Structure of PECVD Si:H films for solar cell applications

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Abstract

The structure of undoped Si:H films and solar cells deposited under different hydrogen concentration and substrate temperatures were studied. The characterization techniques used were XRD, Raman spectroscopy, TEM, optical absorption, and hydrogen effusion. The high concentration films were amorphous in the as-deposited state but crystallized upon annealing at 700\textdegree{}C. Middle and low concentration films were nanocrystalline (nc) and remained nc up to 800\textdegree{}C annealing. A theoretical explanation is given for the stability of these films. Such films, on glass substrates, had optical absorption spectra close to those of amorphous material. The solar cell samples, showed some nc morphology in all-concentration states.

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1. Introduction

Progress in silicon thin film based solar cell technology has been made by using stacked systems combining hydrogenated amorphous silicon (a-Si:H) wide band gap top cells with hydrogenated microcrystalline (\textmu{}c) silicon bottom cells as a lower band gap element. Efficiencies up to 12\% were reached [1] for such stacked cells while for
single junction μc Si cells efficiencies of 8.5–10.7% were reported [1–3]. In the literature the term μc is applied to all small crystallites; when we refer to our own films we will make a distinction between nanocrystalline (nc) films having crystallites of 1–100 nm; μc films with crystallites >100 nm, <10 μm and polycrystalline films of grain size greater than 10 μm. For the deposition of high quality μc-Si:H, usually the VHF (80–100 MHz) plasma enhanced chemical vapor deposition (PECVD) method is applied with hydrogen-diluted silane as a process gas [4]. Since most commercial a-Si:H solar cells are produced by using RF (13.56 MHz) PECVD, the growth of μc-Si:H by this method is of technological importance, particularly because this frequency is a recognized frequency for industrial applications. Recently, it has been demonstrated that RF PECVD is also capable of producing high-quality μc Si films at high deposition rates [5,6]. Efficiencies of up to 8% have already been obtained at i-layer growth rates of 5 Å s⁻¹ [6]. For these high efficiency, high growth rate, solar cells a high deposition pressure was an essential prerequisite. This paper focuses on solar cells and films prepared under such a high-pressure regime.

It is well known from silicon integrated circuit processing [7,8], that CVD silicon films deposited from silane/hydrogen mixtures are amorphous if the substrate temperature (in a hot wall reactor) does not exceed 580–590°C. Above this deposition/annealing temperature, Si films are μc; an average grain size of 0.1–1 μm is typical. In the case of PECVD the Si:H film structure in the as-deposited state is either amorphous or μc depending on a number of PECVD process parameters. These are mainly the SiH₄/H₂ flux ratio (r), also referred to as the silane concentration, the glow discharge power, the gas pressure in the reactor, and the substrate temperature [2,6]. The i-layer is especially important because it is responsible for light absorption and the subsequent charge carrier generation/separation and for photovoltaic stability under continuous illumination (Staebler–Wronski effect [9]). Thus, it was found that an optimum combination of solar cell operational parameters is obtained in a junction cell with the i-layer consisting of a mixed, amorphous–μc structure. The μc-Si was shown to be produced via low concentration SiH₄/H₂ [10].

Regarding the structure, a specific “columnar” structure with an incubation amorphous sublayer of a/μc-Si:H in the as-deposited films was demonstrated in Refs. [11–15] for n-Si:H on glass and on SiO₂/Si substrates at Tₛ = 200°C in a PECVD reactor with f = 13.56–116 MHz [11–13]. Specifically, a structure of columnar crystalline Si film growth inside an a-Si matrix was proposed in Ref. [17]. The ⟨110⟩ texture of the columnar μc-Si:H was found to be dominant in Si:H films deposited with a high r plasma on SnO₂-covered glass substrates at Tₛ = 200°C in a PECVD reactor with f = 110 MHz [15].

Much work has been done in the study of H evolution from a-Si [16,17]. From the temperature spectrum of H evolution, substantial information has been obtained concerning the bonding of H to Si and the internal structure of a-Si.

