http://webbook.nist.gov/chemistry/mw-ser.html

- 23. Ferreira, I., Silva, V., Águas, H., Fortunato, E. & Martins, R. Mass spectroscopy analysis during the deposition of a-SiC:H and a-C:H films produced by hot wire and hot wire plasma-assisted techniques. *Applied Surface Science*, **184**(1–4), 60-65, 2001.
- 24. Chowdhury, A. I., Klein, T. M., Anderson, T. M. & Parsons, G. N. Silane consumption and conversion analysis in amorphous silicon and silicon nitride plasma deposition using in situ mass spectroscopy. *Journal of Vacuum Science & amp; Technology A*, **16**(3), 1852-1856, 1998.
- 25. Gabriel, O., Kirner, S., Klick, M., Stannowski, B. & Schlatmann, R. Plasma monitoring and PECVD process control in thin film silicon-based solar cell manufacturing. *EPJ Photovolt*, **5**, 55202, 2014.
- 26. Vassallo, E., Cremona, A., Ghezzi, F. & Ricci, D. Characterization by optical emission spectroscopy of an oxygen plasma used for improving PET wettability. *Vacuum*, **84**(7), 902-906, 2010.
- 27. Kirner, S., Gabriel, O., Stannowski, B., Rech, B. & Schlatmann, R. The growth of microcrystalline silicon oxide thin films studied by in situ plasma diagnostics. *Applied Physics Letters*, **102**(5), -, 2013.
- 28. Weakliem, H. A., Estes, R. D. & Longeway, P. A. Ion–molecule reactions in a direct current silane glow discharge. *Journal of Vacuum Science & Comp; Technology A*, **5**(1), 29-36, 1987.
- 29. Xu, S., *et al.* Improve silane utilization for silicon thin film deposition at high rate. *Thin Solid Films*, **520**(2), 694-696, 2011.
- 30. Nishimoto, T., Takai, M., Miyahara, H., Kondo, M. & Matsuda, A. Amorphous silicon solar cells deposited at high growth rate. *Journal of Non-Crystalline Solids*, **299–302**, **Part 2**(0), 1116-1122, 2002.