Evolution of porous silicon crystal structure during storage in ambient air

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Abstract. Both double- and triple- crystal X-ray diffraction techniques (X-ray DCD and TCD techniques) together with transmission electron microscopy (TEM) were employed for the investigation of structural changes in porous silicon (PS) layers during prolonged periods (up to 6800 hours) of their storage in ambient air. Apart from the Bragg reflection from the Si substrate, the diffraction pattern contains an additional maximum caused by the presence of the PS layer with an increased lattice parameter. The position of this peak shifts to smaller Bragg angles and its intensity decreases as the time of storage in air increases. In addition, the profiles of such peaks become clearly asymmetric. In this case, Gaussian curves were used to reach a fit to the experimental X-ray rocking curves. All samples were biaxially bent due to compressive stresses that arise as soon as 10 min after electrochemical process. The values of lattice strains along the surface normal ($\Delta d/d_\perp$) and lateral deformation ($\Delta d/d_\parallel$) were estimated to be $\sim +10^{-3}$, $\sim -10^{-5}$ respectively. The analysis of diffraction curve evolution shows a gradual destruction of the crystal lattice caused by the air oxidation process.

1. Introduction
It is well known that as-prepared porous silicon (PS) reacts strongly with oxygen in ambient air and both the structural and optoelectronic properties can continuously evolve with the storage time [1]. Therefore, it is important to know what happens with the crystal structure of PS layers during so called “ageing”. In [2] it was concluded that the lattice parameter of a porous layer along the normal to the surface is larger than that in bulk Si, i.e. PS experiences some lattice expansion. That gives rise to sample bending caused by biaxial compressive stresses. The goal of this work is to present new data that could concern the changes in the structure of PS layers stored for prolonged periods of time. In this communication, the changes in structural characteristics and the level of PS layer deformation were investigated by double and triple- crystal X-ray diffraction (DCD, TCD) techniques and TEM to elucidate their dependence on the anodization regimes and time of ageing in air.

2. Experimental details
PS layers were formed by the electrochemical etching of boron-doped (p-type) silicon wafers (orientation <100>, resistivity: 10 $\Omega$cm) under natural lighting. The area exposed to the electrochemical etching solution was about 10 mm in diameter. The electrolyte consisted of 1:3=HF(48%):H$_2$O mixture. Several micrometer thick porous layers numbered as 1, 2, 3 (see Table 1) were prepared. These samples are characterized by equal total electric charge passing through the
electrolytic cell. Another series of samples studied (3, 4, 5) had equal etch times (see Table 1). After the formation of PS layers the samples were rinsed in de-ionized water and dried at 60°C for 5 min.

For the X-ray DCD and TCD techniques symmetric (004) and asymmetric (224) Bragg geometries of X-ray intensity measurements were taken using CuKα radiation. All X-ray measurements were carried out on the central exposed area (±4mm) which had a homogeneous porous layer. The total storage time was more than 8 months, and each specimen had been measured at different times, starting from 10 min immediately after anodic etching. The integral specimen porosity was determined by the measurement of photoelectrical absorption coefficient of the X-ray beam passing through the PS layer on Si. The microstructure of PS layers was examined by plan view and cross-sectional transmission electron microscopy (XTEM).

3. Results

3.1. Parameters of porous layers: thickness and porosity

The calculated values of porosity and the thicknesses of PS layers measured by SEM on a cleaved sample surface are listed in Table 1.

| sample # | current density mA/cm² | etching time min | thickness PS µm | porosity % |
|----------|------------------------|-----------------|-----------------|------------|
| 1        | 100                    | 1               | 3.7             | 65         |
| 2        | 50                     | 2               | 4.3             | 60         |
| 3        | 10                     | 10              | 7.9             | 56         |
| 4        | 50                     | 10              | 23              | 64         |
| 5        | 100                    | 10              | 47              | 68         |

Table 1. Regimes of anodization and parameters of PS layers

In Table 1 it can be seen that the porosity of samples numbered 1-3 decreases as the current density reduces. At the same time, the PS layer thickness increases with longer etching time. The increase in PS layer thickness results from the higher value of charge crossing the electrochemical cell. These dependences are in agreement with previous work [3].

3.2. Stresses and strain in PS layers

Immediately after preparation, all PS samples were bent with positive curvature. The macro curvature of samples was measured by the angular shift of (004) Bragg reflection from the Si substrate while scanning the specimen in the X-ray beam. It was observed that for all stages of ageing in ambient air the bending, caused by biaxial compressive stresses σi in PS leading to lattice expansion along [100], was homogeneous (spherical) and positive. The dependence of stresses calculated according to Stoney’s formula during the storage times is seen in Fig. 1. For all samples, their curvature increases with time. Sample 1 shows the largest rate of change in biaxial compressive stress along specimen surface σi which occurred during the first week of storage. This sample has a high value of porosity and is the thinnest PS layer; the rate of change decreases almost to zero after 1.5 months. This observation indicates a gradual distortion of the PS skeleton and a change in the elastic constant of PS.