It seems clear that detailed knowledge of the i-layer structure and H evolution process (pore system, and crystallization of a-Si) could help in the manufacture of more reliable and effective solar cells. We also note that there is little data concerning the i-Si:H film structure for films deposited by the RF-PECVD method using H
diluted SiH₄. This article reports studies on the structure of such films, thin and thick, and their optical properties. We focus on the crystallinity as a function of silane concentration and on the Si:H films thermal stability. Special attention is given to hydrogen effusion from the Si:H films and their defect structure in the as-deposited state. We also study the microstructure of real solar cells. Specifically, the object of this paper is to study by various techniques the i-layers of μc cells both on independent substrates and as part of the solar cells themselves. While all other deposition parameters were the same, the deposition temperature and SiH₄ concentration were varied in a range which was shown previously to produce high efficiency μc solar cells.

2. Experimental equipment and techniques

The intrinsic and doped silicon films were prepared in a multi-chamber diode-type PECVD reactor with an electrode area of 150 cm². Intrinsic silicon films were deposited on SiO₂/Si (100), on glass, and on NaCl substrates. Texture-etched ZnO (sputtered) coated glass [18] served as substrate for the solar cells. All solar cells described in this paper were deposited in the p–i–n deposition sequence “superstrate configuration”, as shown in Fig. 1. While the substrate size was 10 × 10 cm², the cell area was 1 cm², defined by the Ag back contact. A μc p-layer [19] was used for all cells. The n-layer was phosphorus doped a-Si:H. In the following experiments only silane concentration and substrate temperature during i-layer deposition were varied (see Table 1). Deposition pressure and plasma power were fixed at 7 Torr and 60 W, respectively. For all doped layers identical deposition parameters were applied. All silicon layers were prepared using solely 13.56 MHz excitation frequency. The growth rate was ~6 Å s⁻¹.

We estimated the crystallinity in our Si:H material by XRD analysis, by Raman spectroscopy, and by transmission electron microscopy (TEM). XRD analysis was

![Fig. 1. Schematic of the configuration of a solar cell, showing the textured ZnO substrate, the deposited p, i, and n Si layers, and the Ag back contact. The sketch is not to scale.](image-url)
carried out using a Philips powder diffractometer with CuKα radiation. Raman measurements were performed, using a DILOR micro-Raman monochromator. The 514.5 nm green line from an argon laser with an output power of 0.2–1.2 mW was used. This power was found to be low enough to prevent any artifacts due to crystallization in the illuminated area, even when focused onto the sample surface by the optical system of an Olympus BH2 microscope in a spot diameter of ~1 μm. A transmission electron microscope (TEM) JEM-1000 (1 MeV acceleration voltage) with a heating stage was used. TEM samples of thick films for cross-section analysis were produced by ion milling. To study details of the film structure in the as-deposited material and during heating in vacuum in the temperature range of 200–800°C we used non-supported ~500 Å thick films deposited over cleaved rock salt substrates and then floated in water on grids.

Optical absorption measurements were made by the photodiffractometry spectroscopy (PDS) method on samples grown on glass substrates.

Hydrogen effusion experiments (see Ref. [16] for details) were done with a heating rate of 20°C min⁻¹ on samples grown SiO₂/Si substrates. The solar cells were characterised by standard I–V measurements under illumination (AM 1.5, 100 mW cm⁻², 25°C).

### Table 1
Preparation conditions of the films and solar cells (SiH₄/H₂ silane concentration ratio and substrate temperature during deposition)

<table>
<thead>
<tr>
<th>Film or cell no.</th>
<th>SiH₄/H₂</th>
<th>Ts (°C)</th>
<th>Film Raman shift (cm⁻¹)</th>
<th>Crystalline size (nm)</th>
<th>Percent crystallinity</th>
<th>Cell eff. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Film</td>
<td>Cell</td>
<td>r(%)</td>
<td>Film</td>
<td>Cell</td>
<td>Film</td>
</tr>
<tr>
<td>F1</td>
<td>NaCl</td>
<td>C1</td>
<td>0.8</td>
<td>140</td>
<td>518.5 ± 0.06</td>
<td>6</td>
</tr>
<tr>
<td>F2</td>
<td>C2</td>
<td>0.8</td>
<td>190</td>
<td>518.5 ± 0.06</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>F3</td>
<td>C3</td>
<td>0.8</td>
<td>270</td>
<td>518.6 ± 0.08</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>F4</td>
<td>N4</td>
<td>C4</td>
<td>1.0</td>
<td>140</td>
<td>514.5 ± 0.15</td>
<td>2</td>
</tr>
<tr>
<td>F5</td>
<td>C5</td>
<td>1.0</td>
<td>190</td>
<td>500.5 ± 1.97</td>
<td>0.8</td>
<td>6</td>
</tr>
<tr>
<td>F6</td>
<td></td>
<td></td>
<td>1.0</td>
<td>270</td>
<td>Am</td>
<td>Am</td>
</tr>
<tr>
<td>F7</td>
<td></td>
<td></td>
<td>1.5</td>
<td>140</td>
<td>Am</td>
<td>Am</td>
</tr>
<tr>
<td>F8</td>
<td></td>
<td></td>
<td>1.5</td>
<td>190</td>
<td>Am</td>
<td>Am</td>
</tr>
</tbody>
</table>

