Stress characteristics of suspended porous silicon microstructures on silicon

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Abstract. The mechanical properties of porous silicon (PS) microstructures on crystalline silicon (c-Si) were investigated. Micro-Raman spectroscopy was applied to probe stresses in PS micro-hotplates in the form of cantilevers. Important information was obtained for the stress distribution across cantilevers supported at one edge. The structural stability of thermally treated PS after long time exposure in air was also investigated. The results can be used for optimization of microsensors based on the PS microstructures.

1. Introduction
Porous Silicon (PS) has attracted significant interest over the last years due to its potential usage in various fields of applications. PS membranes have been effectively used as material in low power thermal sensors and radio-frequency (rf) devices and for local thermal isolation. Optimization of the mechanical properties of PS layers as well as stress control is a main issue that has to be considered for most of these applications. Stresses can affect the integration of PS devices in microelectronic circuits since they can lead to severe curvature of the wafer. The effect is more severe when PS layers are released from the c-Si substrate. In this case, even mechanical failure can occur due to the fast relaxation of high stresses.

In a recently published work [1], we have studied in a systematic way the stress characteristics of suspended PS membranes as a function of the thermal treatment of porous silicon. In this work, we extend the previous results to include alternative micro-hotplate designs in the form of cantilevers that can be used for thermal sensor applications.

2. Experiment
For the PS layers, p type (100) silicon wafers (c-Si) with resistivity 1-10 Ωcm were used as a starting material. Anodization was carried out in an electrolytic cell at current density of 20 mA/cm² and anodization time of 5 min. Layers with porosity of 60% and thickness of 4 µm were formed. The test structures studied were micro-hotplates in the form of cantilevers. The details of the fabrication process of the micro-hotplates are reported elsewhere [2]. Micro-Raman measurements were performed in backscattering geometry along the [100] direction under excitation with the 488 nm line of an Ar⁺-laser at a low power of 0.2 mW microscopically focused to a spot of 1 µm in diameter. The scattered light was spectrally analyzed by a Jobin-Yvon micro-Raman spectrometer (T-64000) equipped with a CCD-detector.

3. Results and discussion
Figure 1 is a SEM image (top and side view) of a PS cantilever device of 60% porosity. Each cantilever has the dimensions of length x width x thickness = (210 x 20 x 4) µm. One edge of the
cantilevers is incontact with the c-Si substrate and the other is free. The cantilevers have been subjected to a two step oxidation process at 300 and 650 °C for 1 hour.

Raman spectra recorded along the long side of a cantilever, at various distances from its supported edge are shown in figure 2. The spectra consist of a narrow peak of c-Si at 521 cm⁻¹ and a broad, less intense band of PS at frequencies lower than the frequency of the bulk. The peak of the bulk is observed since light penetrates through PS to the underlying c-Si substrate. The peak at 352 cm⁻¹ from the laser (20135 cm⁻¹ absolute) is an Ar⁺-laser plasma line. With reference to c-Si, the observed Raman-frequency shifts of the PS cantilever bands are partially due to the porosity of the cantilever and partially due to the mismatch and thermal strain generated in the cantilever by the support. The strain-dependent frequency shift can be easily separated from the porosity-dependent shift by comparison of the spectra of the investigated PS cantilevers and the spectra of free-standing PS with the same porosity as that of the cantilevers. For the cantilevers of figure 1, a Raman spectrum of the free-standing material is included in figure 2.

The Raman spectra of PS can be decomposed in several sub-bands assigned to nanocrystallites of different sizes within the porous layer. The average nanocrystal-size, estimated from the full width at half maximum of the Raman-bands [3-4], was 2 nm. As demonstrated in figure 3, these sub-bands were fitted with a combination of Gaussians, while the c-Si peak was fitted with a Lorentzian. The red
frequency shift of the free-standing PS bands with respect to the c-Si peak is due to the lowering of crystal symmetry originating from the presence of silicon nano-crystals and the size reduction within the porous matrix. The frequency shift of the PS bands of the cantilevers is due to both, size reduction (red-shift) and strain (blue-shift). For the following strain/stress analysis, the Raman frequency of free-standing PS was taken as reference and the blue frequency shift of the cantilever bands (towards the peak of bulk silicon) was attributed to built-in strains in the cantilever structure originated by the differences in the lattice-constants and the thermal coefficients of the PS epilayer and the c-Si substrate.

