Structure-related strain and stress in thin hydrogenated microcrystalline silicon films

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Abstract. The stress/strain relation for hydrogenated microcrystalline silicon (μc-Si:H) films in the thickness range 10 to 200 nm was studied. It was found from wafer curvature measurements that all deposited films exhibit compressive intrinsic stress, which decreases with film thickness. This finding is in agreement with the stress level seen from the shifts in Raman spectra. The strain was approached through the Raman Mechanical Coefficient for the thin films and was estimated to be \(-1.4 \times 10^{-5}\) (cm\(^{-1}\)/MPa). The Raman spectra indicated highly crystalline films. The deconvolution of the spectra into Lorentzian components revealed inclusion of defective nanocrystallites and amorphous phase as well. The fractions of the different constituents were estimated. The contribution of the defective nanocrystallites to the overall stress in the films has been interpreted.

1. Introduction
The mechanical characterization of thin films is of great importance for their use since device functionality and reliability depend strongly on mechanical parameters. In the field of microcrystalline silicon films a range of diagnostic and deposition techniques has been applied to achieve further enhanced transport properties [1-4]. The relation between these properties and mechanical properties of very thin films of microcrystalline Si remains to be at issue. The results published by J. Trask et al. show that one of the ways to reach better properties is by creating films with larger grains [5] as it is found in this study. The grain and column boundaries play a particularly important role in determining electronic properties of the film, since most of the electrically-active defects are located there [6].
However, the nucleation process is a complicated one and thus, the film structure is sensitive to several factors. Apart from the process parameters, the film structure is a function of film thickness as well. It is known that the crystallinity increases with the film thickness, especially when the deposited films of μc-Si:H are obtained through PECVD method [5]. Some authors characterized microcrystalline silicon material using Raman spectroscopy and found that the optimized nc-Si:H material does not show an incubation layer [7]. In our study it is suggested that growth does pass through this stage. Bearing all this in mind, and that the microstructure of silicon films is physically related to stress/strain characteristics, in this paper attention is drawn to correlate the Raman stress induced shifts with the stress level as independently determined from wafer curvature measurements. The thickness dependence of the stress, of the Raman peak position, of the linewidth of this peak, and film morphology is studied. Here stress/strain characterization is implemented for the very early stages of deposition, since studies in the above mentioned context are still lacking. The results of this study will be used for an easier characterization of microcrystalline silicon thin films via stress/strain apprehension which is essential for reliability of device performance. The knowledge of structure related stress and strain could be applied for elaboration of technology for fabrication of films with desired parameters.

2. Experimental

Hydrogenated microcrystalline silicon thin films were deposited by RF (13.56 MHz) plasma enhanced chemical vapour deposition (RF PECVD) in a capacitively coupled (CCP) reactor on (111) silicon substrates. Before film deposition the Si substrates were coated with a thin layer of a-Si:N:H to avoid epitaxial film growth. Substrate thickness, $d_s$, was $380\pm25\mu m$, and film thickness, $d_f$, was varied between 10 and 200 nm. The film thickness was estimated by modelling of ellipsometric spectra. This range is intentionally below that normally used in solar cell applications in order to reveal the stress condition in the early stages of deposition. A process gas mixture of tetrafluoride, SiF$_4$, H$_2$ and Ar was used for the deposition of the μc-Si:F:H films. The films were prepared, maintaining a constant gas pressure of 3 Torr in the deposition chamber. Since the film properties are very sensitive to the plasma process, low substrate temperature of 200 °C was chosen in this experiment.

Stress values, $\sigma_f$, were determined by the classical method of wafer bending and elastic parameters, Young modulus, $E$ and Poisson’s ratio, $\nu$, were calculated using Stoney’s formula (1) [8]. The last term in parentheses in (1) represents the deformation $\varepsilon$ of the film-substrate system; $R_{f+s}$ and $R_0$ are the radii of curvature of Si substrate with film and without film, respectively. The error in the radii determined by curvature measurements was 10%. The thermal component of the stress is not considered, since it is equal for all samples and hence does not influence the stress evaluation with film thickness. Thus, the stress calculated by (1) characterises the intrinsic stress for the film bulk.

\[
\sigma_f = \int_0^{d_f} \sigma dz = -\frac{1}{6} \left( \frac{E}{1-\nu} \right) d_s^2 \left( \frac{1}{R_{f+s}} - \frac{1}{R_0} \right)
\]

