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STRUCTURAL CHARACTERIZATION OF $\mu\text{c-Si:H}$ FILMS PRODUCED BY R.F. MAGNETRON SPUTTERING

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Microcrystalline silicon thin films were produced by R.F. magnetron sputtering. The microstructure of these films has been studied by X-ray diffraction, transmission electron microscopy (TEM) and Raman spectroscopy. Average values of crystalline size and strain obtained by the different techniques used are critically compared and the reasons for the differences are discussed.

1. Introduction

Hydrogenated microcrystalline silicon ($\mu\text{c-Si:H}$) has attracted considerable attention as a potential new material for electronics devices such as solar cells, thin films transistors and MOSFETs. This interest is based on a higher electrical conductivity of this material compared to amorphous silicon (a-Si:H). Nevertheless, electrical conductivity and other physical properties relevant for those applications are strongly influenced by the thin film microstructure of $\mu\text{c-Si:H}$. Solids made out of nano(micro)particles have physical properties different of those of the conventional material due to electronic or vibrational confinement effects and also due to surface effects. Hydrogen content and bonding type, optical gap, absorption coefficient and electrical conductivity are strongly influenced by the microstructure of $\mu\text{c-Si:H}$ thin films.

Within the frame of this article we will describe the microstructure of $\mu\text{c-Si:H}$ thin films and the related experimental techniques.

For the purpose of the structural characterization we used X-ray diffractometry (XRD), transmission electron microscopy (TEM) and Raman spectroscopy. Besides the conventional techniques the Raman spectroscopy is an interesting technique for studying structure, geometry and type of nanoparticles.

The thin films were grown by reactive RF sputtering. Generally these films are described as consisting of spherical crystals (c-Si) embedded in an amorphous matrix (a-Si:H). The grain size ranges typically from 3 to 100 nm, whereby the lower limit is defined by thermodynamical considerations.

2. Experimental

Microcrystalline silicon thin films were grown by reactive RF sputtering on corning glass substrates[1]. Five different samples were prepared. The deposition conditions are summarised in table I. The thicknesses of the films varied from 0.24 to 2 μm . The growth temperature was maintained constant during all the growing process at $T = 250^\circ\text{C}$.

Table I .Growth conditions of the samples and thickness (d)

Sample	rf Power W	pH ₂ Pa	pAr Pa	d nm
a1	80	0.39	0.23	241
a2	200	0.16	0.78	1362
a3	150	0.35	0.23	1760
a4	80	0.16	0.78	642
a5	100	0.16	0.78	632

The crystallite size as obtained by different experimental techniques may have different values depending on the dimensional parameter associated with respective technique and the analysed area. TEM analysis reveals directly the crystal size although in a certain direction and topological position. From XRD the average linear dimension of regions of coherent scattering of the X-rays in a certain crystallographic direction is obtained. In Raman scattering lineshape is affected by the crystallite size and vibrational confinement due to the finite size of the crystals as discussed below.

2.1 X-ray diffraction

A typical X-ray spectrum of $\mu\text{c-Si:H}$ thin film is shown in figure 1. Three diffraction peaks of c-Si are visible. The relatively large background under the (111) diffraction peak is caused by the amorphous Si matrix and also the glass substrate. A gaussian profile was used for fitting this contribution (not presented in the figure 2).

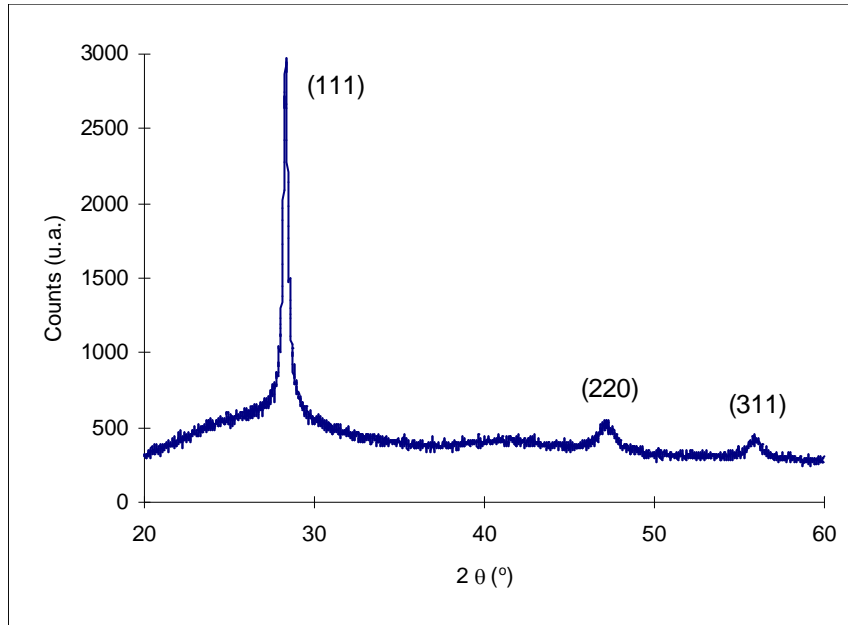


Figure 1: X-ray spectrum of a microcrystalline silicon sample a3.

