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# Structural characterization of crystallized Si thin film material by HRTEM and Raman spectroscopy

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Comparative structural analyses of a crystallized, 60 nm thick silicon film deposited on quartz substrate were performed using high resolution transmission electron microscopy (HRTEM) and Raman spectroscopy (RS). Both methods suggest high degree of crystallization of the film. The material of the film consists of crystalline grains with sizes up to 20 nm (HRTEM) and the mean size of the grains is ~4 nm (RS). HRTEM results suggest large scatter of the crystal orientations of the grains. The existence of boundary defects between grains grouped in large agglomerates was also detected by HRTEM. RS analyses indicate large compressive strain in the system and the existence of high pressure Si phases in the material of the film.



**1 Introduction** Thin crystalline Si films situated on glass or polymer-based flexible substrates are advantageous materials for large area electronics and photovoltaics (PV) due to sufficient quality/price ratio (see Ref. [1] for the latest review). Moreover, nanometer-thick Si layers in $Si/SiO_2$ multiple quantum wells (MQW) attract growing interest due to their potential applicability in PV, microelectronics, photonics, bioelectronics, etc. Quasi-direct and controllable band-gap and advanced carrier-transport properties are predicted for such MQWs [2–7]. Substantial improvement and reliable control of the crystalline quality of thin Si films and Si nano-layers in $Si/SiO_2$ MQWs remains a priority task [2], since only high degree of crystallinity can lead to suitable electrical and PV characteristics of the films.

The process of thin Si film and $Si/SiO_2$ MQW preparation implies deposition of amorphous-Si (a-Si) layer(s) onto a substrate such as crystalline-Si (c-Si), quartz, etc., followed by crystallization of the a-Si layers applying heat treatments or laser annealing [2, 8–11]. Recently light-induced solid phase crystallization (LISPC) [12] was also successfully applied to $Si/SiO_2$ MQWs.

A structure of thin Si films can be investigated with several experimental methods such as X-ray diffraction (XRD), X-ray scattering (XRS, SAXS, GISAXS), transmission electron microscopy (TEM) and Raman spectroscopy (RS). However, employment of X-ray methods is problematic for the case of $Si/SiO_2$ MQWs due to extremely small volumes of the material. TEM and especially high-resolution TEM (HRTEM) investigations are capable of distinguishing a-Si and nanocrystalline Si (Si-nc) phases in the $Si/SiO_2$ MQWs (see e.g. [11, 13, 14]). Since the crystalline structure can be directly observed in HRTEM, the interpretation of the images seems straightforward. However, the preparation of high quality specimens necessary for HRTEM investigations can be challenging and time consuming. On the other hand, RS does not require additional sample preparation and explores much larger volumes of samples, thus allowing detection of small

residual a-Si inclusions in the crystallized material. Analyses of RS spectra, besides detection of various phases of Si, i.e. a-Si, c-Si, high pressure phases, etc. [15], allow estimations of the mean size of the crystallites and average strain in the structure [16, 17]. The ratio of crystalline material volume to the total Si volume in the film, the so-called crystalline fraction $F_{CR}$, can be estimated using integrated intensities of RS signals from crystalline and from other Si phases [18, 19]. However, such an approach was questioned in Ref. [20]. Since the structural parameters have a decisive influence on the electrical properties of thin Si films, we decided to perform a direct comparison of RS and TEM results for the relatively simple case of a single 60 nm thick crystallized Si layer.

## 2 Sample preparation and experimental details

**2.1 Si film fabrication** Remote plasma enhanced chemical vapour deposition (RPECVD) was employed for fabrication of $SiO_2/Si/SiO_2$ structures on quartz substrates. Preliminary cleaned, 350 μm thick quartz plates with area of $10 \times 10\,mm^2$, were introduced into a CVD reactor for the subsequent deposition of undoped a-Si and $SiO_2$ films using controlled $SiH_4$ and $O_2$ gas fluxes. The deposition was performed at 250 °C. The thicknesses of the deposited layers were: 5 nm $SiO_2$ buffer layer deposited directly onto the quartz substrate, 60 nm a-Si layer and 110 nm thick $SiO_2$ capping layer. The sample was annealed in a furnace at 1050 °C for 30 min in an inert $N_2$ atmosphere after the deposition. The annealing conditions were optimal for obtaining a high degree of crystallization.

**2.2 HRTEM: sample preparation and experimental details** In order to perform HRTEM analyses very thin lamellas have to be prepared from the samples. Such lamellas were produced using a focused ion beam (FIB) instrument. The preparation related artefacts were reduced by post-FIB processing of the lamellas using a Duo mill tool from BAL-TEC instruments, equipped with an argon-ion source and operating at low energy (2 kV). The final thickness of the lamella could be estimated as $\leq$40 nm.

