SMALL-ANGLE X-RAY SCATTERING FROM LIGHT EMITTING POROUS SILICON AND SILOXENE

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ABSTRACT

We studied the microstructure of two types of light emitting porous silicon (PS), as-etched and rapid thermal oxidized and of material prepared according to the siloxene recipe by Small-Angle X-Ray Scattering (SAXS). In all three types of samples we found particles with nanometer dimensions. The average particle size in as-etched PS is in good agreement with results achieved by TEM and X-ray diffraction. Shape analysis shows, that the PS skeleton consists of cylindrical shaped particles with an average heigth of 20 Å and a diameter of 40 Å.

1. INTRODUCTION

The discovery of efficient light emission from porous silicon (PS)[1] opens new prospects for Si-based optoelectronics. In relation to this, also siloxene[2], which is known for its light emission for a long time[3], attrackts more attention. At the moment there is a big controversy about the origin of the light emission mechanism in PS. More than 12 hypotheses have been proposed, which can be divided into three groups: 1) hypotheses considering pure quantum size effects[1], 2.) such relating the light emission to the existance of luminous molecular agents (siloxene[2] or hydrides[4]) on the PS internal surface and 3.) hypothesis concidering quantum size particles with surface electronic states[5]. The siloxene molecules $Si_6H_{6-n}O_{3+n}$ are made responsible in ref. 2 for the light emission from PS, but neither the mechanism of light emission[6] nor the microstructure[7] of the siloxene samples are conclusively figured out. The observation of increased PL intensity from PS samples after complete oxidation of their internal surface[8,9], made the siloxene molecule related explanation unlikely. There is amazing similarity between the PL spectra of as-etched and rapid thermal oxidized PS on one side and of of as-etched PS and material prepared according to the siloxene recipe on the other (Fig 1a). The appearent compositional inconsistancy to IR transmission data (fig. 1b) motivated us to compare the microstructure of the three types of samples. For this purpose we started a systematic small-angle X-ray scattering study. With the PS samples we carried out a detailed investigation to get information on the average remnant size, shape and anisotropy of the Si skeleton. These results are compared to recent SAXS[10] observations on similar PS samples.

After shortly summarizing the main aspects of SAS in chapter 2, we describe the samples and the SAS camera in chapter 3. Results are presented and discussed in chapter 4.

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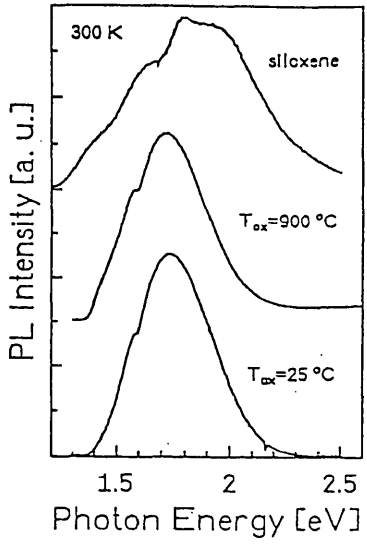


Figure 1a: PL spectra from siloxene, as-etched PS and RTO PS

Figure 1b: IR transmission spectra from a) siloxene, b) as-etched PS and c)RTO PS

2. SAXS

SAXS, the diffuse scattering in the vicinity of the transmitted beam, is sensitive to variations in the scattering-length density, i.e. the electron density, on a length scale of several Å to several 100 Å. Here only the most important aspects and equations shall be introduced. For a more detailed description of the theory and technique of SAXS we refere to[11].

If the sample under consideration consists of isolated, randomly distributed objects (particles) of electron density ρ_P, surrounded by a medium of electron density ρ_M, the scattering amplitude is given by

$$A(q) = (\rho_P - \rho_M) \int_{-\infty}^{+\infty} F(r) e^{iqr} dr$$

$$F(r) = \begin{cases} 0 & r \text{ ends at a point outside the particle} \\ 1 & r \text{ ends at a point inside the particle.} \end{cases} \quad (1)$$

$|k_0 - k| = q = 4\pi/\lambda \sin(\theta/2)$ is the modulus of the scattering vector, θ the scattering angle, λ the wavelength of the X-rays, k_0 and k the wave vectors of the incident and scattered wave, respectively. The observed intensity is proportional to the square of the amplitude of the independently scattering objects:

$$I(q) \sim \sum A(q) \cdot A^*(q) \quad (2)$$

The summation has to be performed over all particles illuminated, parameterized by a distribution of their shapes and sizes. Irrespective of the particles shape the linear dimension may be estimated using Guinier's approximation:

$$I_G(q) = I(q=0) \cdot e^{-q^2/3R_G^2} . \quad (3)$$

R_G is the socalled Guinier radius or radius of gyration. I(0), the intensity scattered in the direction of the incident beam, is given by the electron density contrast

$$I(q=0) = \Delta\rho^2 \cdot V_P^2 \quad (4)$$

with $\Delta\rho = \rho_P - \rho_M$ and V_P volume of the particle.

