

DEVELOPMENT OF NANOCRYSTALLINE SILICON SOLAR CELLS GROWN BY LEPECVD: OPTIMIZATION OF THE INTRINSIC LAYER FOR PIN STRUCTURES

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ABSTRACT: Low-energy plasma-enhanced chemical vapour deposition (LEPECVD) is a new technique for growth of hydrogenated microcrystalline silicon ($\mu\text{-Si:H}$) at high growth rate. For all existing growing techniques, a silane dilution threshold exists below which the material's electronic and optical properties are crystalline-like and above which they are amorphous-like. As known in literature, optimized $\mu\text{-Si:H}$ materials for photovoltaics are always grown around this threshold. Our previous studies have demonstrated that up to 10% silane dilution ($d = [\text{SiH}_4] / ([\text{SiH}_4] + [\text{H}_2])$), the grown material showed a rather crystalline behaviour. Therefore our present study focuses on higher dilution samples (30 and 50%) characterized electrically (dark and illuminated conductivity) and structurally (confocal Raman spectroscopy) in order to identify this dilution threshold for LEPECVD. The conductivity measured in a solar cell configuration allowed us to draw only a semi-quantitative picture. This was, however, sufficient to reveal that reducing the silane flow (from 20 to 12 sccm) leads to an increase of the structural homogeneity in the growth direction, of the surface crystallinity, and of the conductivity (dark and illuminated) while varying the silane dilution induces nearly no change of these properties. Then, from a conductivity criterion, the most suitable material seems to be obtained at a flow of 16 sccm of silane and a dilution d of 30%. However, this material shows an inhomogeneity of the microstructure in the growth direction which could be detrimental to the performance of the solar cell.

Keywords: Thin Film, $\mu\text{-Si:H}$, PECVD, Contact, Photoconductivity

1 INTRODUCTION

Hydrogenated microcrystalline or nanocrystalline silicon ($\mu\text{-Si:H}$ or nc-Si:H) is considered as one of the most promising materials for photovoltaic applications, mainly due to its potential in reducing the costs of solar cells [1]. In this publication $\mu\text{-Si}$ is used as a synonym for both micro- and nanocrystalline Si materials.

In this framework, low-energy plasma-enhanced chemical vapour deposition (LEPECVD) [2], like HWCVD (Hot Wire CVD) and VHF (Very High Frequency)-PECVD, is one of the new techniques developed for growing $\mu\text{-Si}$ at high enough deposition rates to lift one of the most important obstacles towards its industrial application.

As observed previously, a suitable $\mu\text{-Si}$ material for photovoltaics is a compromise between a crystalline material (low optical absorption, high electrical conductivity) and amorphous material (high optical absorption, low electrical conductivity) [3]. For all existing growth techniques, a silane dilution threshold exists (regardless of other deposition parameters in a first approximation) below which the material's electronic and optical properties are crystalline-like and above which they are amorphous-like. As a consequence, an optimized $\mu\text{-Si}$ material for photovoltaics is always grown with a dilution around this threshold value to take advantage of a relatively high conductivity (reducing the electrical losses) and a relatively high optical absorption (reducing the optical losses). This kind of material is called a transition material.

Our previous study [4] on samples grown at a dilution ranging from 2 to 10% showed a lateral dark conductivity (σ_d) in the range of 10^{-6} S/cm and an illuminated conductivity (σ_{ill}) of the same order which is typical for c-Si . As previous TEM analyses [5] showed that, in addition to the nanometre-scaled crystallites, a columnar structure in the growth direction exists, we can reasonably presume that the electrical properties are

anisotropic. Considering that the current flow in a solar cell will be normal to the i -layer surface (in the growth direction), we have found that it would be more relevant to measure the conductivity in solar cell configuration [4].

The present work focuses on the investigation of 1 μm thick samples grown at a dilution of 30 and 50% for different silane flows.

We investigate the change in microstructure and conductivity of the $\mu\text{-Si}$ layer due to different dilution ratios and silane flows. The optimum material deposited so far is analyzed.

The microstructure is characterized by confocal Raman spectroscopy and the conductivity by its measurement in the dark and illuminated state while the samples show a solar cell configuration.

The constraints imposed by the measurement in solar cell configuration are discussed.

2 EXPERIMENTAL

2.1 Material

One micrometer thick intrinsic $\mu\text{-Si:H}$ films are grown on ITO coated glass substrates ($R_{\text{sheet}} = 10 \Omega/\square$ on 7059 Corning glass) with high deposition rates (between 1.5 and 4 nm/s) using the LEPECVD process.

