Non-linear annealing effect on Raman scattering of porous silicon layers

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We have analyzed the Raman scattering spectra of as-prepared and high temperature vacuum annealed porous silicon (PS) layers. The Raman spectra were used to analyze changes in the porous silicon crystallinity following the annealing. The spectra indicate that the effect of annealing depends non-linearly on the temperature. The maximal amount of PS phase and α-Si (amorphous silicon) phase is observed for annealing temperature at 1000°C. The annealing at temperatures higher than 1000°C leads to the recrystallization of α-Si phase.

1. Introduction

Preparation and characterization of materials on the nanometer scale have provided new physics in reduced dimensions and novel structures. The interest towards porous silicon (PS) layers formed by anodic etching of silicon substrates is determined mainly by their possible application as a part of opto-electronic devices and by the possibility to be used as an insulator in new class of silicon on insulator (SOI) technology. Recently observed non-linear decrease in photoluminescence and resistivity of porous silicon after vacuum annealing is very important from application point of view [1,2]. Two opposite concepts are in explanation of the transport properties and light emitting of PS structures. The first concept explains the transport properties and photoluminescence by the quantum confinement of electron/hole current in the PS columns [3]. The second attributes the properties of PS to the amorphous phase only, formed in the PS during anodic etching [4,5]. The advantage of the use of Raman probing of PS is the possibility to clarify the structure of the PS layers, to analyze the different phases included in the PS layer, and to optimize their application [6,7].

In this paper, a detailed study is presented of Raman scattering from PS layers over the 800–1200°C range. A large broadening and asymmetry of the TO band is observed after high temperature vacuum annealing. Different spectral components have been derived, belonging to α-Si, c-Si and PS phases. Their non-linear behavior with temperature allows us to estimate the relative weight of these phases in the layers.

2. Experimental details and sample preparation

The substrates used for the experiments were p-type B-doped silicon wafers, (100) oriented with resistivity of 15 Ω cm. The PS layer was formed on the front side of the wafers by anodic etching in an electrolytic cell in HF (40%): C\textsubscript{2}H\textsubscript{5}OH = 2:1 at the current of 10 mA/cm\textsuperscript{2}. The thicknesses of PS layers were measured by SEM being about 5 mm. The Raman spectra were measured using Ar\textsuperscript{+} laser as an excitation source and a triple Joben-Yvon T64000 spectrometer equipped with a charge coupled device (CCD) detector and a microscope of 1 μm resolution. The annealing of the samples has been carried out by rapid thermal annealing (RTA) technique. The annealing of the samples has been carried out in vacuum 5 \times 10\textsuperscript{-5} Torr at different temperatures in the range of 800–1000°C and for different duration of the annealing.
3. Experimental results and discussions

Raman spectra of our PS samples registered under different RTA conditions are shown in Fig. 1. The spectrum of the samples annealed at 800°C for 30 s are practically the same as that of the as-prepared samples (spectrum a), while considerable differences can be seen in the spectra of samples obtained after higher temperatures annealing (b–e). Besides the well-known transverse optical mode (TO) at 521 cm⁻¹, the spectrum a contains a peak at 304 cm⁻¹ together with two kinks at 230 and 435 cm⁻¹ (2TA overtones), weak bands at 630 and 670 cm⁻¹ (TA + TO combinations) and a peak at 920–1010 cm⁻¹ (2TO overtone) [8]. Evidently, all weaker bands in this spectrum correspond to the second order Raman scattering of bulk crystalline silicon c–Si.

![Overall Raman spectra of PS samples subjected to different annealing conditions](image1)

Fig. 1. Overall Raman spectra of PS samples subjected to different annealing conditions; (a) as-prepared; (b) 1000°C, 15 s; (c) 1000°C, 60 s; (d) 1200°C, 15 s; (e) 1200°C, 60 s.

With increasing the RTA temperature up to 1000 and 1200°C, the spectra (b–e in Fig. 1) are changed. The bands at 150 (TA) and 310 (LA) cm⁻¹, corresponding to the one-phonon density of states of a–Si, appear. Also, 630 cm⁻¹ band that agree well with the TA + TO combination of a–Si is present. The main change at this annealing is connected with the TO mode. Its evolution with increasing the annealing temperature is presented in Fig. 2, where the sequence of the spectra is the same as in Fig. 1. It can be seen that the spectrum b consists, at least, of two bands; one peak centered at 521 cm⁻¹ and another one, less intensive, but much broader, at about 512 cm⁻¹. These peaks correspond to Si–Si modes in the PS originated from very large crystallites and nanocrystallites respectively [2]. In the spectrum c (Fig. 2) only the broad PS peak is observed. However, after the next RTA procedure, the PS contribution to the spectra is strongly reduced.

The relative amount of c–Si, PS, and the a–Si phases, included in the PS layers may be obtained by analyzing the corresponding Raman bands. The deconvolution of the 450–550 cm⁻¹ spectral region into only two components is not satisfactory, implying the presence of additional bands. The precise deconvolution of the spectra b–e made by fitting with gaussians and lorezians, shows a more or less pronounced shoulder on the low-frequency tail at 480 ± 5 cm⁻¹, which corresponds to the TO band of a–Si. The deconvolution of the spectrum c, which is typical for our PS enriched samples, consists of tree peaks corresponding to c–Si, PS, and a–Si phases (Fig. 3). The a–Si - like character of the b–e spectra indicates rather strong order-disorder effects in the samples. The percentage weight R of different phases, a–Si, PS, and c–Si, have been estimated from the integral spectral intensities of the corresponding characteristic bands.