The HRTEM studies were conducted on a FEI Titan 80-300 TEM equipped with an aberration corrector and operating at 300 keV. The contrast of a HRTEM image originates from the coherent superposition of primary and of scattered electron beams and is related to the projected atomic structure of Si-nc. For better atomic resolution, the images were taken in negative Scherzer focus (NCSI) imaging mode, in an aberration-corrected TEM, based on the adjustment of negative spherical-aberration coefficient of the objective lens of the TEM microscope [21].

**2.3 RS: measurement details and estimation of structural parameters** Raman spectra with spectral resolution $0.05\,cm^{-1}$ were recorded by means of a micro Raman spectrometer (Dilor XY) equipped with frequency doubled Nd:$YVO_4$ cw laser with wavelength 532 nm. We used low power density of the probe beam ($<1.4 \times 10^5\,W/cm^2$) to minimize local heating of the samples during the measurements. The spectra were recorded in the range of wavenumbers 160–700 $cm^{-1}$ and with the signal integration times ~60 s. To obtain the RS spectrum of the film, a spectrum related to the substrate quartz was detected separately and subtracted from the overall spectrum of the sample. Precise calibration of RS peak positions was performed using spectral line from standard Hg lamp.

The Si-nc volume fraction in the material could be roughly estimated using $F_{CR} = (I_{Si\text{-}nc})/(I_{TOT})$ expression, where $I_{Si\text{-}nc}$ is the integrated intensity of the Si-nc signal and $I_{TOT}$ that of the sum of all silicon phases [18, 19]. Therefore the RS spectra detected from the film were fitted with the peaks related to various Si phases for estimation of $F_{CR}$. Besides that, spectral parameters of the Si-nc peak, i.e. full width at half maximum, FWHM and a spectral position of maximal intensity, $\nu(I_{MAX})$ allow estimation of mean size of crystallites, $s_{nc}$ and of a value and sign of mean internal strain, $\varepsilon$ in the film [16, 17]. Namely, $s_{nc}$ determines $\nu(I_{MAX})(0)$ at $\varepsilon = 0$ and FWHM of the peak. On the other hand, strain affects only $\nu(I_{MAX})$. Therefore, first $s_{nc}$ and $\nu(I_{MAX})(0)$ were obtained from FWHM of the peak and then $\varepsilon$ was estimated from a difference between $\nu(I_{MAX})$ and $\nu(I_{MAX})(0)$.

## 3 Results

**3.1 HRTEM results** A HRTEM image of a cross-section of the crystallized Si layer and of the neighbour layers is presented in Fig. 1. Si nanocrystals grown with various crystalline orientations can easily be distinguished. Si-nc grains, orientated in various directions are well-connected and form almost perfect crystalline film. Although the crystalline structure of Si-nc grains is clearly visible in HRTEM images, deduction of their dimensions, $s_{nc}$ and of crystalline fraction $F_{CR}$ is not straightforward. Both, small, i.e. $s_{nc} < 3$ nm, and large with $s_{nc} \approx 20$ nm grains could be found in the image at the same time. First, the grains have irregular shapes, i.e. the extent of Si-nc grains differs for different directions. Next, HRTEM images provide information only 'in plane' of the image and it is not possible to get information in-depth of the film. Thus due to a possible superposition of the structures positioned at various depths in the film the estimations of $s_{nc}$ and $F_{CR}$ are problematic. The HRTEM images suggest that small grains tend to connect to each other and form agglomerations. Locations without crystalline structure also can be found in the image of the film. These areas may contain a-Si or Si-nc orientated in highly indexed directions with respect to the electron beam direction. The latter possibility is related to the fact that in HRTEM only atomic columns with orientations nearly parallel to the electron beam can be detected.

After crystallization most of the grains in Si film have the diamond cubic crystal structure (space group Fd3m). An experimental image in which the [110] zone axis is perpendicular to the sample plane and parallel to the viewing direction is presented in Fig. 2. The projected crystalline

