Studies on grain boundaries in nanocrystalline silicon grown by Hot-Wire CVD

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Abstract

The use of a tantalum wire in Hot-Wire Chemical Vapour Deposition has allowed the deposition of dense nanocrystalline silicon at low filament temperatures (1550ºC). A transition in crystalline preferential orientation from (220) to (111) was observed around 1700ºC. Transmission Electron Microscopy images, together with Secondary Ion Mass Spectrometry measurements, suggested that no oxidation occurred in material obtained at low filament temperature, due to the high density of the tissue surrounding grain boundaries. Greater amount of SiH_3 radicals formed at these temperatures seemed to be responsible of the higher density.

Keywords: nanocrystalline silicon, Hot-Wire CVD, oxygen incorporation
Subject Index terms: N100, C185, O155

1. Introduction

Hot-Wire Chemical Vapour Deposition (HWCVD), also called Thermocatalytic CVD, has been applied to the deposition of nanocrystalline silicon (nc-Si:H) and has been postulated as an alternative to well-established plasma CVD techniques due to its simplicity and ability to achieve higher deposition rates. The differences between both techniques result in different species generated, different secondary gas phase reactions and the lack of ion bombardment in the case of HWCVD. These facts lead to a different set of suitable technologic parameters to obtain device-quality material. In particular, contrary to what happens in Plasma Enhanced CVD (PECVD), where dense nc-Si:H is obtained at substrate temperatures close to 250ºC [1], moderately high substrate temperatures (>400ºC) seem to be required in HWCVD to achieve dense material [2]. This need of a significantly higher deposition temperature in HWCVD than in PECVD limits the type of substrate and solar cell structures available.

The main drawback of nc-Si:H deposited by HWCVD at low substrate temperatures (~200ºC) is its low density and high porosity, as it consists mainly of silicon crystallites surrounded by porous grain boundaries. This high porosity favours a very fast oxidation when the samples are exposed to air. This oxidation also affects the deposited solar cells and causes an irreversible degradation in their performance after some days of exposure to air.

In this paper we focus on the obtaining of dense nc-Si:H by HWCVD at low substrate temperature (200ºC) using a tantalum wire. Tantalum, when compared to tungsten, has an insignificant silicide formation, so it makes it possible to work at lower filament temperatures (T_f) [3]. Since the species generated on the surface of the hot filament are highly dependent on its temperature, we have concentrated on the effects of this key parameter on the structure and chemical stability of the layers.

2. Experimental

All nc-Si:H samples were deposited onto Corning 1737 glass and Si(111) in a HWCVD reactor, as described elsewhere [4]. The dissociation of the gases was achieved by means of a 3-loop basket-shaped tantalum filament the upper part of which is placed 3 cm below the substrate. The filament was heated at temperatures in the range of 1500-1850ºC. The substrate temperature was kept at 200ºC and a process pressure of $3.8x10^{-2}$ mbar and a gas mixture consisting of 4 sccm of silane and 76 sccm of hydrogen were used. It is important to notice that due to the geometry of our reactor a change of 300ºC in T_f did not affect the substrate temperature significatively. Without substrate holder heating, the sample temperature reaches 150ºC with the filament geometry used in this work at its maximum temperature.

The thickness and deposition rate of the samples were measured with a Dektak profilometer. The crystalline fraction of the samples was deduced from Raman spectroscopy. Crystalline preferential orientation and grain size were obtained from X-Ray diffraction (XRD). Hydrogen and oxygen content (C_H, C_O) were obtained from Fourier infrared (FTIR) spectrometry following Curtins and Veprek [5]. The oxygen content of the samples and its evolution was also analysed from Secondary Ion Mass Spectrometry (SIMS) measurements. Transmission Electron Microscopy (TEM) has been performed to one of the dense films.

3. Results

In order to study the effects of the Ta T_f on the structure and chemical stability of nc-Si:H layers, several samples were deposited at wire temperatures between 1500 and 1850ºC.