The films are deposited at substrate temperatures of 250°C, using SiH_4 and H_2 as precursor gases. The dilutions are 30 and 50% with silane flow values of 20, 16 and 12 sccm.

Further details of both the deposition process and the sample growth can be found in [5-7].

2.2 Configuration for conductivity measurements

We evaporate $5 \times 5 \text{ mm}^2$ square-shaped contacts on the $\mu\text{-Si}$ layer (up to 6 contacts per $5 \times 5 \text{ cm}^2$ substrates) followed by an annealing step at 180°C in Ar atmosphere for 90 min.

For the study of the contact properties 3 different metals or metal stacks for the $\mu\text{-Si}$ contact are studied: Al (1000 nm), Ag (1000 nm), Ti/Pd/Ag (50/50/1000 nm). In all cases a maximum distance of 5 mm between the ITO contact and $\mu\text{-Si}$ contact is ensured.

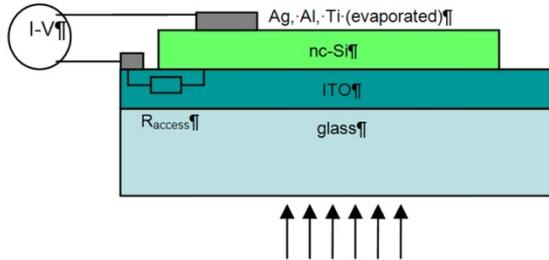


Figure 1: Schematic principle of conductivity set-up in solar cell configuration.

The measurement itself was performed using a standard IV measurement setup (Fig. 1) in a sun simulator under AM 1.5 conditions keeping the sample temperature at about 25°C.

2.2 Confocal Raman Spectroscopy

Raman measurements are carried out at room temperature with a Jobin Yvon LabRAM micro-Raman system in backscattering configuration, equipped with a LN₂-cooled charge-coupled device camera. Crystallinity depth profiles are obtained combining the powerful properties of the confocal optics with a He-Ne laser at 633 nm, penetrating about 1 μm in $\mu\text{-Si}$. However, the crystallinity depth profiles are shown without providing the depth of the detected film region with respect to the surface. In fact, in the case of a confocal microscope, the optical thickness strongly depends on the refractive index of the examined material, which cannot be accurately determined in the case of a biphasic material due to its inhomogeneous structure.

The crystalline volume fraction χ_c , which was obtained from each Raman spectrum, is calculated on the basis of the method proposed by Smit et al. [8], using as reference a completely amorphous sample grown at 200°C and $d = 100\%$.

3 SOLAR CELL CONFIGURATION STUDY

3.1 Measurement and interpretation

The measured IV curves have various nonlinear shapes or, more precisely, locally linear parts as seen in Fig. 4.

Considering that the nonlinearity at low voltage is present whatever type of metal is used for contacting, we assume that it is the ITO/ $\mu\text{-Si}$ contact which has a Schottky character, rather than the metal/ $\mu\text{-Si}$ contact.

Based on these considerations we build a very simple model that could explain these curves at least qualitatively.

In this model, we assumed that the ITO/ $\mu\text{-Si}$ contact is Schottky, and can behave like a solar cell under illumination, and that only the $i\text{-}\mu\text{-Si}$ layer resistance is dependent on the illumination.

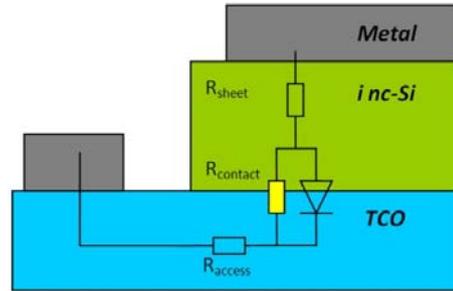


Figure 2: Model developed to explain the observed IV curves.

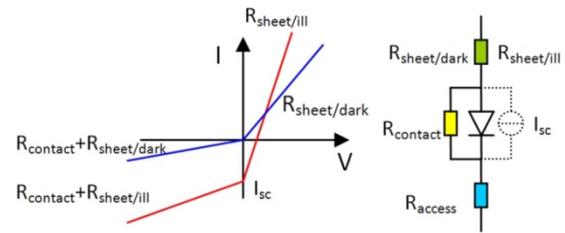


Figure 3: Schematics of the double slope effect in the IV curves.