From X-ray diffraction, average crystal size and thin film strain can be obtained by fitting a pseudo-Voigt function ($pV(x)$) to each diffraction peak[2]. This function is the weighted sum of a Gaussian $G(x)$ and a Cauchy function $L(x)$:

$$pV(x) = I_p (\eta L(x) + (1 - \eta) G(x)) \quad (1)$$

where η is the percentage of Cauchy component and I_p is a constant.

The crystallite size and the average strain are generally related to the Cauchy component and Gauss component[3, 4], respectively using the integral breadths, β_C and β_G :

$$D = \frac{\lambda}{\beta_C \cos \theta} \quad (2)$$

$$\langle \varepsilon^2 \rangle^{0.5} = \frac{\beta_G}{4 \tan \theta} \quad (3)$$

where λ is the wavelength of the copper $K\alpha_1$ radiation ($\lambda = 1.50456 \text{ \AA}$), and θ is the diffraction angle.

In other simulations of the same diffraction patterns the peaks were simulated by a simple Cauchy function. From these data the crystal size can be obtained but, of course, no information on the average crystalline strain. In figure 2 the fitting using these two methods is shown.

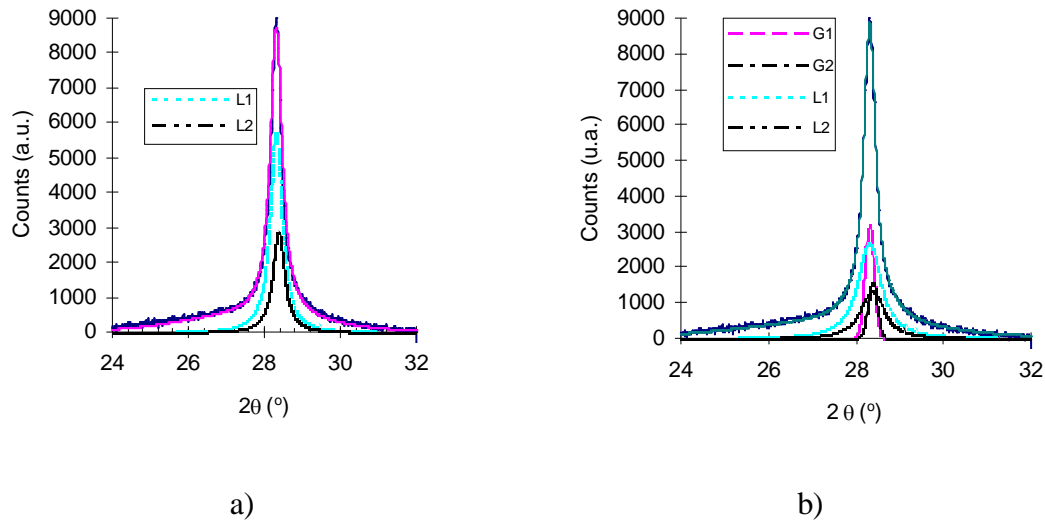


Figure 2: Detail of (111) peak of sample a3 and fitting components. a) using a simple Cauchy function. b) using the pseudo-Voigt method. G and L indicates the Gauss and Lorentz components, respectively. 1 and 2 indicates $K\alpha_1$ and $K\alpha_2$, respectively. The experimental and fitted curve are the coincident full curves.

Corrections for background, spectral width, $K\alpha_2$ radiation and instrumental peak broadening were performed following methods described elsewhere[5].

2.2 Raman Spectroscopy - Strong Phonon Confinement

Raman scattering is in principle a powerful technique although several experimental effects must be taken into account:

- i) The peak frequency of the 1st optical phonon decreases with increasing temperature owing to anharmonic effects.
- ii) $\mu\text{c-Si:H}$ thin films crystallise easily.
- iii) thin film strain (and stress) shifts the phonon frequency. The thermal strain mismatch of thermal thermal expansion coefficient of substrate and film when cooling from deposition temperature to room temperature is about 0.09%

Therefore to avoid these effects, the thermal heats due to the laser power must be strictly controlled. For that we used 0.68 mW of power on the sample with a 514.5 nm argon laser.