The situation of a strained cantilever is described in ref. [5]. For a cantilever oriented with its short side (20 µm) along the x-axis (x // [010]) and its long side (210 µm) along the y-axis (y // [001]), the stress profile corresponding to the Raman frequency shift (measured in backscattering along the z-axis, z // [100]) is obtained under the assumption that the cantilever structure is subjected to a uniaxial stress σ in the y direction. By application of a uniaxial stress, the triple degenerate phonon of c-Si splits in a singlet and a doublet, polarized perpendicular and parallel to the stress direction [6]. Thus, in the present case (σ // [001]), the phonon threefold degeneracy splits into a doublet polarized in the xz plane and a singlet polarized along y. According to the selection rules of Raman scattering, for a material of cubic symmetry, only the doublet is observed in backscattering along z and its frequency shift is given by [5]:

\[ \Delta \omega_d = \frac{\omega_0}{k_{11}S_{12} + k_{12}(S_{11} + S_{12})} k \omega_0 \sigma / 2, \]  

where \( \sigma \) is the stress, and \( \omega_0, \ k, \) and \( \ S \) are the Raman frequency, the phonon deformation potentials, and the elastic compliances of the non-strained material, respectively.

Based on Eq. 1, the stress \( \sigma \), responsible for the bending of the cantilevers (Figure 4), was calculated from the Raman frequency shift of the measured spectra according to:

\[ \sigma = \frac{2\Delta \omega_d}{\omega_0 \left( k_{11}S_{12} + k_{12}(S_{11} + S_{12}) \right)} \]  

by using the elastic constants of PS, after extrapolation of values known from the literature [7-8], and the phonon deformation potentials of c-Si instead of those of PS that are still unknown.

Figure 4 is a close SEM image of the bent cantilevers studied.

The stress distribution in dependence of the distance from the supported cantilever edge is depicted in figures 5a and 5b. Since the Raman spectra of the cantilevers were decomposed in more than one sub-bands (figure 3), stress values were obtained for the first two bands lying on the high and the low energy side of the Raman spectrum, respectively. The contribution of the third Raman band was neglected because, even in the case that it was present (as in figure 3), it was rather weak. With respect to the frequency of free-standing PS, the stress values calculated from the frequency shift of the PS band on the high energy side of the Raman spectrum \( \Delta \omega_{1\text{-strain}} \) (figure 5a, full circles) are in the range of \( \sigma_1 = (0.1-0.2) \) GPa (figure 5a, open circles), while those calculated from the frequency shift of the PS band on the low energy side of the same Raman spectrum \( \Delta \omega_{2\text{-strain}} \) (figure 5b, full squares) are in the range of \( \sigma_2 = (1.8-2.2) \) GPa (figure 5b, open squares); the minus sign designates compressive stresses. As can be seen, stresses increase slightly with the distance from the supported edge. Taking in account that each sub-band is related to a sub-group of nanocrystallites with a specific typical size, a
mean stress value can be estimated by averaging over the stress values of all the sub-groups/sub-bands weighted by the contribution of each sub-group/sub-band to the overall PS Raman band (as defined by the ratio of the integrated intensity of each sub-band to the overall band). This averaging procedure leads to stress values in the range \( \sigma = -(0.5-0.7) \) GPa.

Previous Measurements performed on the same cantilevers one year ago reveal a similar distribution of the existing stresses. The stress values deduced from \( \Delta \omega_{1,\text{strain}} \) and \( \Delta \omega_{2,\text{strain}} \) vary in the range \( \sigma_1 = -(0.0-0.3) \) GPa and \( \sigma_2 = -(1.5-2.0) \) GPa, respectively. This is an experimental indication that long time exposure of thermally treated PS layers in air does not significantly affect the structural quality of the porous microstructure.

4. Conclusions
The stress characteristics of PS micro-hotplates used in microsensors in form of cantilevers were investigated by micro-Raman spectroscopy. It was found that: a) the stress distribution across cantilevers supported at one edge depends strongly on the cantilever geometry and increases slightly with the distance from its supported edge, and b) PS treated thermally in \( O_2 \) at moderate temperatures appears to be structurally stable. The information obtained is useful for optimizing the design and the fabrication process of microsensor devices.

5. References
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