3.3. Structural changes in PS during its “ageing” in ambient air

In order to understand the behaviour of compressive stresses in PS, its crystal structure was investigated by X-ray DCD and TCD techniques. For all initial PS samples, the first DCD curves both in symmetric (004) and in asymmetric Bragg geometry (224) with grazing incidence and exit angles show a well defined PS peak that lies at smaller Bragg angles than that of the Si substrate (Δθ~400°).
This indicate a lattice expansion in the direction perpendicular to sample surface. In the TCD measurements, an anisotropy of scattering from the PS layer was discovered: FWHM rocking curve for the \(\theta\)-scan \((w_{\text{PSi}} \approx 10-15''\), due to micro disorientation) was 3-4 times less than that for the \(\theta\)-2\(\theta\) scan \((w_{(\theta-2\theta)} \approx \text{up to } 50''\), due to dilatation). This result shows that strain (variations in lattice plane spacing along [100]) is the main reason for broadening of the rocking curve in the initial PS layer. It should be noted that the \(\Delta \theta\) value (peak shifting) increases with ageing time. Using Bragg’s formula, one can calculate the positive deformation \(\Delta d/d\perp\) in the PS layer along [100]. For all samples, the rocking curve parameter \(w_{\text{PSi}}\) increases with duration of air storage, and the DCD rocking curve becomes significantly asymmetric. This asymmetry is related to the appearance of additional PS reflection peaks at smaller Bragg angles. Similar rocking curve behaviour is observed for the TCD \((\theta\text{-}2\theta)\) rocking curves for all PS samples. For example, the changes in \(\Delta \theta\), \(w_{(\theta-2\theta)}\), \(\sigma_{\parallel}\) and \((\Delta d/d)\perp\) values for sample 4 are listed in Table 2. As mentioned, the DCD rocking curves as well as TCD ones are gradually transformed to asymmetric profiles, and by using a Gaussian fit the experimental asymmetric rocking curve can be decomposed into several sub-peaks. The TCD \((\theta\text{-}2\theta)\) (004) rocking curve for sample 3 is shown in Fig. 2 as an example. The Gaussian fit makes it possible to reveal three sub-peaks which correspond to different PS layers. Similar rocking curves were observed in [4] for PS layer prepared by the stain-etch technique. The different parts of the PS layer after its air storage for 2660 hours can be seen in the TEM image of Fig. 3. The electron diffraction pattern (inset) shows that the Si skeleton retains its crystal structure with <110> orientation. The weak diffuse rings in Fig. 3 confirm the presence of an amorphous phase which is a result of the PS layer oxidation.

A typical PS structure after prolonged storage in air is presented in Fig. 4. This sample shows a high concentration of small single pores and their agglomeration. The size range of single pores was estimated to be 3 - 8 nm and the Si crystallites were measured to be 3 - 10 nm. As seen in Fig. 4 (inset), the area occupied by the Si crystallites (dark contrast) is significantly less than that of the silicon oxide (grey contrast). This is a result of the PS degradation in air, but nevertheless the Si crystallites keep their initial crystal orientation (Fig. 3, inset).

Measurement of the lateral deformation in PS \((\Delta d/d)_{\parallel}\), was performed using asymmetrical (224) DCD rocking curves, recorded at both grazing incidence and exit geometries. This allows us to calculate the difference between the inclination angles of (112) lattice planes in PS and Si [5]. Thus, the lateral deformation value \((\Delta d/d)_{\parallel}\) was estimated to be \(-10^{-5}\).
**4. Conclusion**
Gradual structure changes in PS during prolonged period of ageing in ambient air (up to 6800 h) have been studied by X-ray techniques. All specimens suffered biaxial compression stresses 10 min after their fabrication. The lattice strains along the surface normal are positive and equal to ~ +10^{-3}, two orders of magnitude larger than the lateral strains of ~10^{-5}, i.e. the relaxation of the PS skeleton is insignificant. The analysis of changes in X-ray rocking curves shows a step-by-step distortion of the crystalline PS skeleton by oxidation with an increase in strain and disorientation of nanocrystallites in it. In thick PS layers, aged up to 8 months, two types of crystallite sizes were revealed (~5 nm and ~0.15 µm) on the basis of the DCD rocking curve analysis. The existence of a PS multilayer structure exhibited by TEM agrees with the analysis of the X-ray TCD (\(\theta-2\theta\)) asymmetric rocking curves.

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