For small crystals the wave function of the optical phonons is not a plane wave but a localized wave originating a relaxation in the selection rule of wave vector conservation. Thus phonons with non-zero wave vector can participate in the Raman process resulting in a red shift and broadening of the peak. This is the basis of the Strong Phonon Confinement (SPC) model.

For a given crystal of size D the wave function becomes:

$$\psi(q_o, r) = W(r, D)\phi(q_o, r) \quad (4)$$

where $\phi(q_o, r)$ is the wave function for a phonon of wave vector q_o in an infinite crystal and $W(r, D)$ is the phonon weighting function. In the literature different SPC models, each with its respective weighting function can be found [6, 7, 8, 9, 10]. Within the frame of this work spherical microcrystals and a gaussian weighting function were assumed for the fitting of the Raman spectra:

$$I(\omega) \approx \int_0^1 \frac{\exp(-q^2 D^2 / 4a_o^2) d^3 q}{(\omega - \omega(q) - \omega_s)^2 + (\Gamma_0 / 2)^2} \quad (5)$$

where Γ_0 is the linewidth of c-Si including instrument contribution ($\Gamma_0 = 4.0 \text{ cm}^{-1}$), $\omega(q)$ is the phonon dispersion relation, q is given in units of $2\pi/a_o$, a_o is the lattice constant of c-Si ($a_o = 0.357 \text{ nm}$), D is the average size of the crystals and ω_s is the Raman shift due to the strain (ε) given by:

$$\omega_s = -3 \gamma \varepsilon \omega_o \quad (6)$$

where $\omega_o = 521 \text{ cm}^{-1}$, γ is the Gruneisen constant and takes the value 1.

For the dispersion of the LO phonons in c-Si we consider:

$$\omega^2(q) = A + B \cos(\pi q/2) \quad (7)$$

where $A = 1.714 \times 10^5 \text{ cm}^{-2}$ and $B = 1 \times 10^5 \text{ cm}^{-2}$ as determined by neutron scattering [11].

In figure 3 a typical Raman spectra of microcrystalline silicon is shown. The Stokes peak in the vicinity of 520 cm^{-1} is generally attributed to the transverse optical mode (TO) of crystalline silicon. The band at $\omega \approx 480 \text{ cm}^{-1}$ is associated with the amorphous phase.

To analyse the Raman spectra, we used a Gaussian profile for the amorphous TO structure and the crystalline profile is calculated based on the Strong Phonon Confinement (equations 5 and 7) [6, 12]. For some samples the contribution of near surface atoms at $\omega = 505 \text{ cm}^{-1}$ is need to obtain acceptable curve fits as seen in figure 3.

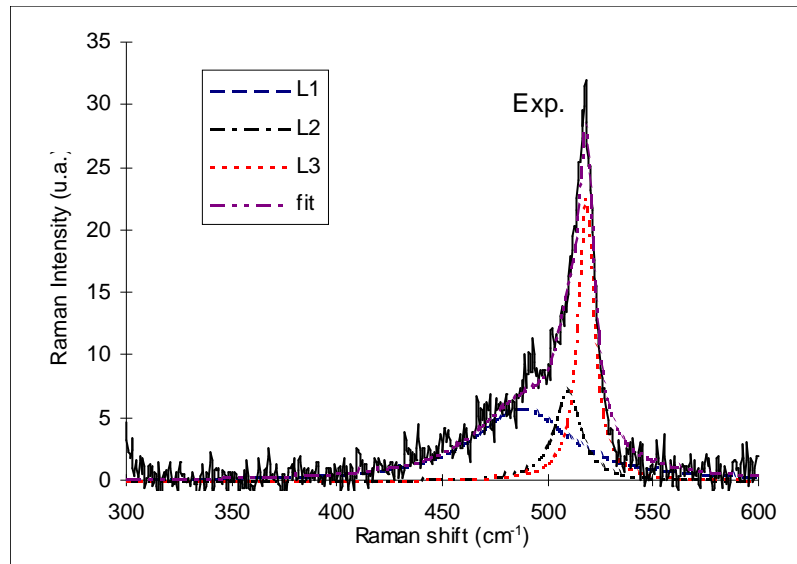


Figura 3: Fit of the Raman curve of $\mu\text{c-Si:H}$ (sample a3) showing the 3 contributions: L1, L2 and L3 are the contributions of a-Si:H, surface atoms and c-Si, respectively.