Also given are the results of Raman spectra measurements: the position of the crystalline peak in the films (Film Raman shift), the crystallite size calculated from it [20] and the percent crystalline contents of the samples. Finally, the last column is the solar cell efficiency.

#### 3. Experimental results and discussion

The experiments covered by this report were performed on four sets of samples, prepared as described in Section 2. Two sets (F sets) of Si:H films of 1 μm thickness, deposited on SiO₂/Si and on glass substrates, were intended for the study of the isolated intrinsic layer in solar cells. This layer is the thickest deposited layer in a solar cell, and is where most of the solar energy is absorbed. Another set (N set),
deposited under the same conditions as the F sets, but of 30 nm thickness on NaCl substrates, was used for some of the TEM measurements, and a set (C set) was of true solar cells, in which the intrinsic layer was deposited under the same conditions as that of the corresponding F and N samples.

The samples were studied as a function of $r = \text{SiH}_2/\text{H}_2$, the silane concentration and of substrate temperature. Three concentrations were used: 0.8% (lr), 1% (mr) and 1.5% (hr). The substrate temperatures were 140–190°C, and 270°C as shown in Table 1. Thus, the study was focussed on the close vicinity where the amorphous to μc transition occurs.

3.1. Si:HiSiO$_2$/Si system, as-deposited state

XRD spectra of Si:H films deposited at 140°C on amorphous SiO$_2$/(001)Si substrates by PECVD with different SiH$_4$ concentrations are shown in Fig. 2. The sample corresponding to low concentration (curve 1) exhibits an XRD spectrum typical for nc material slightly textured along $\langle 110 \rangle$ axis. Spectrum 3 (high concentration) is characteristic of an amorphous layer. The intermediate concentration SiH$_4$ plasma produced semi-amorphous Si:H film giving low intensity but distinct XRD peaks with non-expressed texture. Raman spectra of Si films are given in Figs. 3a and b. The deconvoluted Raman spectrum is composed of three main peaks. A sharp peak around 510–520 cm$^{-1}$ is the zone center phonon of the crystalline component of the microcrystals. The frequency and the width of this peak depend on the size of the microcrystals [20]. The smaller the crystal size, the lower is the frequency and larger is the line width. Phonon confinement and stress are the cause of the shift and the broadening of the Raman line [20]. On the other hand, the Raman spectrum of the amorphous component of the Si:H represents the broadened phonon density of states [21] which is composed of two main bands corresponding to the optical and acoustical zone edge phonons around 480 and

![Fig. 2. Curves 1, 2, 3: XRD spectra of Si:H films grown on SiO$_2$/Si substrates with minimum, intermediate, and maximum SiH$_2$ concentration $r = \text{SiH}_4/\text{H}_2 = 0.6\%$, $0.9\%$ and $1.5\%$, respectively, and $T_s = 140$°C. Curve 4 is a reference spectrum of a thick polycrystalline Si sample.](image)
380 cm$^{-1}$, respectively. Figs. 3a and b show that the fit of the Raman spectra is made up of three Lorentzian components: one around 520 cm$^{-1}$, one around 480 cm$^{-1}$, and one around 400 cm$^{-1}$.

In Table 1, we report the percentage of the crystalline content of each sample. It was calculated from their Raman spectrum which is illustrated in Fig. 3. We used the deconvoluted Raman peak intensities to determine the crystalline percentage, $P$, of the intrinsic films [11]. The equation employed was: $P = 100(I_{520})/(I_{480} + I_{380} + I_{520})$, where $I_{520}$, $I_{480}$, and $I_{380}$ are the intensities of the crystalline, amorphous and peaks, respectively. The crystalline component decreases significantly with increasing SiH$_4$/H$_2$ ratio, as can be seen by comparing F1, F4, F7—F2, F5, F8—and F3 and F6 which are sets of samples, each set grown at a fixed temperature with varying $r$. Similarly the crystalline component is seen to decrease with growth temperature, as
can be seen by comparing the crystalline content of sets F1–F3 and F4–F6, each set consisting of samples grown at different temperatures, but at a fixed \( r \).

