Stress measurements in polycrystalline silicon films grown by hot-wire chemical vapor deposition.

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Stress measurements were carried out by the X-ray powder diffraction technique known as the "$\sin^2\Psi$-method" for polycrystalline silicon films grown by hot-wire chemical vapor deposition. Results show homogeneous biaxial stresses ranging from 110 MPa (tensile) to -210 MPa (compressive). The results are interpreted in terms of the dependence on the growth parameters and post-deposition oxidation. The deposition parameters that could be expected to give unstressed films by this technique, which are shifted to lower temperatures compared to other deposition methods, and the ability to measure stresses in randomly oriented polycrystalline silicon layers by this technique are shown in this paper.

Keywords: *Residual Stress, polycrystalline Silicon, Hot-Wire CVD.*

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1. Introduction

Nowadays, polycrystalline silicon (poly-Si) films are used for a variety of applications, such as sensors and micromachining, microelectronics or large area devices for flat panels and solar cells. There is a great interest in novel deposition techniques that yield large-grain material with good structural and electrical properties at relatively low temperatures and fast deposition rates. In poly-Si films, structural quality is significantly affected by residual stresses, which could be related to the growth dynamics [1], thermal mismatch between film and substrate [2], recrystallization of amorphous phases [3] or thermal oxidation of the material [4], giving rise to degradation or high levels of structural defects. For this reason, the control of stresses is a key to obtaining good quality films.

Macrostresses in poly-Si films have been measured through the curvature of the substrate [5] or X-ray topography [6], whereas microstresses have been determined by MicroRaman Spectroscopy [7] or X-ray diffraction techniques such as peak shape analysis [8]. In this work, we have used an X-ray powder diffraction technique, the "$\sin^2\Psi$-method", which is a suitable technique for the analysis of residual stress in randomly oriented polycrystalline specimens, which could present other contributions to the Raman peak position that would hinder the interpretation of the results.

The "$\sin^2\Psi$-method" [9] is based on the variation of the strain with the observation angle Ψ. From a powder sample, it is possible to obtain a diffraction peak for large variations of the observation angle Ψ. The method consists of measuring a certain diffraction peak in the $\theta/2\theta$ mode for different Ψ-tilts. For every value of Ψ, the peak is measured from the same family planes but for different grains from a macroscopic illuminated area, with their diffracting planes oriented at an angle Ψ to the plane of the substrate. Strain is determined for every Ψ-tilt from the position of the peak, which is related to a lattice spacing. For the case of biaxial homogeneous stresses (finite stresses only on the plane of the film) the plot of strain vs. $\sin^2\Psi$ is linear [10] and the stress in the plane of the substrate is related to the slope of this plot through the values of the Young's modulus and Poisson's ratio (assuming the

material to be isotropic). When strains are present in the growth direction, the $\sin^2\Psi$ plot shows two different but symmetric arms for the values of $\Phi=0$ (positive Ψ) and $180°$ (Pseudo-negative values of Ψ), which is known as "Ψ-splitting". Inhomogeneous stresses lead to scattered data in the $\sin^2\Psi$ plot [11].

2. Experimental

Residual stresses were measured for poly-Si films grown at low substrate temperatures (T_s) and fast deposition rates (r_d) on fused silica and Si(111) substrates without removing the native oxide layer, by the Hot-Wire chemical vapor deposition (HW-CVD) method described elsewhere [12]. Samples showed a columnar structure from the interface, with absence of amorphous phases in the Raman spectra, and no significant differences were observed in the morphology between samples on both substrates. Grain sizes varied from 0.3 to 1 μm and the crystallites were randomly oriented. Post-deposition contamination has been studied in a previous paper [13], showing an increase in the oxygen signal at the grain boundaries, and a concentration depth profile constant along the whole thickness of the films. The O/Si signal ratio obtained by Secondary Ion Mass Spectrometry (SIMS) increases as the T_s and the grain size decrease. The main deposition parameters, mean grain size estimated from Scanning Electron Microscopy (SEM) planar views and the O/Si SIMS signal ratio are summarized in Table I