All deposited samples had thicknesses around 1 µm. The deposition rate stayed almost constant (2.3 - 3.2 Å/s) in the whole range of T_f used in this study. This can be attributed to the geometry of the filament and the gas inlet in our system that result in a high probability of the silane molecules to collide with the filament surface.

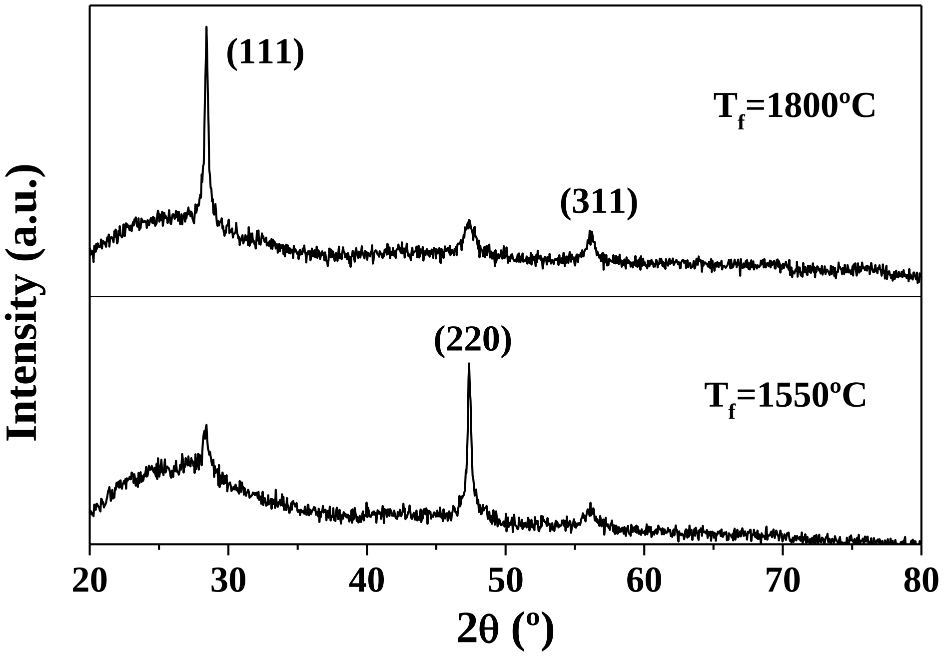

Fig. 1. X-Ray diffraction patterns corresponding to samples with similar thickness (1µm), deposited at filament temperatures of 1800 and 1550ºC.

Raman measurements of the films performed with the laser beam being incident from the top side showed a crystalline fraction of 95% regardless T_f. Differences in the crystallographic preferential orientation were found at different T_f. XRD showed (220) crystalline preferential orientation for samples grown at low T_f (below 1650ºC). On the other hand, nc-Si:H layers obtained at T_f above 1700ºC exhibited (111) crystalline preferential orientation, as can be seen in fig.1 for 1550 and 1800ºC. The intensity ratio of crystalline orientations ($I_{(220)}/I_{(111)}$) had its maximum at 1550ºC, as can be observed in Fig.2. This figure also shows that grain size values obtained are in agreement with the intensity ratio. (220) grain size decreased with increasing filament temperatures from 50 nm to values around 15 nm whereas (111) grain sizes increased from 10 nm at 1500ºC to 70 nm at 1850ºC.