Table 1 also shows the Raman Shift of the crystalline component of the films grown on glass substrates. When the SiH\(_4\)/H\(_2\) ratio, \( r \) increases, the crystalline Raman frequency tends to decrease, and there is no crystalline component for samples F6–F8. For a 0.8% SiH\(_4\)/H\(_2\) ratio, the Raman shift is growth temperature independent, however, this shift decreases significantly with increasing temperature when \( r \) equals 1%.

Additionally, the size of the crystallites is reported in Table 1. This size is calculated using the method proposed by Ossadnik et al. [20], based on unstressed samples, using the formula they give for the least-squares fit in their Fig. 1. The size has been deduced from the Raman frequency rather than from the line width which gives a less reliable result [20]. We have also calculated the crystallite size from the XRD peak width at half maximum, using the Sherrer equation [22]. Though the XRD size calculation gives results of the order of twice as large as the Raman calculation, there is a good correlation between the two measurements.

In Fig. 4 we present a cross-sectional TEM picture of film F4 in the as deposited state. One can observe conical type crystallization with an amorphous “incubation layer”. In the conical regions the dominant component is formed by many very small nanocrystals, and a few larger ones. A detail of the incubation layer and the tip of a conical crystallized region is seen from the high resolution TEM in Fig. 5.

As just seen, the hydrogen concentration plays an important role in the Si:H film structure formation. The transition from crystalline to amorphous structure proceeds in a narrow range of hydrogen concentration. A similar narrow transition range has been observed by others [23].

Optical absorption spectra of the low concentration (lr) nano crystalline film, medium concentration (mr), and high concentration (hr) purely amorphous Si:H

![Fig. 4. Cross-sectional TEM of ~1μm thick Si:H films on SiO\(_2\)/Si substrate, as-deposited state. Note conical type crystallization with an amorphous “incubation layer” Film F4: \( T_s = 140^\circ\text{C} \), \( r = 1\% \).](image)
films are different, as seen in Fig. 6, which was obtained by photo deflection spectroscopy (PDS) [24]. It is seen by extrapolating the straight section of the curve to the abscissa that, as expected [15,25], the hr films have a larger band gap than the lr films. We find that a relatively small amount of the amorphous phase (≈20%, see cross-sectional TEM picture in Fig. 4) dramatically changes the absorption spectra so that the spectrum of the mr-film is close to that of a-Si:H (hr) in the visible, and close to the nc-Si:H in the infrared. This gives them an absorption spectrum similar to that, which is obtained, from stacked amorphous/polycrystalline cells.

The temperature dependence of hydrogen effusion of several films is shown in Fig. 7a. These data are important because it can provide us with information on the porous structure in the films, since this information cannot be extracted from TEM data. Three different ranges a, b and c can be distinguished. As was explained in previous work [17], the low-temperature peak a (at T ≈ 400°C) corresponds to hydrogen desorption from internal surfaces followed by H₂ motion through

Fig. 5. Microstructure (cross-sectional high-resolution TEM image) of Si:H film, in the as-deposited state. The amorphous/crystalline interface is shown in the inset. Note thermally grown SiO₂ substrate. Film F4: T_s= 140°C, r = 1%.
interconnected voids in the Si:H matrix, peak \( \mathbf{b} \) is assigned to atomic H outdiffusion and peak \( \mathbf{c} \) is associated with effusion of \( \text{H}_2 \) trapped in small not interconnected voids. Fig. 7b shows in schematic form the inferred type of defects associated with the different hydrogen evolution peaks. Also noted in Fig. 7a is the efficiency of single junction solar cells with i-layers produced under the same deposition conditions. It is seen that the highest efficiency (6%) was obtained with material in which the isolated intrinsic layer showed a mixed amorphous-crystalline phase with only a shoulder in the range of the LT (interconnected voids) effusion range. This might suggest that Si layers without interconnected voids or other extended defects are preferable for solar cell production, since these defects probably reduce the mobility of charge carriers, thus reducing the efficiency of the solar cells. This hypothesis needs further confirmation because the structure of \( \mu \)c Si films are apparently different when integrated in solar cells instead of deposited on glass substrates, as will be shown in Section 3.3.
3.2. Stability of the thin unsupported Si:H films upon heating from 300°C to 800°C

The TEM data of the as-deposited Si:H ~ 300 Å thickness N films, with low r, Fig. 8a exhibited a non-textured nc structure with a median grain size of ~20 nm and some filaments of amorphous phase. It is interesting to note that the amorphous phase in the (a+c)-Si sample obtained at r = 1% and T = 140°C (Fig. 9a) shows residual amorphous phase areas which did not vanish during vacuum annealing.