Raman spectra were obtained by LabRAM HR micro-Raman spectrometer equipped with CCD detector and laser excitation wavelengths of 632 and 514 nm. Objective with a magnification of 100x was used. The peak position accuracy is below 0.02 cm$^{-1}$. Usually shorter wavelength is used to increase the Raman signal and to decrease the signal arising from the substrate. The penetration depth, i.e. the probed volume of the film, is determined also by the wavelength. Taking into account the absorption coefficients of μc-Si:F:H films [9,10] we can assume that 632 nm beam probes the whole film volume, so that the Raman stress results can be correlated with the stress results taken from the curvature measurements. Using lower wavelengths can substantially decrease penetration depth [11], for μc-Si:F:H films the decrease amounts to 3 times [4]. Therefore, Raman scattering at 514 nm and confocal experiment are applied to reduce the depth penetration and to better resolve the different phase fractions (crystalline/amorphous) in the films.
The morphology of the films is observed by Scanning electron microscope – JEOL JSM 5300.

3. Results and discussions

The properties of the thin films are largely dependent on the state of stress/strain in the film. Strain in a thin film can be caused by several factors, including: lattice mismatch between film and substrate, thermal expansion coefficient differences, and different phase inclusions during growth process. The approach taken for the work presented in this paper was to examine the film properties as a function of film thickness, since such dependence gives an opportunity to discuss stress/strain relation.

We extract the effects of strain from stress dependence on the film thickness. Figure 1 shows this dependence. It also shows that the type of the stress is compressive for all films studied. The evolution character of stress follows the change in the Raman peak position (figure 2) for excitation wavelength of 632 nm as a function of the film thickness. As the film thickness increases, the Raman peak is moved towards lower frequencies, but still higher than the values for unstressed bulk crystal Si, which is 520.7 cm\(^{-1}\). From the point of view of stress characterization, this means that development of compressive stress occurs [12], as in fact found from the curvature measurements shown in figure 1.

From the structural point of view, the presence of peak at about 521 cm\(^{-1}\) (figure 2) corresponds to films that are mostly crystalline. Another result ensues from the peaks position shift with film thickness, and it is that an evolution of film microstructure during growth is obtained, as will be discussed further.

![Figure 1](image1.png)

**Figure 1.** Mechanical stress values at different film thickness. Line is a guide to the eye.

![Figure 2](image2.png)

**Figure 2.** Raman shifts measured at 632 nm excitation wavelength for all film thicknesses.

Another proof in confirmation of the crystallinity of films structure is the observed (not here) constant with film thickness value of 3 cm\(^{-1}\) for the full width at half maximum (FWHM). The value of this quality for crystalline Si is given to be 1.22 cm\(^{-1}\) in [13]. This result is in agreement with published by Faraci et al. who found FWHM = 3 cm\(^{-1}\), which they ascribed to a great number of nanocrystallites of about 100 nm size in the film [14]. Furthermore, the observed crystallites by SEM in this study are also of 100 nm size (figure 3). Thus, constant halfwidth and constant grain size are manifestation of (nano)crystallinity observed by two different analysis.

Figures 4a and 4b show the deconvoluted Raman spectra measured at 514 nm excitation wavelength for μc-Si:F:H films with thickness of 10 and 200 nm, respectively. For the thinner films the contribution of the c-Si substrate is considered, as shown in figure 4a. In thickness coordinates, the Raman peak position is shown at figure 5 for all film thicknesses studied. Together with the 521 cm\(^{-1}\) peak characteristic for crystalline films two other features are observed, at around 480 cm\(^{-1}\) and

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Figure 3. SEM images for films of 10 nm (a), 50 nm (b) and 200 nm (c) thickness.

Figure 4. Deconvoluted Raman spectra measured at 514 nm excitation wavelength for μc-Si:F:H films of 10 nm (a) and 200 nm (b) film thickness.

515 cm\(^{-1}\). The peak frequency of the Raman bands was determined from Lorentzian fits of the data. The shoulder at 480 cm\(^{-1}\) indicates the presence of an amorphous fraction in the film. The low-
wavenumber peak at around 515 cm\(^{-1}\) is usually assigned to a phase of defective nanocrystallites, which belongs to crystalline part of the nanocrystals, as determined by Raman emission cross-section ratio in [4]. The presence of peak at 515 cm\(^{-1}\) can be also attributed to smaller than 10 nm size of the grains as found recently [9] by Raman profiles that used a bimodal size distribution of crystallites. From modelling of Raman spectra, some other authors estimated that the peak at about 515 cm\(^{-1}\) corresponds to grain size of about 3 nm [14]. Similar result has been obtained by means of Raman scattering for nanocrystalline silicon films [15]. According to the positions of the crystalline peak, the mean crystallite size was calculated there as being 3.5 nm. Based on these considerations, a suggestion could be drawn that namely defective nanocrystallites are smaller sized nanocrystallites in this study. However, SEM analysis was not able to show them (figure 3).