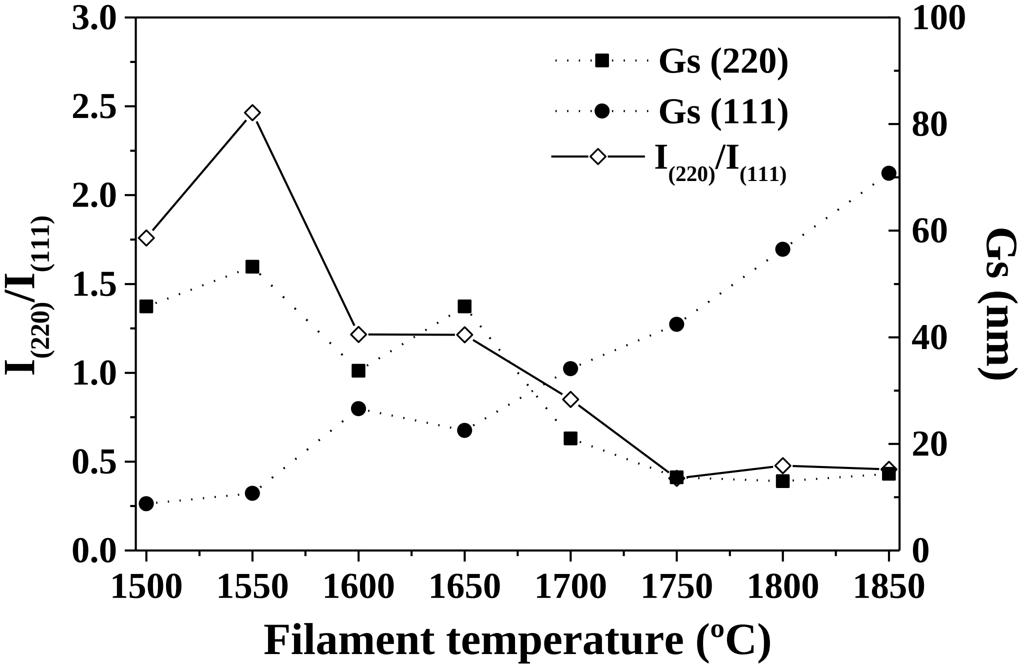

Fig. 2. Grain sizes in (111) and (220) crystalline preferential orientations and intensity ratio of crystalline orientations ($I_{(220)}/I_{(111)}$) as a function of the filament temperature.

Hydrogen content of the samples, calculated from the Si-H wagging band of the FTIR spectra, decreased as T_f was increased, changing from values of C_H=7% at 1500ºC to values of 3% at high filament temperatures. FTIR spectra also allowed us to study the degree of oxidation of our samples and its evolution with time. Fig. 3 shows the Si-O bands measured three months after the deposition of the nc-Si:H layers and there it can be seen that the average C_O diminished with decreasing T_f. Saturated C_O up to 18.5% were obtained after long time air exposure for samples deposited at high T_f whereas values below 2% were obtained at T_f below 1600ºC. Further air exposure of the layers under illumination, which enhances the oxidation process and allows a faster reaching of the saturated oxygen content, did not enlarge the peak.