To check structure stability, all three film categories, lr, mr, and hr were annealed up to 800°C, that is, close to the recrystallization temperature of polycrystalline Si [7]. This was done also to detect and study structural changes of the material which might also occur when solar cells are exposed for extended times to elevated ambient temperatures. It also seemed worthwhile to check the structure of these films at high temperature because of the thin amorphous “incubation layer” seen in Si:H films deposited on SiO2/Si substrates even in the case of low concentration plasma deposition.

The results are shown in Figs. 8b and 9b, and 10: (i) the lr films hold their initially nc structure up to high temperature having almost no trend to a change in crystallinity; (ii) in mr films (Fig. 9) only the amorphous component transforms...
gradually (with increasing temperature) to the nc structure; (iii) the hr films (Fig. 10), which were initially amorphous, demonstrate upon annealing a classical Avrami behavior of crystallization via random nucleation and grain growth [26] that is detectable by in-situ TEM at 700–750°C. Low nucleation rate (of the order $10^5–10^6 \text{cm}^{-2} \text{s}^{-1}$ at 700°C) and relatively large grain growth rate (≈ 1 nm s$^{-1}$ at 700°C) are typical for the a-Si:H amorphous-to-crystalline transformation [27]. An average grain size of the order 1 μm was obtained. The incubation time, $t_0$ for the beginning of crystallization of the hr films at 700°C and 800°C ranged from 10 to 1 min, respectively.

Therefore, we see from TEM studies that our PECVD process with hydrogen-diluted silane creates three main categories of Si:H films with a structure crucially influenced by the concentration-factor: the lr ($r = 0.8$) films which are nc with an grain size of the order of 20 nm, the hr ($r = 1.5$) are amorphous films, and the mr films ($r = 1$ for $T_s = 140$°C) present an amorphous–crystalline mixed structure.

### 3.3. Intrinsic Si:H layer inside a real solar cell structure, Ag/n-aSi/i-Si/p–ncSil/Zno(textured)/glass

In Fig. 11, the Raman spectra of solar cell C4, and film F4 are shown. Solar cell C4 gave the highest efficiency of the series. The spectra of the other solar cells were
qualitatively very similar to this one, differing only in the crystalline content, as detailed in Table 1. However, the Raman spectra behavior of the intrinsic layer in solar cells is markedly different from that of the films grown on SiO₂/Si substrates, as can be seen in Fig. 11 and Table 1. In contrast to the F films, in the cells the crystalline content changes relatively little. In all cases the crystallite Si peak around 519 cm⁻¹ has a higher frequency in the cells than the corresponding frequency in the F films, which means the crystallites are larger in the cells than in the films. This is also brought out in Table 1. We have added on Table 1a column indicating the efficiency of the cells. There appears to be an inverse correlation between the crystallite size and the efficiency of the cells, it being higher for the smaller crystallites. This trend is illustrated in Fig. 12. This correlation should be considered tentative because the curve on which it is based has few points.

Fig. 9. (a) Plan-view TEM of Si:H film deposited with intermediate SiH₄ concentration: (a) nc in the as-deposited state (some amorphous areas shown by arrows); (b) the film is μc after annealing at 800°C for 1 h. Film N4: Tₚ = 140°C, r = 1%.