Stress was characterized in a Philips MRD diffractometer in the Parallel Beam mode, featuring a texture goniometer that allows controlled rotations of the samples about the three axes (figure 1a). The $\theta/2\theta$ scans were measured with the unfiltered CuK_α line (1.54 Å). Although the (111) diffraction peak was analyzed in some cases, the (220) diffraction peak was chosen because of the preferential orientations of these samples and the absence of background at low diffraction angles due to the amorphous substrate. The latter peak was measured in the range of 2θ between 44 and $50°$ for Ψ-tilts from 0 to $80°$, for both $\Phi=0°$ and $180°$, giving 16 lattice spacings, which were obtained from the fitting of every single peak to

a Pseudo-Voigt function with the $K_{\alpha 1}$-$K_{\alpha 2}$ and background corrections. The "time per step" setting was modified to take into account the reduction of the diffracted intensity with the increase of Ψ, according to the rocking-scan data. The values of stress were calculated assuming that Young's Modulus and Poisson's Ratio values for poly-Si are 160 GPa and 0.17, respectively [14].

3. Results and discussion

The diffraction peaks obtained were symmetric and nearly lorentzian for all the samples, with full width at half maximum (FWHM) values increasing with the decrease in T_s. This may indicate the presence of microstresses, related to the presence of defects, or size effects, but these differences are not significant since these values are near the FWHM of the peaks obtained from powder standards. Fig.1b shows the calculated values of lattice spacing vs. $\sin^2\Psi$ for the sample S1. For this sample, grown at the highest values T_s and r_d (500 °C, 37.1 Å/s, respectively), the behavior was linear with a positive slope related to a moderate tensile stress. Samples S2 and S4 were characterized on two different substrates, namely fused silica and Si(111) with the native oxide layer. Thermal mismatch between substrate and film would lead to tensile stress during the cooling process following the growth from T_s to room temperature for the case of samples grown on fused silica, and a slight compressive effect (if any) for the case of Si substrates. Figs. 2a and 2b show the $\sin^2\Psi$ plots for the samples S4 and S4C, respectively. The values of stress obtained for each sample were very similar on both substrates, which seems to indicate that in this range of T_s (280-400 °C) there is no influence of thermal mismatch between substrate and film. The same measurement was carried out in the sample S4 from the (111) peak, without substantial changes in the value obtained for the stress. The dispersion between the points for $\Phi=0$ and 180° for the first value of Ψ, which is a general trend for all the samples, could be related to an effect of the variation of the penetration depth: for low values of Ψ the influence of the deeper zones is

greater than for higher angles. Stress gradients with depth or inhomogeneous stresses in the film-substrate interface would lead to such data scattering.

Fig. 3 shows the values of stress plotted vs. T_s and the same data as a function of r_d and the thickness of the films. Sample S3 was the least stressed film, with a calculated value very near that of the error bar, which is of the same order as other linear plots in the series. Samples S5 and S6 were grown at the same T_s but with slightly different r_d. The values for stress are similar for both cases, suggesting that the influence of r_d is lower. The most remarkable finding is the contrast between tensile stress for the film grown at higher temperature (S1) to the others, which presented compressive behavior. For both plots, the stress was compressive for lower values of T_s and r_d and it became tensile for higher values. Both parameters determine the growth dynamics before the film nucleation: high T_s and low r_d promote rearrangement of the arriving species, giving rise to relaxed and compact films, whereas low temperatures and high deposition rates lead to a low mobility of the impinging particles, giving rise to shadow effects, porosity and stressed layers [15]. Another factor that could influence these results is the effect of the post-deposition oxidation at the grain boundaries: at lower T_s, the decrease in the grain size determines a higher degree of oxidation [13], and so a higher compressive stress related to it. Both explanations are supported by the biaxial nature of all stresses, which is in agreement with the columnar structure of the films, and the fact that the sample featuring tensile stress (S1) is less oxidized. On this basis, both effects could play a role in the interpretation of the results. The high level of oxidation of the samples grown at lower temperatures, which can explain the compressive stress component, would be superimposed to the fast growth effect, which gives rise to the tensile component that increases with r_d. Moreover, the dominant component at low T_s and r_d seems to be the compressive one, related to the oxidation, whereas the tensile component may be the most important for higher values of T_s and r_d. In order to ascertain the importance of each effect, residual stress analysis of as-deposited samples, in which the oxidation contribution would be negligible, are being carried out. The deposition parameters suggested by the trend of the stress data for obtaining good structural quality poly-Si layers by HW-CVD are shifted to

lower temperatures, compared to other techniques, such as LPCVD [16] or RTCVD [17]. This fact could be related to the high level of atomic hydrogen in the growth atmosphere, giving rise to the selective etching of weak Si-Si bonds, which are thus substituted by Si-H bonds. In this way, the growth of amorphous phases in the film, responsible for residual stresses in the growing layer, is hindered, giving rise to unstressed and polycrystalline films for lower T_s than in other methods.