![Deconvolution of the Raman spectrum of a PS sample annealed at 1000°C for 60 s](image2)

Fig. 2. TO Raman band of annealed PS samples; (a) as-prepared; (b) 1000°C, 15 s; (c) 1000°C, 60 s; (d) 1200°C, 15 s; (e) 1200°C, 60 s.

![Deconvolution of the Raman spectrum of a PS sample](image3)

Fig. 3. Deconvolution of the Raman spectrum of a PS sample annealed at 1000°C for 60 s. The peaks characteristics are given in Table 1.
Table 1. Characteristics of deconvoluted peaks shown in Fig. 3.

<table>
<thead>
<tr>
<th>Peak position [cm(^{-1})]</th>
<th>Bandwidth [cm(^{-1})]</th>
<th>Band profile</th>
<th>Peak area</th>
</tr>
</thead>
<tbody>
<tr>
<td>486.1</td>
<td>73.8</td>
<td>Gaussian</td>
<td>125841</td>
</tr>
<tr>
<td>512.3</td>
<td>26.4</td>
<td>Gaussian</td>
<td>53728</td>
</tr>
<tr>
<td>520.7</td>
<td>3.6</td>
<td>Lorentzian</td>
<td>21031</td>
</tr>
</tbody>
</table>

The sum of the percentage weight for each individual sample is 100%, which means that no additional Raman bands are considered. The dependence of R of the different phases on the annealing temperature is shown in Fig. 4. Its highly non-linear behavior is evident. This behavior is a result of the balance of the processes of amorphpization and recrystallization at the given temperature. For temperatures below 1000°C the amount of the c-Si phase decreases with increase in the annealing temperature and annealing time at the expense of the increase in the PS and a-Si phase. It is important to note that a strong correlation is observed between a-Si and PS phases. This fact is due to decreasing of the feature size of the PS nanocrystallites. At temperatures below 1000°C some part of the crystallites converts into a-Si phase. At temperatures above 1000°C a-Si phase starts to agglomerate, giving addition to the c-Si Raman signal.

![Fig. 4. Relative weight of different phases vs annealing temperature.](image)

This considerations of the non-linear annealing behavior of the PS layers are also supported by the existing theory of the effect of the phonon confinement in the small (< 4 nm) nanocrystallites on the TO silicon Raman band. A typical Raman spectrum taken from high porosity porous silicon sample (50%) is shown in Fig. 5. The shape of Raman spectrum may be explained by phonon confinement in nanocrystallites which are periodically distributed in the depth of the PS layer [10]. The main feature of the PS Raman spectrum is a TO shift towards lower frequencies in comparison to the standard c-Si Raman spectra, and a specific asymmetric broadening. The asymmetric Raman shape may be calculated by the phonon confinement model [9,10]. The best approximation of the spectra could be achieved by Gaussian presentation of the Furrier coefficient $I(0,q)\leq$ of the phonon confinement function for micro-crystalline silicon [9]

$$|c(0,q)|^2 = \exp[-q^2L^2/(4a^2)]$$

where $a$ is the lattice constant of Si, $L$ is the characteristic dimension of the nanocrystallites which form the PS, and $q$ is the wavevector. $L$ is either the diameter of an infinite cylinder or the diameter of spherical particles. Using this model the Raman line shape may be calculated by

$$I_c(\omega) = \frac{q_{max} d\Omega|c(0,q)|^2}{[\omega - \omega(q)]^2 + (\Gamma/2)}$$

The best fitting of the Raman spectrum, presented in Fig. 5, is obtained for dimension of nanocrystallites $L$ of 1.6 nm. The asymmetry of the Raman shape sharply increases for nanocrystallites with dimensions less than 4 nm. The peak position also varies depending on the size of nanocrystallites [7] being 512 cm\(^{-1}\) for $L = 3.6$ nm, and 504 cm\(^{-1}\) for $L = 1.0$ nm.

Using the Raman spectra shown in Fig. 2 we have evaluated the feature size of the nanocrystallites of the considered PS layers. The spec-
trum of the as-prepared PS layers is very close to the Raman spectrum of crystalline silicon, peaking at 521 cm\(^{-1}\). The asymmetry of the spectrum is negligible because the size of the silicon nanocrystallites in the as-prepared PS is greater than 4 nm. The annealing of the samples at temperatures of 1000\(^\circ\)C increases the asymmetry of the Raman PS band. The broadening of the spectra after RTA may be connected with decrease of the nanocrystallites dispersed in the PS matrix. The calculated nanocrystallites feature size of the samples annealed at this temperature for 60 seconds is about 2.5 nm, while 15-second-annealing results in nanocrystallites with feature size of about 3.2 nm. The RTA procedure at 1200\(^\circ\)C for 15 seconds also leads to a decrease of the nanocrystallites size to 3.5 nm, but the longer annealing time of 60 seconds has no remarkable effect on the TO bandwidth.

4. Conclusions

The Raman scattering of the PS layers indicates markedly a non-linear change of the microstructure of the layers after high temperature vacuum annealing. We have found a clear evidence of a–Si phase in our PS samples subjected to RTA. The amount of a-Si phase, being correlated with the volume fraction of PS phase, is maximal in samples annealed at about 1000\(^\circ\)C. This fact supports the conception of highly disordered intergrain tissues, whose volume fraction grows with decreasing grain and broader the size distribution. Applying the phonon confinement model, the size of the nanocrystallites has been found to be about 2.5 nm for samples annealed at 1000\(^\circ\)C.

Acknowledgments

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References