3. EXPERIMENTAL DETAILS

The PS samples were prepared on p-type (B-doped) silicon (100) wafers (resistivity between 1 Ωcm and 5 Ωcm) by electrochemical etching in 50%HF in C_2H_5OH (volume ratio 1:1) with current densities between 30 mA/cm^2 and 300 mA/cm^2. The thickness of the layer is controlled by the etching time and was 10 μm in our case. Samples stored under ambient conditions are named as-etched PS in this work.

The PS samples with oxidized internal surface[8] have been prepared by rapid thermal oxidation (RTO) in dry oxygen using commercial RTO-apparatus (Heat-Pulse 610). The oxidation temperature varies in the range up to 1200°C, the oxidation time was 30 s.

The siloxene samples fresh (green powder) and annealed (red powder) have been prepared and provided by the Stuttgart group[2].

SAXS measurements were performed at a rotating Mo-anode X-ray generator (Rigaku) working at 10 kW. The Mo-Kα-line (λ=0.71 Å) was selected by a pyrolithic graphite monochromator. A spot of 1x1 mm^2 of the sample was illuminated by a beam with a divergence in direction of q of 2.0 mRad. The scattered radiation was recorded using a linear position-sensitive detector. By changing the sample to detector distance between 310 mm and 900 mm we obtained a q-range of 0.01 Å^{-1} to 0.6 Å^{-1}. The scattering of the PSi layer was obtained by substracting the electronic noise and background scattering in the usual way. Measurements of a reference sample showed no significant scattering from the 0.5 mm thick Si substrat.

4. RESULTS AND DISCUSSION

a. As etched sample

Fig. 2 shows the scattering from a 50 mA/cm^2 (75% porosity) as-etched PS sample. The central part ($q < 0.04$ Å^{-1}) is covered by a beam stop. The general trend of the scattering cur-

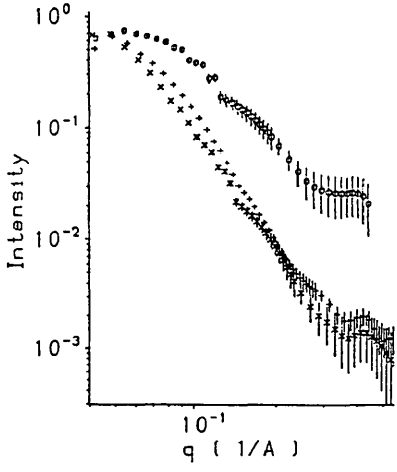


Figure 2: log-log-plott of normalized scattering intensities from PS together for different tilt angles ϕ.
——, +: $\phi = 0^o$;
- - - - -, x: $\phi = 30^o$;
–·–·–, o: $\phi = 70^o$.

part ($q < 0.04$ Å^{-1}) is covered by a beam stop. A fit to the inner part of the scattering curve yields a Guinier radius of 24 Å. The overall shape of I(q) shows that scattering originates from particles with a well defined size (Guinier-region) but no simple shapefunction. In contrast to ref. 10 we find no distinct Porod-region, the asymptotic slope for large q is of the order of 1. To get information about the shape of the particles in the layer, we tilted the sample about two perpendicular axes:

- Tilting about the direction of the incident beam, perpendicular to the surface, resulted in no significant variation in I(q).

- In fig. 2 we also included scattering curves obtained by tilting the sample about an axis lying in the surface, perpendicular to the X-ray beam direction. There is a clearly visible dependence on the tilting angle ϕ, reflecting the different cross sections perpendicular to $\mathbf{k}_o$. In fig. 3 we give the different R_G obtained from fits to the inner part of the scattering curves. A detailed analysis of the entire scattering curves shows that the measured intensities may be attributed to scattering from disc shaped particles with an average diameter of 40 Å and a higth of 20 Å with a size distribution approximated by a gaussian with a width of 5 Å. The "porod"-slope of -1 may be explained by sharp edges and tiny connections between different particles. Due to the complex structure of this highly disordered system, we assume, that more than a qualitative fit can not be expected with a reasonable number of parameters. It should be stressed, that the surface is parallel to the x,y-plane. Additional measurements reaching smaller scattering angles ($q_{min} = 0.01$ Å^{-1}) showed no