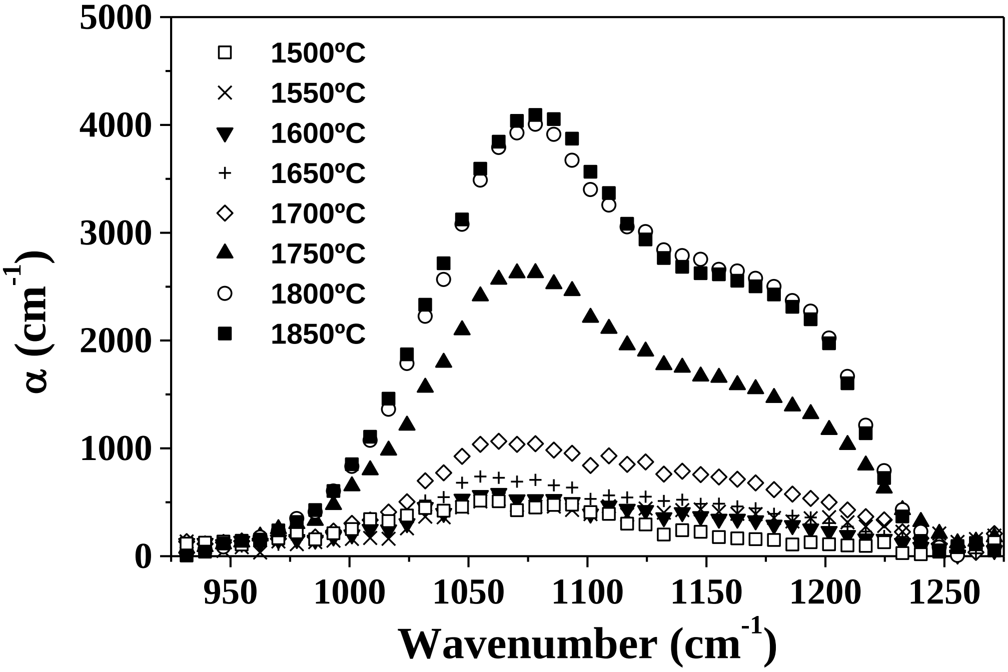

Fig. 3. Si-O absortion bands measured by FTIR three months after the deposition for samples deposited at filament temperatures between 1500 and 1850ºC. Oxygen content changes from 2% in samples deposited at low T_f to 18.5% at high T_f.

The low value of the average oxygen content in samples deposited at low T_f suggested us that the oxidation process in these films was limited to a superficial layer. In order to investigate the distribution of oxygen in the films, SIMS measurements of two of the samples were carried out – samples grown at 1550 and 1800ºC were chosen. Fig. 4 shows oxygen compositional profiles performed by SIMS half a year and a year after the deposition of the samples. That grown at 1800ºC showed an oxygen content uniform from the top of the sample to the sample-substrate interface. The amount of oxygen incorporated in the sample grown at 1550ºC decreased as we approached the substrate from a value close to 10^{20} cm^{-3} at the top of the sample to a value of $4x10^{18}$ cm^{-3} near the interface, with an almost constant concentration around $6x10^{18}$ cm^{-3} inside the film. The SIMS depth profile clearly showed that oxygen incorporation in this case was limited to a more superficial layer. Constant oxygen concentration of about $3x10^{18}$ cm^{-3} inside the film has been reported for device quality compact nc-Si:H deposited by HWCVD at moderately high substrate temperatures [6]. The bulk value of oxygen concentration of our samples is also comparable to that of microcrystalline silicon deposited by VHF CVD ($2x10^{18}$ cm^{-3}) [7]. It has also to be noticed that the ratio of C_O between both samples calculated from the FTIR spectra was in agreement with the ratio of integrated oxygen concentration measured from SIMS depth profiles. SIMS measurements carried out one year after the deposition of the samples showed that the amount of oxygen incorporated in the film grown at 1550ºC had not changed whereas the oxygen content in the sample deposited at 1800ºC was still uniform but had increased from 10^{20} cm^{-3} to $2x10^{20}$ cm^{-3}.