Considering that the contact resistance can be of the same order of magnitude as the resistance of the $\mu\text{-Si}$ layer, R_{contact} and R_{sheet} are in series in reverse bias while only R_{sheet} is taken into account in forward bias. Fig. 4 shows the two different slopes of the measured IV curves.

At a bias larger than 1 V absolute other effects lead to a supralinear behaviour. We suppose that:

- in forward bias, there is a space charge limited current (SCLC) which occurs at low voltage due to the small interelectrode distance (the thickness of the film is around 1 μm) [4];
- in reverse bias, the SCLC and/or the so called punch through phenomenon lead to a sharp increase of the current due to the very quick extension of the depletion region with the voltage (non intentionally doped material and low thickness) that reach the back electrode [9].

These phenomena mean that the conductivity measurements are only useful up to 1 V absolute.

3.2 Metal contact configuration study

The following observations have been made:

- Ti/Pd/Ag contacts show the most linear behaviour under illumination, however the high current values and the perfectly linear characteristics lead to the assumption that the Schottky contact is mostly short circuited through pinholes that can be observed just by the eye.
- IV curves with Al contacts show the 2-slope phenomenon previously described. However, the low current value and some instability during measurement in combination with low reproducibility allow us to conclude that the contacts are not reliably established. We then could conclude that Al has not formed a homogeneous contact with Si.

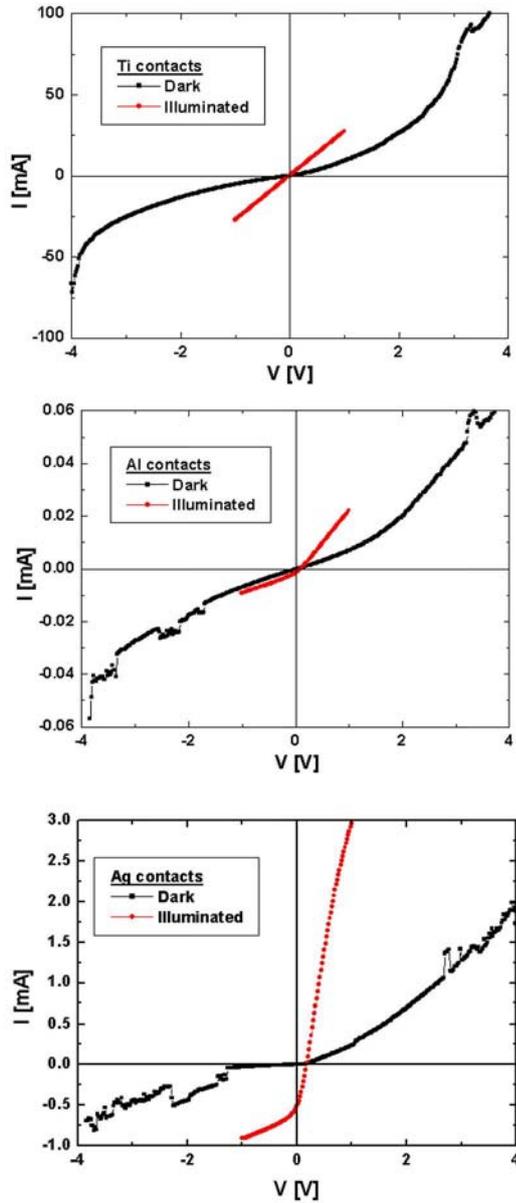


Figure 4: Typical IV curves from Ag, Al/Ag, and Ti/Pd/Ag contacts

- Ag contacts lead to true solar cell-like IV curves. A fitting procedure according to our model (Fig. 2) was possible only when taking into account an ideality factor of 2 for the diode which is characteristic of high recombination in the space charge region. The fitted very high value of the saturation current of this diode is consistent with a very low minority carrier lifetime which is well known in the literature for this kind of material. The high stability and reproducibility of the measurement lead us to think that Ag makes a reliable Ohmic contact on Si which allows the true nonlinear behaviour of the ITO/ μ c-Si contact to be observed.

Concerning the method itself we have to notice that (with these contact geometry parameters) the access resistance is of the same order of magnitude as the μ c-Si material resistance when the material conductivity reaches 10^{-5} S/cm. Such values could be obtained in the case of the illuminated conductivity of a good μ c-Si

material. This could lead to an underestimation of the conductivity of the material.