3. Results and Discussion

3.1 Transmission electron microscopy

Thin films deposited by sputter deposition process show, as is generally observed, a columnar structure with diameter varying between 50 and 150 nm depending on the growth conditions[1]. From the TEM analysis the crystalline fraction and the average grain size were obtained. Figure 4 shows the diffraction image of two samples. The different rings (due to the different planes of c-Si) are clearer in the sample a1 than in a2 illustrating that a1 is more crystalline than the other. The planes spacing obtained using a horizontal profile through the center of the diffraction images are in agreement with literature data for c-Si.

Analysing the dark field images (figure 5) of a1 and a2 a considerable difference between these two samples can be observed. At the lower magnification the crystals of a1 seem to be much bigger than the crystals present in sample a2. When increasing the magnification it is easily verified that the crystals in a1 sample are agglomerates of several smaller crystals. For a2 sample the average size is about 50 Å.

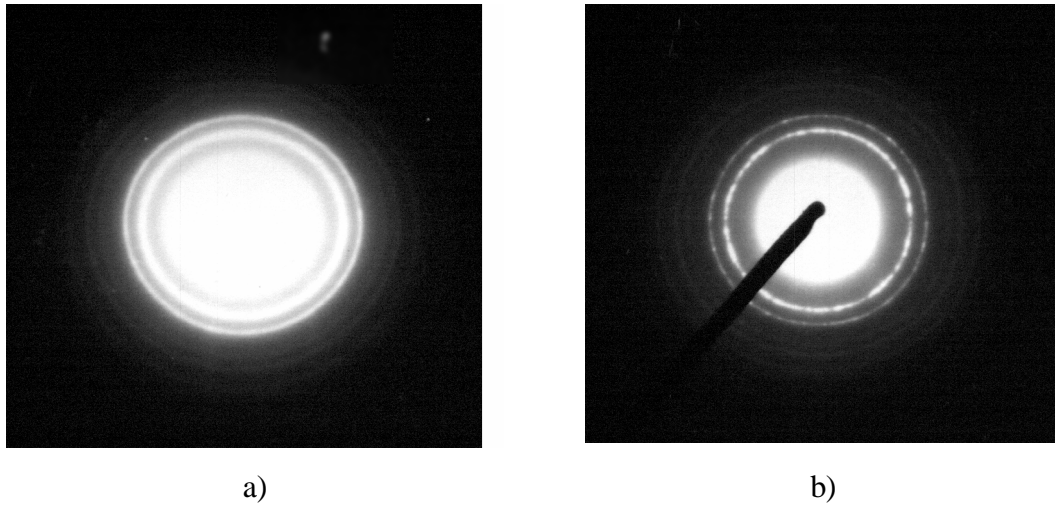


Figure 4. Diffraction image of two samples. a) sample a2; b) sample a1.

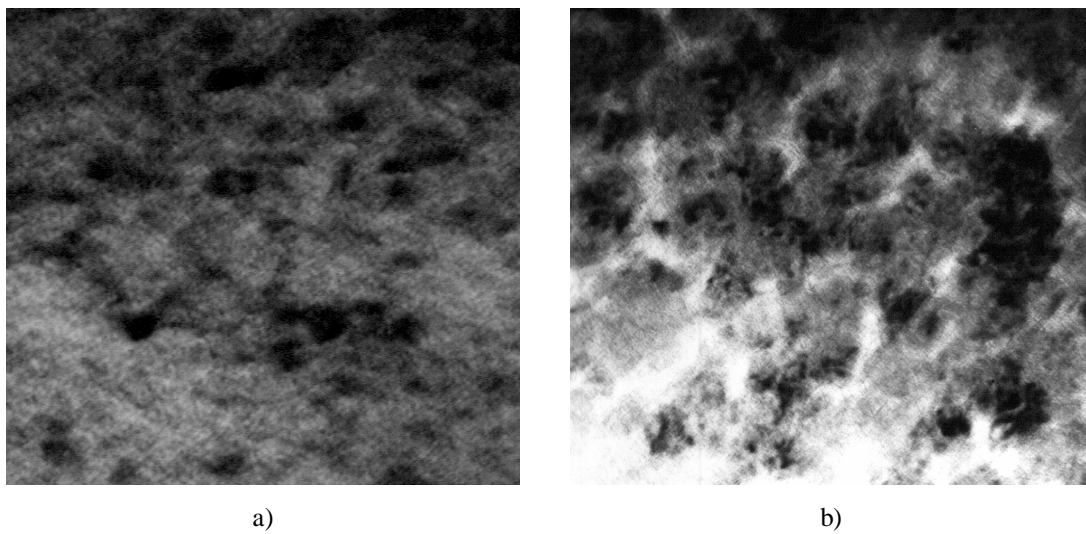


Figure 5. Dark field images of two samples at 300Kof magnification (1cm =6nm). a) sample a2 (2.09 cm x 3.14 cm), b) sample a1 (6.84 cm x 5.67 cm).