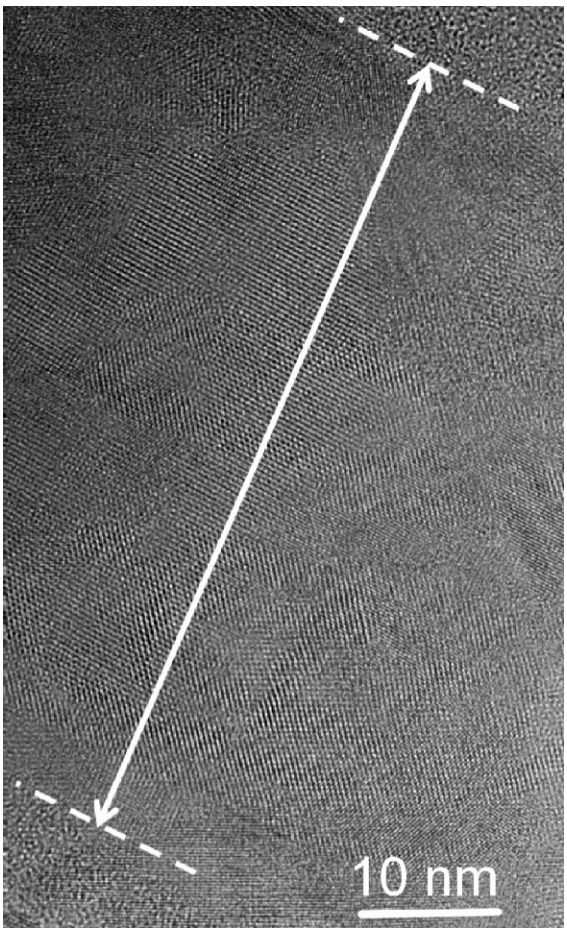


**Figure 1** Cross-sectional HRTEM image from crystallized Si film. Location and direction of the film is indicated with double-sided arrow and with dotted lines.

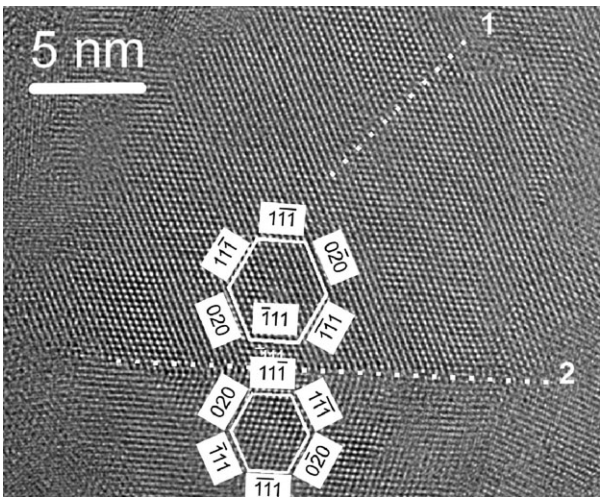


**Figure 2** Cross sectional HRTEM image along the [110] zone axis of the structure. Line 1 shows a stacking fault. Two Si-nc crystallites form a twin boundary located along line 2.

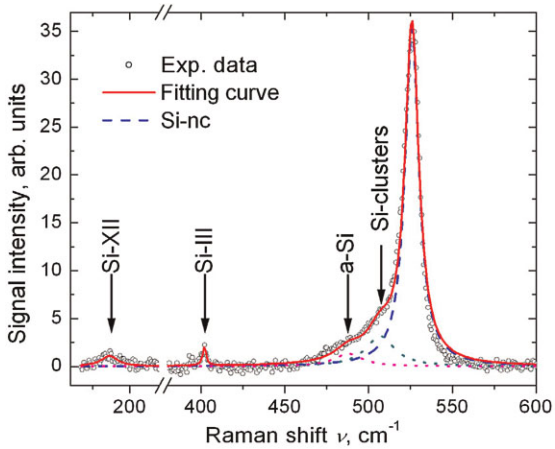


**Figure 3** (online colour at: www.pss-a.com) Raman spectrum detected from the crystallized Si film. The experimental data points were fitted with peaks related to Si-nc, Si-clusters (Si-nc precursors with dimensions <1 nm), a-Si and high pressure Si phases, i.e. Si-XII and Si-III.

distances in the <200> and <111> directions are 0.406 and 0.380 nm, respectively. Image shows that large agglomerate of Si-nc grains is formed inside the Si layer. The image illustrates the atomic structure of planar defects in thin-film silicon. The line 1 follows an intrinsic stacking fault in which adjacent layers are shifted slightly and line 2 shows the twinning plane in which the upper layers are mirror-inverted with respect to the lower layers.

**3.2 RS results** A Raman spectrum originating from the crystallized film is presented in Fig. 3. In the same figure fitted peak curves and a cumulative fitted spectrum are presented. Assignments of Si peaks to various Si phases shown in the figure were done in accordance with Ref. [15].