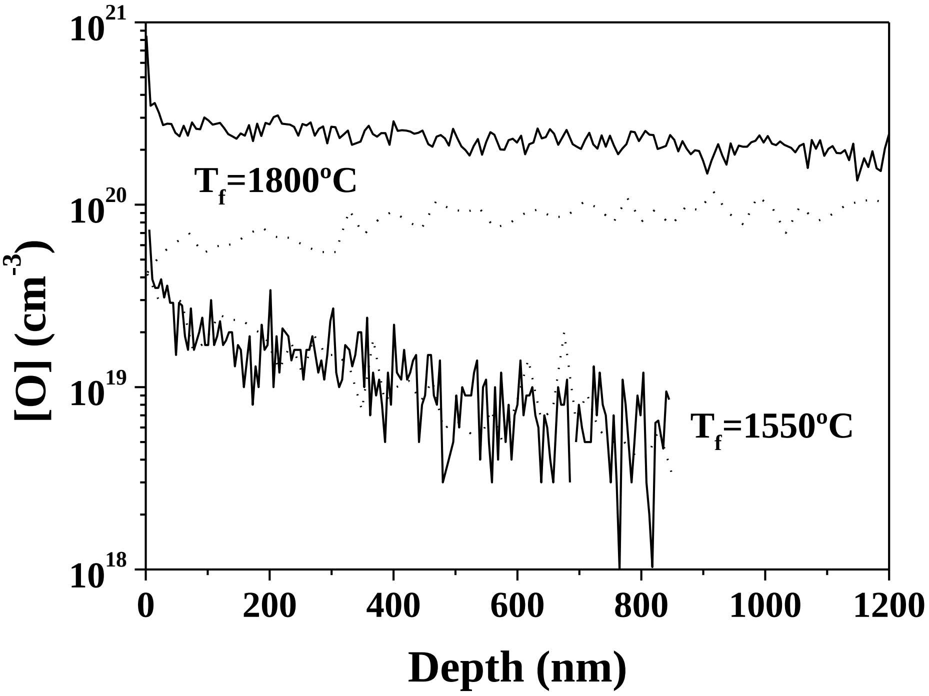

Fig. 4. Oxygen concentration depth profiles measured by SIMS for samples deposited at 1550 and 1800ºC. Dot lines correspond to measures performed half a year after the deposition of the samples and straight ones to those carried out a year after the deposition.

Results up to now suggested that films grown at low T_f had denser tissue among grain boundaries. In order to study this material more thoroughly, TEM and High-Resolution TEM (HRTEM) measurements of the sample deposited at 1550ºC were performed. Columnar grains in the direction of growth were observed. Contrary to what has been reported for compact nc-Si:H deposited using a W filament and at higher substrate temperatures, these grains did not present an inverted conic shape [8] but were more parallel in the vertical direction. TEM cross-sections, like the one in fig. 5, also showed that the sample had a superficial roughness of around 15 nm. The rms roughness measured with AFM was in agreement with this value. HRTEM photographs pointed out the presence of crystalline domains very near the substrate (30Å), evidencing that the crystalline growth took place from the very first formation stages. Finally, planar view images showed a wide distribution of grain sizes between a few and 100 nm, even though the majority of grains had sizes among 10 and 30nm. Fig. 6 shows a planar view TEM image where grains surrounded by white lines can be seen. These lines, which are clearly observable in the double magnification image in the upper right part of the figure, correspond to areas having a lower density than the crystalline grains [9], which can be attributed to an amorphous tissue surrounding the grains.