The TEM cross-sectional view (Fig. 13) also confirms the increased crystallinity of Si:H in the real stacked structure: no incubation amorphous sublayer existed in the
middlediluted Si:H. This is in contrast with the film grown on SiO$_2$/Si under the same conditions, as was shown in Fig. 4. An almost ideal oriented texture of ZnO metallization over glass is observed in the SAD shown in Fig. 13.
4. Discussion

4.1. Difference between intrinsic Si:H films inside solar cells and on SiO₂ substrates

Because the origin of increased crystallization in the as-deposited state of Si:H in solar cell structures was not clear, we decided to investigate the question further.
Looking at the structure of the cell (Fig. 1), one can suspect a number of causes for the immediate crystallization of the i-layer: The first possibility is the presence of the thin μc p-Si layer deposited before the i-layer. However, other possibilities should also be considered. These are the influence of the highly crystallized ZnO layer, which is unlikely, because in our previous work [28] we have shown that the ZnO layer itself actually inhibits metal (Ag) induced crystallization in the Ag/ZnO/a-Si:H system. Neither ZnO:Al nor Zn metal, present in small amounts inside the ZnO, stimulated a-Si:H transformation in the system both in the as-deposited state or under vacuum annealing up to 600 °C. Another cause could be the rough texture of the ZnO layer used to increase optical absorption in the cell. A further possibility may have been the influence of Ag metal diffusion from the rear ohmic contact that is not protected with a ZnO buffer layer. We looked at the Ag i-layer interface with HRTEM, and found that even under in-situ annealing for 15 min no increased crystallization was observed. To settle definitely the question, we investigated also i-layers grown directly on textured and non-textured ZnO. No increased crystallization occurred in these samples.

Therefore, we can definitely state that the factor that produces the “crystallization shift” in the solar cell structure is the contact during the growth and/or annealing process of the intrinsic Si:H with the μc p-layer in the p–i–n deposition sequence.

Incidentally, in the course of our experiments, we observed that Si:H films deposited on a ZnO substrate had 2–3 times shorter “incubation lengths (time)” than the same films deposited on SiO₂. This feature, which was also detected by Neuchatel’s group [39], requires explanation. The most likely difference between SiO₂/or ZnO/ substrates for Si:H crystallization lies possibly in the difference of mismatch at the SiO₂/Si:H and ZnO/Si:H interfaces.

4.2. Correlation between TEM and Raman results

From the results presented, it is seen that the TEM and Raman results of this research are consistent, especially as far as identifying the relative crystalline content of the samples. Regarding the determination of the crystallite size, there is a discrepancy of a factor of three between the two methods. One has to realize in the first place that the Raman beam probes a sample area orders of magnitude greater than the high resolution TEM. Furthermore, in estimating the average size of nanocrystals from TEM, no actual statistics were made, the estimate being based on a rough evaluation of what the picture presents. On the other hand, the determination of the average grain size from Ossadnik et al.’s equations [20] provides us with a precise (but not necessarily accurate) and convenient means to compare the size of the of the nanocrystals in different samples, even if the actual average size may differ somewhat from that calculated.

4.3. Stability of Si nanocrystals under vacuum annealing

The results of the TEM in-situ annealing experiments call for an explanation for the stability of the nc material. The observed absence of crystalline growth in nc Si:H
films during their annealing at high temperatures $T_A \approx 1100 \, \text{K}$ differs fundamentally from the quite rapid growth of Si crystallite nuclei in “normal” a-Si:H films at $T \approx 10^3 \, \text{K}$ for about 1 h [27]. This difference results from the absence in the nc Si:H films of certain conditions necessary for crystallite growth. Growth takes place through thermally activated atomic rearrangements or diffusion-like jump in the external crystallite vicinity, which enable Si atoms to join the growing crystallites [29–34]. In order to proceed at reasonable rates, these processes require certain conditions to be satisfied.

1. The presence of a “driving force”, e.g. the evolution of metastable amorphous materials driven towards the more stable crystalline state which has a lower free energy [29–31,35].
2. The presence of a sufficient supply of Si atoms in the immediate external vicinity of the surface of growing crystallites [29–31,35].
3. The temperature should be high enough to ensure a reasonably high value of the rate coefficient, $K$ of the growth [29–31]:

$$K = \Delta \tau^{-1} \exp(-\Delta G/kT) \leq t_g^{-1},$$

where $t_g$ is the annealing time, $\Delta \tau \sim 10^{-12} \, \text{s}$, $\Delta G$ is the free energy barrier, which should be overcome in the course of the material (atomic) rearrangements involved in the crystal growth. For example, the thermal crystallization in a-Si:H has $\Delta G_g \approx 3 \, \text{eV}$ and requires time $t_g \approx 1 \, \text{h}$ at $T \approx 1073 \, \text{K}$ [27]. An increase of $\Delta G_g$ by only about 30% increases the crystallization time by a factor $\approx 1.5 \times 10^4$.

