X-ray reflectivity investigation of multilayer macroporous silicon structures

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Abstract. In this work, the X-ray reflectivity was used to study the porosity of multilayer macroporous silicon samples obtained under various conditions. The porosity calculation is based on a change in the position of the critical angle of total external reflection resulting from a decrease in the density of the porous silicon layer. Our findings show that the absence of photoluminescence in the samples is due to a porosity of about 30 % in the surface layer. The morphological features were characterized by scanning electron and atomic force microscopy.

1. Introduction
Porous silicon (por-Si) is one of the promising materials for nanophotonic devices [1]. Unlike ordinary crystalline silicon (c-Si), por-Si exhibits intense photoluminescence (PL) in the visible range, as well as a large specific surface area. However, the morphology and optical properties of por-Si can vary significantly depending on the preparation technique. For example, the porosity of por-Si synthesized by top-down electrochemical etching changes from the surface to the bulk of the structure. Since PL is a surface phenomenon, with an excitation depth of about 10-30 nm for por-Si [2], it is more correct to use the surface analysis method to establish relationships between porosity and photoluminescence characteristics. It was found in the work [3] that por-Si with a porosity of at least 50 % exhibits PL properties.

Common porosity measurement techniques such as gravimetric method, gas and liquid porosimetry determine the average porosity of a sample and are, therefore, significantly less accurate. In contrast to the above techniques, X-ray reflectivity (XRR) makes it possible to measure the density and hence the porosity of a surface layer about 10 nm thick [4]. In this paper, we discuss the morphological features, a method for determining surface porosity, and PL properties of multilayer macroporous silicon prepared under different conditions. XRR has been successfully used as a convenient non-destructive tool for measuring the porosity of the surface layer of por-Si.

2. Theory
The complex refractive index for the X-ray radiation can be written as [5]

\[ n = 1 - \delta + i\beta = 1 - \frac{r_e\lambda^2}{2\pi} \rho_e. \]  

(1)
Here, $\delta$ and $\beta$ are the dispersion and absorption components, respectively, while $r_e$ is the classical electron radius, and $\lambda$ is the wavelength of X-ray radiation. The electron density $\rho_e$ and mass density $\rho$ are related by the expression

$$\rho_e = fn_a = (Z + f' + if'') \frac{N_a}{A} \rho, \quad (2)$$

where $f$ denote the atomic scattering factor, $f'$ and $f''$ are the dispersion and absorption corrections, respectively, $n_a$ is the concentration of atoms, $Z$ is the atomic number of the chemical element, $N_a$ is the Avogadro constant, and $A$ is the atomic mass.

If we insert $\rho$ into equation (1), we then obtain an expression for the real and imaginary parts of the refractive index

$$\delta = \frac{r_e \lambda^2}{2\pi} \frac{N_a}{A} (Z + f') \rho, \quad \beta = \frac{r_e \lambda^2}{2\pi} \frac{N_a}{A} f'' \rho. \quad (3)$$

In the small-angle approximation and far away from absorption edges [6], the critical angle of total external reflection can be determined according to Snell’s law:

$$\theta_c^2 \approx 2\delta = \frac{r_e \lambda^2}{2\pi} (Z + f') \frac{N_a}{A} \rho. \quad (4)$$

Therefore, knowing the critical angles of por-Si ($\theta_{c-PS}$) and silicon substrate ($\theta_{c-Si}$) allows us to estimate the surface porosity from the relation [7]

$$P(\%) = \left[1 - \left(\frac{\theta_{c-PS}}{\theta_{c-Si}}\right)^2\right] \times 100. \quad (5)$$

3. Experimental methods

Multilayer macroporous silicon structures were formed on the surface of phosphorus-doped crystalline silicon $c$-Si(100) substrates. The one- and two-stage electrochemical etching was carried out in a solution of hydrofluoric acid and dimethylformamide with the addition of hydrogen peroxide and sulfuric acid. The anodizing current density was changed stepwise during the two-stage etching process [cf. Table 1].