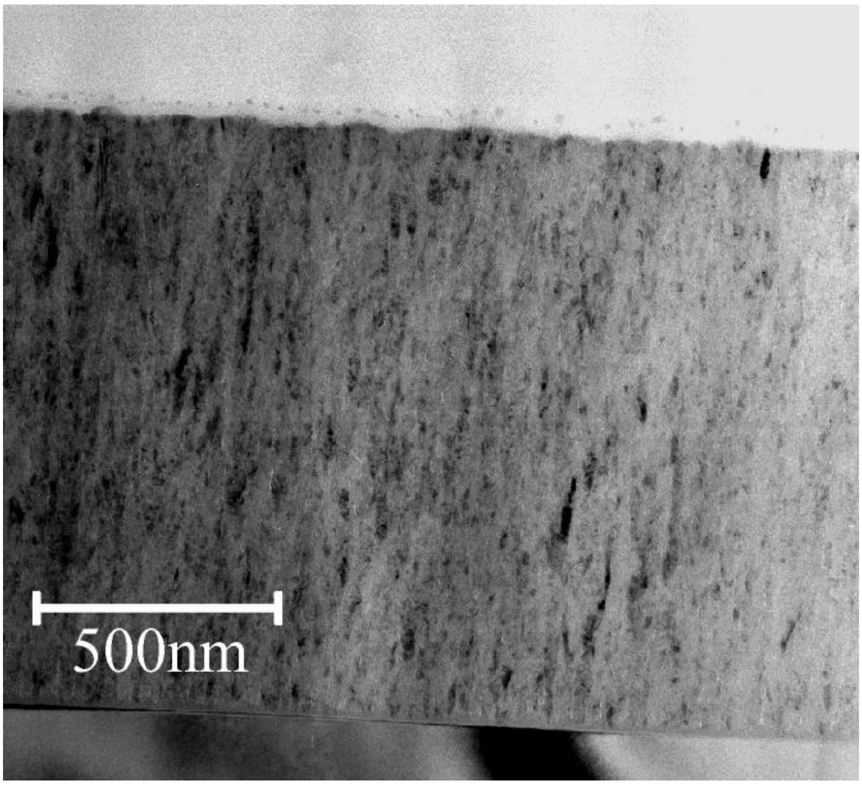

Fig. 5. TEM cross-section image of the sample deposited at 1550ºC. Crystalline growth from the first formation stages and a superficial roughness of around 15 nm can be seen.

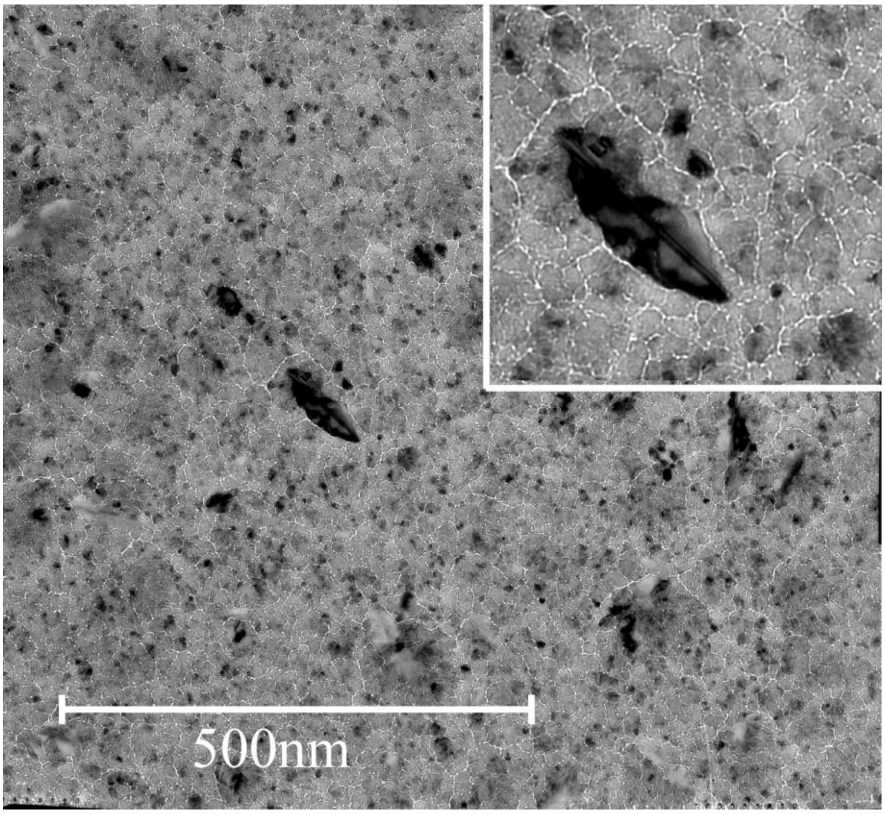

Fig. 6. TEM planar view of the sample deposited at 1550ºC. The inset shows a double magnification image.

4. Discussion

Whereas some preferential (220) growth was early reported with HWCVD for thick samples growth at higher temperatures (>350ºC) [10], it is much more difficult to obtain this preferential growth for thinner samples at lower temperatures. (220) crystalline preferential orientation has been obtained at low T_f in samples with thicknesses slightly lower than 1μm using a Ta filament. This behaviour is different to the one observed with a W wire, where a minimum thickness of 1.5 μm seemed to be required in order to show (220) crystalline preferential orientation instead of (111) [11].