3.4 Recommendations

In the case of lateral conductivity measurements it can be stated that the method is less sensitive for a change in the properties of the layer underneath the contact, so that Ti is the best suited metal for establishing a reliable and low resistance Ohmic contact.

For a conductivity setup in solar cell configuration, or a *pin* solar cell back contact, the integrity of the very thin layer below the contact must be preserved while insuring a good Ohmic contact. We then recommend the use of Ag for this purpose.

The μ c-Si/TCO contact must be Ohmic and we have seen that it is probably not the case using ITO as TCO. However, another TCO can perhaps ensure an Ohmic contact which could make the conductivity measurement in solar cell configuration a reliable technique within the following restrictions:

- The conductivity to be measured should be below 10^{-5} S/cm;
- The measurement should be carried out at low voltage ($|U| < 1$ V), and the linearity must be checked.

4 CONDUCTIVITY AND RAMAN RESULTS

4.1 Conductivity

Due to the nonlinearity of the IV curves, depending on the metal used, but also due to the deposition inhomogeneity, the results presented are only semi-quantitative.

Table I: Summary of growth parameters and conductivity as well as surface crystallinity measurements for the samples studied.

Ref.	$d =$ [SiH ₄] [SiH ₄]+[H ₂]	[SiH ₄] (sccm)	[H ₂] (sccm)	Surface χ_c	Photogain / σ_d
7821	30%	20	46.7	28%	high/low
7823	30%	16	37.3	27%	med/med
7824	30%	12	28	41%	low/high
7825	50%	20	20	36%	high/low
7826	50%	16	16	27%	low/high
7827	50%	12	12	39%	low/high

Considering that low/med/high dark conductivities correspond to 10^{-11} - 10^{-9} / 10^{-8} - 10^{-7} / 10^{-6} - 10^{-5} S/cm respectively, and that low/med/high photogains (ratio of the illuminated conductivity to the dark conductivity) correspond to 1-10/20-500/1000-10000 our conductivity measurements are summarized in Table I.

Using this representation, a low photogain and a high σ_d are characteristics of a crystalline material whereas a low σ_d and a high photogain are characteristics of an amorphous material. In between (medium/medium) lies our targeted transition material.

We observed that reducing the silane flow to 12 sccm has increased the crystallinity at the surface, which is

correlated with an increase of the dark conductivity and a decrease of the photogain.

However, the conductivity depends on the crystallinity distribution of the whole layer, which will be examined in the next section. Therefore, the surface crystallinity data are not necessarily in agreement with the interpretation of the conductivity data.

4.2 Raman spectroscopy

Additionally, Raman spectroscopy allowed us to probe the structural morphology of the material.

We observed that decreasing the silane flow leads to an increase of the crystallinity far from the surface, whereas the difference in surface crystallinity is less pronounced for the 30% (Fig. 4) and 50% dilution samples.