Fitted parameters of the peaks are presented in Table 1. The crystalline fraction for the sample could be estimated as $F_{CR} \approx 74\%$. From the value of FWHM, using Ref. [17] we estimated the mean size of Si-nc grains as $s_{nc} \sim 4.2$ nm. Next, from the $\nu(I_{MAX})$ of the Si-nc peak and from the estimated $s_{nc}$ value, it appears (see [17]) that the compressive strain in the structure was ~4.8 GPa. The slightly asymmetric shape of Si-nc peak (see Fig. 3) suggests large scatter of the Si-nc size values. The presence of large compressive strain correlates well with the appearance of high pressure phases, i.e. Si-XII and Si-III in the RS spectra of the sample.

**Table 1** Fitted parameters of the peaks in the Raman spectra of the crystallized film.

| peak | pos. ($cm^{-1}$) | FWHM ($cm^{-1}$) | area | % of Si |
|---|---|---|---|---|
| Si-nc | 525.87 | 10.0 | 551.2 | 74.15 |
| Si-clust. | 507 | 20.4 | 112.9 | 15.19 |
| a-Si | 488 | 19.5 | 37.2 | 5.01 |
| Si-III | 402 | 4.8 | 15.4 | 2.07 |
| Si-XII | 185 | 13.3 | 26.6 | 3.58 |

**4 Discussion** From the HRTEM analyses it was possible to obtain information about structural peculiarities of the Si-nc grains and their agglomerates. The presence of boundary defects, i.e. twin boundaries, stacking fault, etc., was confirmed for the nano-crystalline material of the film. From the RS results presence of large strain in the film was suggested, which was supported by detection of high pressure phases of Si.

Both experimental methods applied for structural characterization of the thin crystallized Si film showed high degree of crystallization. HRTEM images show presence of crystalline grains filling the volume of the film almost entirely, while RS results suggest high value of crystalline fraction, i.e. $F_{CR} \approx 74\%$. The high level of crystallinity visible in the HRTEM images does not exclude presence of a-Si inclusions in the material of the film, obscured by the crystalline material. On the other hand, several factors can influence the estimations of $F_{CR}$ from the RS results. Possible errors in estimations of $F_{CR}$ value are related to the origin and spectral intensity of the peak at $488\,cm^{-1}$. According to Ref. [20], besides a-Si the peak at $\sim 480\,cm^{-1}$ can originate from grain boundaries (GB). The RS spectrum detected from the $Si/SiO_2$ MQWs completely crystallized in LISPC regime [12] revealed only Si-nc peak at $\sim 520\,cm^{-1}$ with symmetrical Lorentzian lineshape, despite the fact that the structure of the Si layers should contain GBs in that case as well. Therefore, the relation of GBs to the peak at $480\,cm^{-1}$ was not confirmed. On the other hand, peak at $\sim 480\,cm^{-1}$, somewhat similar to a-Si, was detected from stishovit, a variety of $SiO_X$ $(X < 2)$ [22]. Since diffusion of Si atoms to the neighbouring oxide and formation of $SiO_X$ phase there during furnace annealing of the sample can not be excluded, the peak at $\sim 480\,cm^{-1}$ can contain a component related to $SiO_X$. In such a case the estimation of $F_{CR}$ from the RS results would be understated. It is worth to be noted that a peak at $\sim 480\,cm^{-1}$ and that at $507\,cm^{-1}$ were detected in MQWs crystallized by light in non-SPC regime [12] as well. Altogether, we can state a good agreement between HRTEM and RS results in analysing the crystallinity of the material.

From the first glance there exists disagreement between sizes of Si-nc grains obtained from HRTEM and RS results. However, one should keep in mind that RS suggests a mean value for the size of the grains. The asymmetric shape of the Si-nc peak indicates a large scatter of the actual grain sizes. On the other hand observation of small size grains ($<3$ nm) in HRTEM is problematic due to concealing of their images by the large grains. Taking into consideration the above details, the agreement between the HRTEM and RS results in analysing of Si-nc dimensions can be recognised as quite satisfactory.

**5 Summary** Results obtained by HRTEM and by RS during investigations of structural parameters of 60 nm thick crystallized Si film showed nice agreement. Both methods showed that the film contains high density of Si-nc grains with mean size about 4 nm (RS) and a large scatter of individual sizes (from $s_{nc} < 3$ nm to $s_{nc} \sim 20$ nm, HRTEM). The fraction of crystalline material in the film exceeds 70%. HRTEM results suggest large scatter in orientations of the Si-nc grains and presence of boundary defects between the neighbouring grains. RS revealed high average compressive strain ($\sim$4.8 GPa) in the system and the presence of the high pressure Si-III and Si-XII phases in the material of the crystallized film.

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