Apparently the non-fulfillment of the above-mentioned conditions in the nc Si:H films (ncfs) makes the heating of the film up to $T \approx 1073 \, \text{K}$ insufficient to cause the crystallite growth during about 1 h. Possibly substantially longer time at elevated temperatures could cause structural changes in the ncfs.

Let us consider now in detail the main factors responsible for the absence of fast crystallite growth in ncfs of Si:H. First the absence of a substantial “driving force” to promote crystal growth similar to that which exists in a-Si:H films, since the film is already in crystalline form. Second, as a consequence of the high packing density Si nanocrystals in the ncfs, thin layers of inter-crystalline material (ICM) of random thickness and shape separate the nanocrystals from one another. Since the crystallites are essentially pure Si, the ICM contain a relatively low Si concentration Si $< 80$–$90\%$ and a high hydrogen concentration $H > 10$–$20\%$ compared to their average values in a-Si:H. This is due to the dense packing of Si atoms in crystallites, which allows them to accommodate very little H. Consequently most of the H remaining in the sample is concentrated in the ICM in form of SiH$_2$, SiH$_3$ and other multi hydrogen complexes [36]. As a result, a relatively small number of unhydrogenated Si atoms are available in the ICM, specially because it takes several electron volts energy to release H attached to Si [36].

Furthermore, each of the Si nanocrystallites (in the ncf) has as its neighbors other stable Si nanocrystals of random size, random crystallographic orientations, and random, shapes. This is because they have been formed by a great number of highly non-equilibrium random short-term (picosecond) pulses of strong local “heating”
followed by very rapid “cooling” of nanometer regions of the a-Si:H film during its plasma assisted growth. The above pulse heating of the film is caused by fluxes of very many energetic plasma ions impinging on the film surface generating random sequences of huge numbers of short-lived hot spots of a nanometer size and picosecond lifetime [33,35]. We recall that in Fig. 4 one can see that there is an amorphous “incubation layer” of ~200 Å thickness. Since the growth rate of the film is 6 Å s⁻¹, we obtain an “incubation time” of ~35 s. From our previous work [27] we know that this incubation time in unsupported films corresponds to a temperature of 800°C. This confirms that the local effective temperature is much higher than the substrate temperature.

Consequently, (i) There is no driving force to stimulate crystallization. (ii) There are only a relatively small number of Si atoms in the immediate ICM surroundings of the Si crystallites, and this is insufficient to supply the growth of the ncs. (iii) There is a significant mismatch between the crystallographic orientations, surface structures and other properties of randomly oriented and shaped neighboring Si nanocrystals. (iv) There are local internal stresses caused by the mismatch between neighboring crystallites. All these factors contribute to increase the effective ΔG for the growth of the nanocrystals. This lets one understand why the highest annealing temperature $T_\text{A} \approx 1100$ K we used in annealing of ncf of Si:H is insufficient to produce detectable changes in these films during relatively short time intervals employed. We note that, these time intervals are quite sufficient to cause crystal growth in a-Si:H films [26,34]. Therefore, one can expect detectable changes to occur in the ncf of Si:H during longer time intervals and higher temperatures. A similar kind of reconstruction is known to occur in the high-temperature behavior of polyatomic metals and alloys operating for long periods at elevated temperatures [37–39].

5. Conclusions

We have studied intrinsic Si:H films grown by PECVD using SiH₄ concentrations in the vicinity of the threshold to produce either amorphous, mixed, or nc films. From Raman spectroscopy and high-resolution transmission electron microscopy, determinations were made of the crystalline content of the samples and of the size of the crystallites.

The highest solar cell efficiency (6%) of the nc material was obtained when the i layers were deposited under conditions that yield mixed nc–amorphous films on SiO₂/Si and glass substrates. However, it was found that films grown under the same conditions on SiO₂/Si substrates or as part of a solar cell have different properties. The ones that are part of solar cells have a higher crystalline content. This was found to be due to the doped μc Si:H layers in contact with the intrinsic films.

It was observed that the mixed nc–amorphous films on glass substrates have optical absorption in the visible and near-infrared spectrum that seem to make them better materials than either crystalline or amorphous films for solar cell applications.

From hydrogen evolution spectra it was inferred that higher efficiency solar cells are associated with intrinsic material containing less voids.
It was found that the nc films are highly stable even at elevated annealing temperatures, and a theoretical model was presented to account for this. We recall that stability is a very important requirement for solar cells.

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