As mentioned above, the film microstructure is changed as the film thickness changes and as a result, the stress as well. To support this suggestion, amorphous/crystalline fraction analysis using integrated Raman intensities of both phases was conducted. The results are given in table 1. As it is seen, a structural transition from 10 to 200 nm films is observed. The amount of the total crystalline fraction (\(X_c+X_{dc}\)), as extracted from figures 4a and 4b, increases mainly because of the formation of defective or small size crystallites (\(X_{dc}\)) on the expense of the amorphous phase (\(X_a\)). The crystalline fraction of large size crystallites (\(X_c\)) remains almost constant. A rough estimate from SEM images, figure 3, gives a value of the large crystallites of about 100 nm grain size. The increased amount of \(X_{dc}\) implies higher number of crystallites and greater inter-grain boundaries area. Different models have been developed to explain the observed Raman shift in microcrystalline semiconductors [16,17], which point out that the shift arises primarily due to presence of compressive stress and strongly depends on the size of the crystallites. With stress data obtained here, this would mean that defective crystallites with their greater boundaries contribute to relaxation of the stress with film thickness increasing. Considering the growth process and structure, the lowered intrinsic stress by nearly one order of magnitude compared to the stress value of 10 nm film, is a sign of completely built, finally grown film where the intrinsic stress is relieved with the thickness (200 nm film), figure 1.

The results in table 1 show that film growth proceeds through formation of amorphous and crystalline phases, which is in agreement with published in [18-20]. Since the largest part of the intrinsic stress, present at room temperature, has its origin in the growth process a structure-related discussion of the highest stress and its evolution follows. By measuring the radii of curvature before...
and after deposition of the μc-Si:F:H films the nature of intrinsic stress is directly determined in this study as compressive. A number of authors [21-23] have also found compressive stress but in rather thicker μc-Si:H films (1 μm) deposited on a glass substrate [23] or using silane-hydrogen gas mixture [21]. In the latter study, a maximum value of 1 GPa compressive stress has been measured for samples grown just before the transition to microcrystalline material. In this sense, the highest stress level of about 4 GPa for 10 nm thick film is reasonable, taking in view the different deposition conditions used in this study. To explain the stress nature independently of our Raman analysis we note that plasma bombardment induces compressive stress [24]. During the plasma bombardment there are a few components that take part in the film formation. The hydrogen plasma exposure results in a hydrogen-rich subsurface layer [25]. One reason for high stress value is that it is generated by unbonded hydrogen. The film is in a state in which SiH₄ complexes [26] are formed by H insertion into strained Si-Si bonds increasing intrinsic stress [18]. The presence of F atoms enhances this effect and μc-Si:F:H nucleation is initiated. On the other hand, according to [27], in the low temperature PECVD process, films of about 10 nm thickness are at the phase transition of amorphous to microcrystalline film structure. It is referred to as incubation phase [28] but the growth of μc-Si is produced on glass substrate, while in our case, a-Si:N:H sublayer is deposited on the Si substrate surface. This allows us to apply the same approach in analyzing the growth process. A very thin layer is sufficient for this phase transformation to occur as we observe from the Raman study (figure 4a and table 1) that both amorphous and crystalline phases are present simultaneously in the 10 nm film. So, the results about intrinsic stress, shown in figure 1, have led in suggesting that the highest stress favours the initial growth of crystallites. As SEM image of 10 nm film shows (figure 3), the material is at the transition between amorphous/microcrystalline states for which some isolated two-dimensional crystalline fragments on amorphous continuous film background are in nucleation.

Stress data (figure 1), the gradual drop in Raman shift (for both, peak at 521 and 515 cm⁻¹, figure 5) and SEM images with keeping same grain size (figure 3) would lead to the suggestion that μc-Si:F:H films of 50 nm thickness could be classified as being still in incubation phase, following [28] as well. Other authors cite incubation phase extending up to 60 nm [29]. The growth conditions are influenced by both substrate temperature and hydrogen dilution ratio [27]. Structural bonds in this study are less strained, while at 10 nm the film bulk is not enough for stress relaxation and requires much more deformation of the bonds. The finding of grain size of 100 nm in the film construction is consistent with peak found at about 521 cm⁻¹ (figure 4a, b). Nanocrystallites of order of 100 nm were inferred by other authors from modelling of Raman spectra [14]. The reason for larger grain size presence is in films deposition accomplished from SiF₄, as reported in [30]. The crystallite size of 16.8 nm has been estimated for films deposited from SiH₄ at the same temperature, 200 °C, as it is in this study but for 980 nm film thickness [23].