A transition in the crystalline preferential orientation from (220) to (111) has been observed around T_f=1700ºC. Although this transition has not been observed in samples deposited in our reactor with a similar W filament and similar conditions, a similar behaviour has been reported [12] for samples deposited with W filament under different deposition conditions. This fact confirms the catalytic nature of the reactions at the wire, and the importance of the reactor-dependent aspects (filament geometry, and arrangement of substrates, gas inlet and filament) for the obtaining of a suitable technological parameter set which leads to device-quality material.

In HWCVD, the heated filament mainly decomposes SiH_4 into Si and H. These products easily react in gas phase giving as result different radicals depending on the process pressure and the filament to substrate distance. Additional atomic H on the substrate surface is essential to obtain crystalline material. This could be provided by adding H_2 to the gas mixture or by selecting appropriate parameters.

In the samples presented here, the observed results could be due to differences in SiH_4 dissociation at the filament. As reported recently [13], the mole fraction of SiH_4 not being decomposed by a tantalum filament decreases with increasing T_f. This means that at lower T_f there is more SiH_4 left for being consumed in the reaction $SiH_4 + H \rightarrow SiH_3 + H_2$ and, therefore, that more SiH_3 is produced at low temperature. This radical is considered to be the main precursor of the growth of dense a-Si:H and nc-Si:H in PECVD and is likely to provoke that material grown in the adequate conditions (low T_f, in this case) has a dense tissue surrounding grain boundaries.

The resistance of compact device quality nc-Si:H obtained using a W filament [6,8] to oxidation was due to the coalescence of conical grains in the growth direction. This kind of structure has as a result a surface with no tissue among the grains and, therefore, without paths for oxygen to enter the film. Columns observed in our samples were parallel in the vertical direction and did not reach coalescence. This fact together with the low and superficial degree of oxidation achieved by samples grown at low T_f after a long exposure to air suggested a denser tissue among grain boundaries. On the other hand, the dramatic oxidation observed in layers deposited at high T_f from the top to the substrate-sample interface can be attributed to the porosity of the material between grain boundaries. That higher density of the nc-Si:H obtained by HWCVD when using a Ta wire heated at 1550ºC is in agreement with the above mentioned consequences a high production of SiH_3 at low T_f would have.

The use of a Ta filament allowed us to obtain dense nc-Si:H at low T_f. This result is very promising because the use of high filament temperatures enhances the probability of incorporation into the sample of species coming from the filament itself. This contamination has been proven to have a clear effect in the solar cell performance as it worsens the properties of the intrinsic layer [14]. On the other hand, low filament temperatures enhance the formation of silicides at its edge and shorten the filament life. This effect is more dramatic when using a W filament than a Ta one [15]. Different strategies have been investigated in order to avoid this silicide formation like leaving the edges of the filament out of the working vessel [16] or having a hydrogen inlet close to the edges that prevents silane from reaching them [17].

5. Conclusions

A transition from (220) to (111) crystalline preferential orientation has been observed when increasing the Ta T_f from 1500 to 1850ºC. Samples grown around 1550ºC had (220) crystalline preferential orientation despite having thicknesses lower than 1 μm. The fact that crystalline growth took place from the first stages was also evidenced. Samples obtained at low T_f exhibited low oxygen content (<2%) after long time exposure to air. SIMS depth profiles evidenced that the oxygen concentration decreased as the sample-substrate interface approached. The film obtained at 1800ºC had much higher oxygen content (18.5%) and the oxygen profile was uniform from the top of the sample to the sample-substrate interface. This different behaviour can be attributed to the difference in density of the tissue surrounding the grain boundaries, a dense amorphous tissue for samples deposited at low filament temperatures and a porous one when the wire is heated above 1700ºC. Different amount of SiH_3 radical produced at different filament temperatures seemed to be responsible of the change in density observed.

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