The morphology and structure of the specimens were examined by scanning electron (SEM) and atomic force microscopy (AFM) using a JEOL JSM-6380 LV and NT-MDT SOLVER P47-PRO instruments, respectively. A ARL X'TRA diffractometer with a CuK$_\alpha$ radiation, Bragg-Brentano geometry, and three resolution-defining slits was employed for scanning the XRR profiles. The PL spectra were recorded with an Ocean Optics USB4000-VIS-NIR fiber optic spectrometer; a laser diode with a radiation wavelength of 405 nm was used [8].

Table 1. Por-Si sample production conditions (etching mode, anodizing current density $J$, time $t$), thickness of the porous layer $l$, average Si particle size $d$, and surface roughness $\sigma$ obtained from SEM and AFM data; porosity of the surface layer $P$ was obtained by XRR measurements.

| Sample | Etching mode | $J$, mA/cm$^2$ | $t$, min | $l$, $\mu$m | $d$, nm | $\sigma$, nm | $P$, % |
|--------|--------------|----------------|---------|-------------|--------|-------------|--------|
| 1      | one-stage    | 50             | 10      | 25          | 555    | 142         | 29     |
| 2      | two-stage    | 50/15          | 5/5     | 15          | 423    | 140         | 27     |
Figure 1. Histograms of silicon particle size distribution on the surface of por-Si formed under different conditions. The corresponding insets show AFM topographic images 5×5 µm in size.

4. Results and discussion

AFM topographic images and histograms of the silicon particle size distribution of por-Si samples are shown in figure 1. The NOVA software was used for image analysis. Both samples have a porous surface and the same roughness values. However, the sample 1 obtained in a one-stage etching mode has a slightly larger average Si particle size [cf. Table 1]. In figure 2 we have gathered the cross-section SEM images of the macroporous Si samples. The SEM data show

Figure 2. Cross-section SEM images of the por-Si samples.

Figure 3. XRR profiles of the por-Si samples, mesoporous Si [9], and c-Si substrate. The dashed lines indicate the positions of the critical angles.
that the porous layer thickens with increasing current density. The average diameter of the dominant pore type in the samples is 150-200 nm. Our detailed observations of the cross-section SEM images allow us to conclude that the location of the boundary between the layers of the structure is determined by the primary mode of electrochemical etching.

The measured XRR data for the por-Si samples and c-Si substrate are summarized graphically in figure 3. The mesoporous Si XRR profile is also shown for comparison [9]. For incident angles \( \theta \leq \theta_c \) total external reflection occurs and all incoming X-rays are reflected from the surface. The intensity of the X-ray reflectivity curves drops dramatically after passing the critical angle \( \theta > \theta_c \). For reference, the XRR profile of a c-Si substrate was investigated. The critical angle of the c-Si substrate at which the reflected intensity is reduced by half [10] is 0.223° and is close to the theoretical value \( (\theta_{c-Si} \approx 0.22° \text{ for } \lambda = 1.54 \text{ Å}) \) [7]. The porosity of the macroporous silicon samples is determined by the equation (5) [cf. Table 1].

No photoluminescence was observed from the macroporous Si samples with \( P \) of less than 29 % in contrast to mesoporous Si \( (P=79 \%) \). The results are in good agreement with the literature [2, 3, 8], according to which only por-Si with \( P \) above 50 % exhibits photoluminescent properties.

5. Conclusion
In this work we have studied the multilayer macroporous silicon structures prepared by an electrochemical etching method. The surface porosity of por-Si samples was determined using XRR measurements. It was demonstrated that the macroporous Si samples with \( P \) of less than 30 % do not exhibit photoluminescence. These results showed that XRR can be successfully used as a non-destructive method for investigating the porosity of the surface layer of nanophotonics devices based on por-Si.

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