4. Conclusion

The stress measurements carried out in poly-Si films grown at different deposition parameters show a switch from compressive to tensile stresses as the growth temperature and deposition rate are increased. This has been interpreted in terms of the fast deposition rate and the effect of the post-deposition oxidation. The trend shown by these samples indicates that poly-Si films with low stress could be obtained by HW-CVD at r_d around 25 Å/s and T_s in the 350-450 °C range. The value of T_s expected to obtain unstressed poly-Si layers by HW-CVD is lower than those of other deposition techniques, which is of great interest in the production of good quality films for relatively low values of T_s and at high r_d. Moreover, the suitability of the "$\sin^2\Psi$-method" for the residual stresses analysis of randomly oriented poly-Si films has been shown.

Acknowledgement

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Figure Captions

Table I. Deposition parameters, mean grain sizes and oxidation levels for the studied samples. Grain size was estimated from SEM planar views, and the O/Si signal ratio was obtained from SIMS concentration depth profiles obtained with 15 KeV Ar+ sputtering.

Fig. 1. (A) Geometry and angles of the texture goniometer. (B) The $\sin^2\Psi$-plot for the sample S1 with positive ($\blacktriangle$, $\Phi=0°$) and pseudo-negative ($\bullet$, $\Phi=180°$) values of Ψ. The value of the stress was obtained from the slope of the linear regression (dashed line).

Fig. 2. (A) The $\sin^2\Psi$-plot for the sample S4, grown onto fused silica substrate. (B) The $\sin^2\Psi$-plot for the sample S4C, on a Si substrate covered by the native oxide. Symbols are the same as in Fig.1.

Fig. 3. (A) The values of stress vs. the deposition temperature, T_s. (B) Same data plotted vs. the deposition rate r_d and thickness.

Sample	T_s (°C)	Thickness (μm)	r_d (Å/s)	mean grain size (μm)	O/Si signal ratio
S1	500	7.8	43.3	1.0	6.0×10^{-5}
S2/S2C	400	4.8	26.7	0.7	1.2×10^{-3}
S3	330	3.2	17.8	0.7	1.3×10^{-3}
S4/S4C	280	2.0	11.1	0.6	1.8×10^{-3}
S5	210	2.9	16.1	0.3	-
S6	210	3.3	18.3	0.5	-

Table I, D.Peiró et al., Materials Letters.

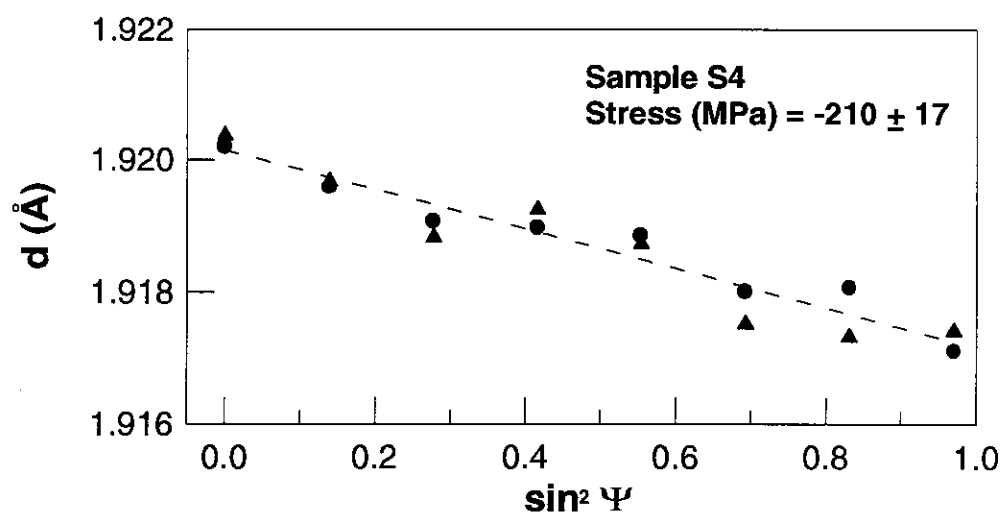A)