As it was mentioned above, a correlation between macroscopic mechanical strain or stress and the local information of the film accessed by Raman Spectroscopy can be found. The reason why such a correlation exists is the common dependence of the Raman signal and the mechanical behaviour on the local nanostructure of the films, which is Hooke’s law or Stoney’s formula (1), but in different terms. Recently, Gouadec and Colomban generalized it, giving the following relation in the case of uniaxial stress [31]:

| film thickness | Xa | Xdc | Xc |
|----------------|----|-----|----|
| [nm]           | %  | %   | %  |
| 10             | 43.5 | 9.4 | 47.1 |
| 200            | 31.6 | 21.8 | 46.6 |
\[ \Delta \omega = S^{c/\sigma} \cdot \sigma, \quad (2) \]

where, \( \Delta \omega \) is the Raman mode shift relative to the unstressed position; \( S^{c/\sigma} \) is the Raman Mechanical Coefficient (RMC), \( \varepsilon \) is the deformation or strain, and \( \sigma \) is the measured film stress in MPa. The physical interpretation of the proportionality coefficient \( S^{c/\sigma} \) is that it combines elastic modulus of the material to the material constants which define the lattice deformation (Raman frequency shift). A linear relationship between the film internal stress calculated by equation (1) and the Raman shift has been accepted by other authors [11,12]. Assuming the same property for our films gives the RMC value of \(-1.4 \times 10^{-5} \text{ cm}^{-1}/\text{MPa} \) for the slope \( S^{c/\sigma} \) (figure 6).

Most of the authors who estimate the stress from Raman shift for different Si materials - from amorphous to nanocrystalline, usually use the same RMC value which is that for c-Si which is \(-5.4 \times 10^{-3} \text{ cm}^{-1}/\text{MPa} \) [32] or its reciprocal value \(-250 \text{ cm.MPa} \) [11,12,23,33]. However, RMC is strictly specific for each material. It should be emphasized that in the present study RMC for \( \mu \)c-Si:F:H is independently determined having the mechanical stress from the curvature measurements. Our RMC value is much lower than for crystalline silicon. In our opinion this result is due to the specific structure of \( \mu \)c-Si:F:H as evident from our SEM and Raman results. As pointed out recently [31] much lower RMC could be related to stress relaxation at grain boundaries and at interphases for nanophase materials.

Actually, the importance of our experiments is also to distinguish between the nature of the stress which accompanies film growth and structural changes in the film (as a reason this stress to appear) and the nature of the externally applied stress, for example. Strong variation of film structure with film thickness (depending on details of the deposition conditions) reflects the evaluated stress. In this study, films are deposited on crystalline Si substrates and not on a glass substrate. The curvature measurement yields the integral value of the film stress, while the Raman shifts are related to the local strain over smaller area of the film. Thus, the RMC contains implications of the physical relevance of the methods for stress determination, namely interference measurements of sample curvature and Raman spectroscopy.

4. Conclusion

Our experimental results show that the very thin films of \( \mu \)c-Si:F:H (up to 200 nm) grow with compressive intrinsic stress as found by the wafer curvature and Raman study. Curvature measurements allow us to experimentally determine the accurate intrinsic stress in the films and to correlate it to Raman shifts. A combined study of the internal stress and Raman shift of the crystalline mode, both measured on the same microcrystalline films, lead us to the value of the RMC material constant for microcrystalline silicon thin films deposited from SiF_4. The constant was estimated to be \(-1.4 \times 10^{-5} \text{ cm}^{-1}/\text{MPa} \). This constant characterizes the film properties resulting from the specific growth process. Besides, from our stress measurements we propose stress related growth of microcrystalline thin films. At the early stage of deposition crystallization is favoured by high stress that develops in the thin films. The mechanical stress is further reduced by an increase of the crystalline fraction linked to incorporation or creation of small size crystallites, the stress being released at their boundaries. We consider the results as giving some light to understand the development of the crystallinity of thin Si films on the base of parallel exploration of stress, Raman spectroscopy and morphology.

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