3.2. XRD and Raman spectroscopy

The lattice constant determined using the different diffraction peaks is consistently $a_0 = 0.546$ nm. We do not expect preferential orientation since the peaks relative intensities of our samples are similar to those of c-Si (see table II).

Table II: The intensity ratio for the different peaks considering the (111) peak as 100%.

	(111)	(220)	(311)
c-Si	100	55	30
a3	100	40	26
a2	100	58	27
a1	100	62	25
a5	100	41	17

From X-ray line profile, the averages grain sizes and the strain are determined using equation (2) and (3), respectively and the results are shown in table III. The D_X values in parenthesis are obtained by the fitting with a simple Cauchy function.

Applying the Strong Phonon Confinement we obtain the crystal size and it is possible to calculate the crystalline fraction using the integrated intensities of the amorphous and crystalline components^[1] (see table III). The higher limit of strain obtained using equation (6) is also shown in table III.

Table III . Crystalline fraction (c), average values of grain size (D) and strain determined by the fitting of the Raman lines and X-ray peaks. Subscripts R, T and X indicate Raman, TEM and X-ray.

Sample	D_X Å	ϵ_X %	D_R Å	ϵ_R %	D_T Å	c_R %
a1	199 (153)	0.9	55	0.1	>60	60
a2	104 (96)	1.8	55	0.1	50	45
a3	163 (157)	0.8	60	0.1		65
a4	182 (130)	1.4	65	0.1		48
a5	156 (129)	2.2	55	0.1		55

Comparing the crystal sizes obtained by TEM and by the fittings of the Raman and X-ray line profile is seen that the Raman and TEM values are similar but in all the samples the crystal sizes obtained by X-ray diffraction are bigger. Some authors consider this difference negligible^[13]. For each sample, the average crystal size obtained using a pseudo-Voigt is bigger than using a simple Cauchy function.

The strain values obtained by XRD are bigger than the maximum value obtained by Raman analysis which is approximately the mismatch strain due to the deposition temperature. The diffraction images obtained by TEM also confirm the absence of strain since the planes spacing are in agreement with the non strained silicon.

4. Conclusions

The microstructure of thin $\mu\text{-Si:H}$ films deposited by reactive magnetron sputtering on glass has been analysed by TEM, XRD and Raman spectroscopy. These films consist in small Si crystals embedded in a matrix of amorphous Si. The crystalline fraction of the films varies between 30 to 70 % depending on deposition conditions. Crystal size as determined by TEM measurements and Raman spectroscopy were generally in agreement and varied between 50 - 80 Å depending again on deposition conditions. Nevertheless, we could not find any conclusive results

on the crystalline fraction of the thin films from the TEM measurements by image analysis. Therefore, the above mentioned results on the sample crystallinity are based on the RAMAN measurements.

Crystal sizes as determined from the XRD experiments are superior to the ones determined by RAMAN spectroscopy and TEM. The difference can not only be explained by the fact that RAMAN spectroscopy identifies the smallest crystal size (the confined one) and XRD an average value for the three different crystal directions. The experimental data were not sufficiently precise to allow a consistent evaluation of crystal size and stress from Gaussian and Cauchy XRD peak fitting by a pseudo-Voigt function. Apparently a simple Cauchy function describes the peaks almost as well as the pseudo-Voigt function and the crystal size determined from the simple Cauchy function is closer to the crystal size determined by RAMAN spectroscopy and TEM.

In addition the RAMAN measurements do not allow a crystal strain superior to 0.1 % as it is calculated from the Gaussian partition of the pseudo-Voigt function. It is also difficult to imagine a stress induced deformation of the hard Si crystals in a relatively soft amorphous matrix.

Generally, RAMAN spectroscopy proved to be an interesting tool when analysing the microstructure of thin $\mu\text{c-Si:H}$ thin films. A thorough peak analysis reveals a relatively complete set of data on the thin film microstructure (crystal size, crystalline fraction and micro-stress). These data can be confirmed and complemented by TEM and XRD measurements.

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