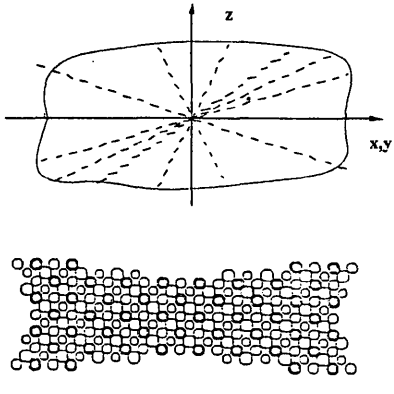


Figure 3: top: Guinier-radii for as-etched PS sample for different tilt angles ϕ. The length of the dashed lines gives the Guinier-radius in the respective direction. The solide line is a guide-to-the-eye.
bottom: Average shape obtained from a fitting procedure. All atoms within 3 (100)-layers are plotted.
In the xy-plane particles are isotropic.

deviation from the extrapolated Guinier behaviour. So we can exclude correlations between different Si particles on a length scale up to 600 Å. Evaluation of the scattered intensity on an absolute scale proved, that the scattering originates from particles of Si or SiO_2 surrounded by vacuum (see eq. (4)).

Our interpretation of the presented data is as follows: The porous layer consists of Si particles with an average size and shape given in fig. 3. The particles are randomly distributed in the layer, connected by 'bridges' of either Si or SiO_x. Comparison with TEM[12] and wide-angle X-ray diffraction yields satisfying agreement. Thus we think our interpretation, attributing the scattering to particles and not to void-volume is correct.

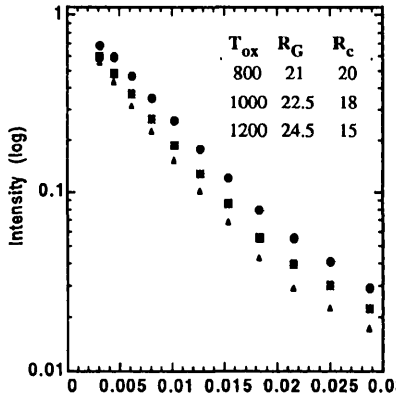
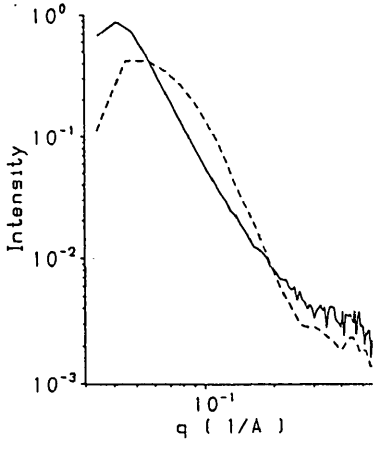


Figure 4: Guinier-plots after RTO. Circles : 800 °C; Squares : 1000 °C; triangles : 1200 °C;
The sample was oriented perpendicular to the x-ray beam. The insert shows the Guinier-radii and calculated c-Si core-radii in Å.

b.) Thermal oxidized samples

To investigate the correlation between the average particle size and the optical properties we measured a series of samples rapidly thermal oxidized at different temperaturesup to 1200 °C. Because of the almost equal average electron-density of c-Si and SiO_2, 0.7 e/Å^3 and 0.66 e/Å^3, respectively, SAXS is not sensitive to changes in the c-Si core of the PS remnants, but to the entire skeleton consisting of Si covered by SiO_2. Our measurements showed, that the size of the remnants grows continuously with oxidation temperature. In figure 4 we present Guinier-plots of a sample oxidized at 800 °C, 1000 °C and 1200 °C; the scattering from the as-etched state is equal to the 800 °C curve. The Guinier-radii are indicated in the figure. Assuming, that the expansion of the Si-Si bond-length under oxidation is the same as at a free surface, we estimated the size of the remaining c-Si core (see fig.4). Thus the blue-shift of the PL spectra[8] is indeed correlated to a decrease of crystalline particle size in PS.



c.) Siloxene

Figure 5: SAS from siloxene (as prepared), compared to SAS from PS.

To learn more about the microscopic structure of siloxene we also measured fresh siloxene powder, as well as samples annealed at 300 °C and 400 °C. Figure 5 shows the scattering from freshly prepared green powder compared to scattering from PS. The evident similarity between both curves indicates a compareable microstructure. The convex curvature of the siloxene curve at low q values reflects a much broader dispersion in particles size. Fitting a size distribution to the measured data, we obtain an average radius of 12Å (spheres) or 7.2 Å (flat cylinders with a heigth to radius ratio of 1:10). Annealing the samples in air resulted in an increase of particle size. Thus we demonstrated that also in siloxene there are quantum size particles which may be reponsible for the light emission. Additional WAXS measurements to claryfy the internal structure and composition of those particles are in progress.

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