B)

Sample S1
Stress (MPa) = 100 ± 20
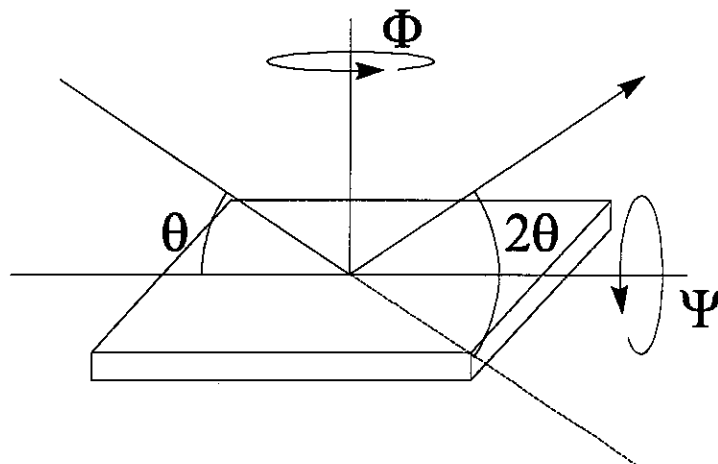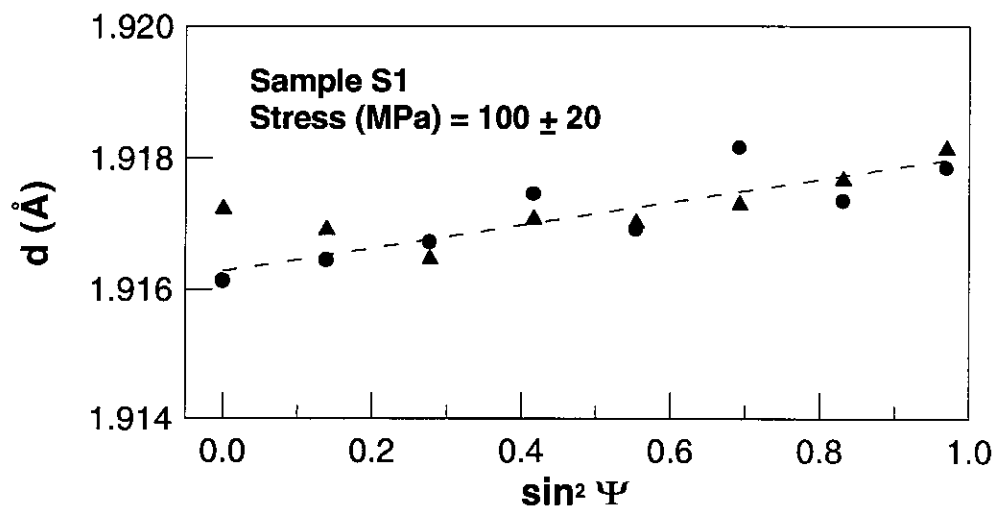
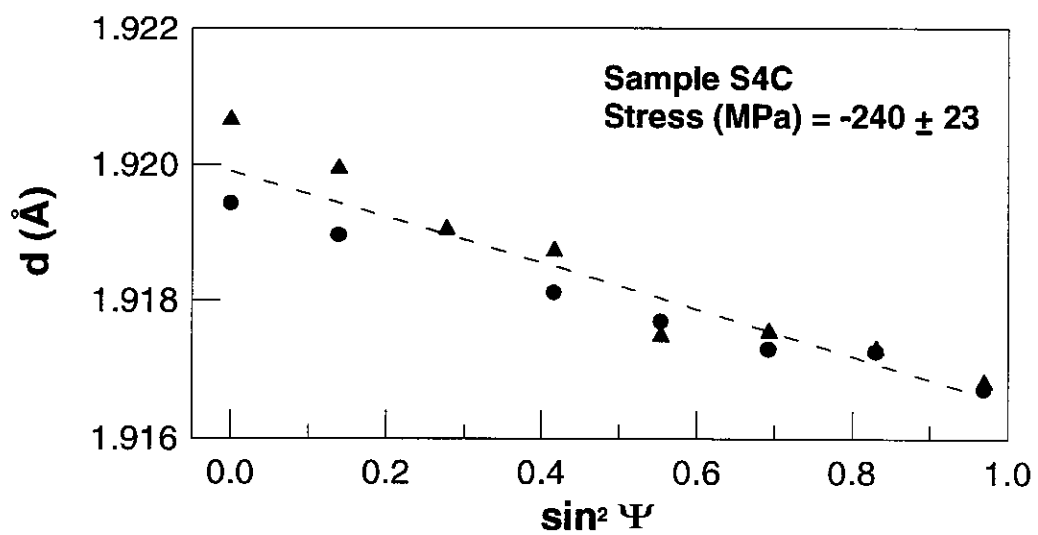