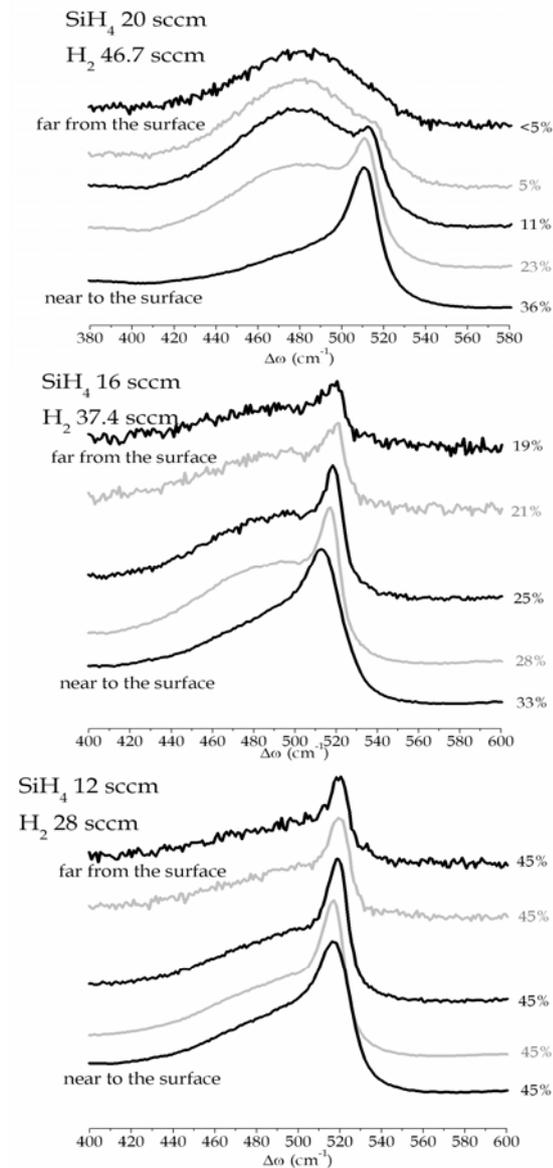


Figure 4: Results from confocal Raman spectroscopy showing the crystallinity of 3 $\mu\text{c-Si}$ samples grown using different SiH_4 and H_2 fluxes, all yielding the same dilution factor (in this case $d = 30\%$).

It has to be remarked that a high silane flow will lead to a higher growth rate and so a more amorphous material at the beginning of the growth, which is in agreement with what we observed here.

The global increase of the crystallinity with the reduction of the silane flow is also in good agreement with the trend observed in conductivity (reduction of the photogain and increase of the dark conductivity).

5 DISCUSSION

We observed no noticeable qualitative difference between 30% and 50% dilution both in conductivity and Raman spectroscopy results.

From the point of view of the conductivity results only, the best results are obtained for the samples grown at $d = 30\%$ with 16 sccm of silane flow. However, the best contact on this sample showed a σ_d of 10^{-8} S/cm and a σ_{III} of 10^{-6} S/cm, which is still one decade lower for both parameters than the material we are aiming for. This leads us to the conclusion that the performances of solar cells made from this material might be lower than expected.

It has been reported in the literature that a structural inhomogeneity of a sample could be a drawback for solar cell applications, due to the inhomogeneous electric field that is induced inside the layer [10]. Therefore a more homogeneous but a more crystalline material might be chosen for the first fabrication of solar cells from this material.

The best material for photovoltaic application grown by LEPECVD has a crystallinity fraction of less than 50%. Indeed, a material with 45% crystallinity (such as that produced at 12 sccm silane flow and $d = 30\%$) behaves as a crystalline material from the conductivity point of view (nearly no photogain). From these data, the interesting range of crystallinity would be between 25 and 35%.

Nevertheless, we have to keep in mind that photogain and dark conductivity are only rough estimators of the quality of a material for solar cells. A more refined analysis could be achieved by estimating the ambipolar diffusion length by Steady State Photocurrent Grating (SSPG) [11]. In combination with the illuminated conductivity data this could give us the normalized mobility lifetime product, which is considered as a reliable indicator of the quality of a material for solar cell applications. Another possibility lies in the estimation of the dangling bond density and the Urbach energy of the valence band tail which could be derived using the absolute optical absorption coefficient. This could be evaluated by Constant Photocurrent Method (CPM), Photothermal Deflection Spectroscopy (PDS) [12] or Fourier Transform Photocurrent Spectroscopy (FTPS) [13].

6 CONCLUSION

The metal contact configuration study allowed us to use Ti/Pd/Ag contacts for lateral conductivity tests and Ag for solar cell configuration conductivity measurement or contacting of solar cells.

A transition in silane dilution was not as clearly identified for LEPECVD as it has been for HWCVD or VHF-PECVD. However, we observe an increase of the

in-depth structural homogeneity as well as the average crystallinity by reducing the silane flow, which demonstrates the large influence of this parameter in $\mu\text{c-Si}$ growth.

A suitable material for solar cell application could be grown with $d = 30\%$ and $[\text{SiH}_4] = 16$ sccm, based on conductivity criteria. However, on a structural homogeneity basis it would be better to use $d = 30\%$ and $[\text{SiH}_4] = 12$ sccm.

Further investigation of the material quality will be performed at a solar cell level.

The conductivity measurements in solar cell configuration could be of interest for obtaining reliable quantitative measurements providing that:

- the TCO/ $\mu\text{c-Si}$ contact is Ohmic;
- the front contact is Ag;
- the measurement is carried out at voltage below 1 V absolute and;
- the conductivity to be measured is not above 10^{-5} S/cm.

In conclusion, promising $\mu\text{c-Si}$ *i*-layers for photovoltaic applications can be grown with high deposition rates and structural uniformity by LEPECVD.

7 ACKNOWLEDGEMENT

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