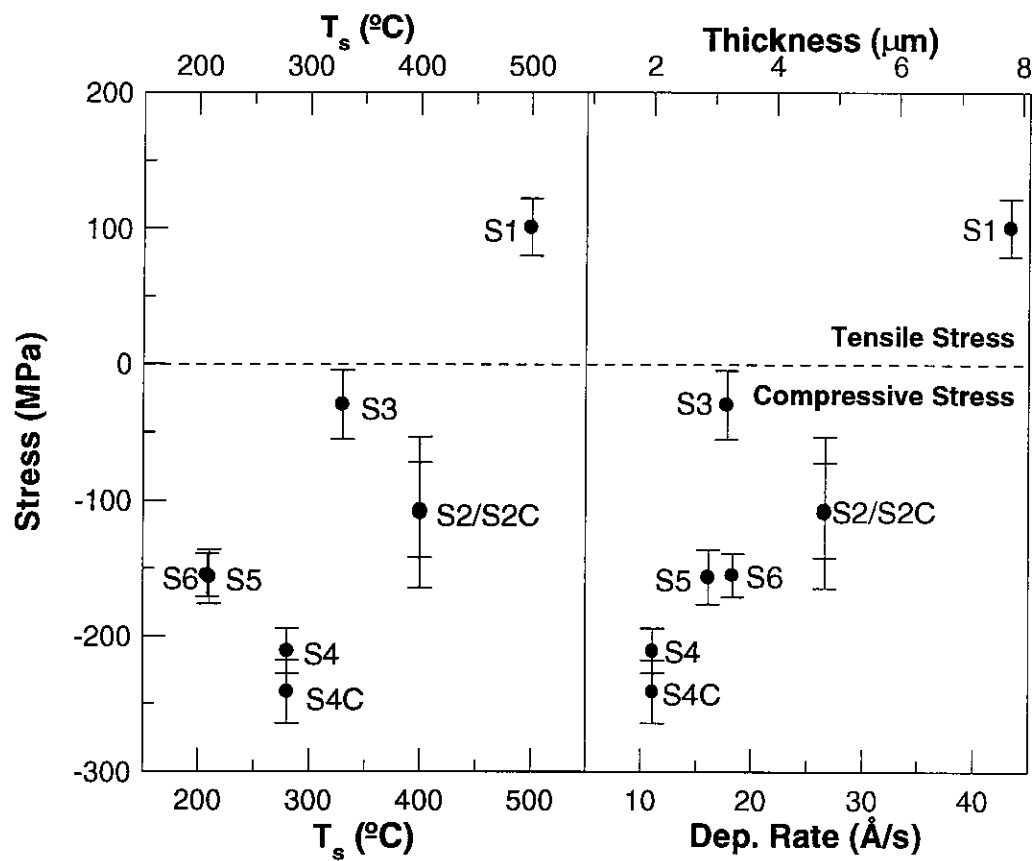Fig.1, D.Peiró et al., Materials Letters.

A)

B)

Fig.2, D.Peiró et al., Materials Letters.

Fig.3, D.Peiró et al., Materials Letters.