

Detection of different states of water and oxide layer in porous silicon by IR spectroscopy

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Different states of water and oxide layer in porous silicon (PS) have been studied by IR spectroscopy method. The water states have been shown to depend on contact conditions between PS and condensed or vaporous forms of water and to determine all the variety of oxidation scenarios. Weakly- and strongly-bonded water states are characterized by different frequencies of stretching bands ν_{OH} . Fine structure of absorption bands of oxygen-silicon complexes ($Si-O-Si$, $SiSi_xO_{4-x}$) has been observed in the IR spectra. We associate it with fractal structure for thin oxide layers. Transition of fractal structure into nearly bulk SiO_2 structure (where LO-TO splitting is observed) with oxide layer thickness growth is considered. The oxide layer states are characterised by the intensity ratio of stretching to deformation bands for considered silicon-oxygen complexes.

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1 Introduction

Porous silicon (PS) is a good model object for studying new fundamental laws in the field of nanophysics, catalytic processes, oxidation and the other chemical transformations in a silicon surface layer. The problem of monocrystalline and porous silicon interaction with oxygen and water is of great importance for many applications. However, the mechanisms of such interaction at atomic scale have not been sufficiently studied yet. Unlike the other physicochemical and thermodynamic methods, spectral study provides information on quantum states and electronic density distribution.

Water takes an active part in PS oxidation, which is important for temporal PS characteristics stability [1, 2]. The environment where PS oxidation takes place has great impact on this process [1–3]. This paper reports combined study of the different water states and oxide structure in PS samples subjected to different treatments.

2 Experimental

PS samples were prepared by anodic etching of $10 \Omega \cdot \text{cm}$ (111) boron doped *p*-Si wafers in solution (48 wt.%) $\text{HF}:\text{C}_2\text{H}_5\text{OH}$ (1:1) at $10 \text{ mA}/\text{cm}^2$ for 5 min. As-prepared (S_0) sample was studied as well as the samples subjected to different treatments at room temperature as follows. Samples S_1^{vap} and S_2^{vap} were exposed to aqueous vapor for 6 and 28 days, respectively. Aging in air was carried out for samples S_1^{air} (2 weeks) and S_2^{air} (7 years). Samples $S_1^{\text{H}_2\text{O}}$, $S_2^{\text{H}_2\text{O}}$ and $S_3^{\text{H}_2\text{O}}$ were immersed in distilled H_2O for 70 min, 20 hours and 3 days, respectively. The other sample $S^{\text{D}_2\text{O}}$ was treated in D_2O during 2 days. IR absorption spectra were obtained at room temperature using a Specord 80M two-beam spectrometer. The bands

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structure of the spectra of the samples discussed below is not related to possible interference in the thin films of porous or monocrystalline silicon.

3 Results and discussion

3.1 Different states of OH groups and molecular water in porous silicon The presence of water in PS has been well detected in many studies by the stretching absorption bands [2, 3], however the possibility of existence of different water states has not been discussed yet. The stretching bands ν_{OH} for the samples exposed to aqueous vapor are shown in Fig. 1a, where tendency of both intensity growth and peak shift of O-H stretching band into low-frequency region with PS oxidation progress can be observed.

Having taken into consideration both the spectral investigations and the possibility of the dissociation processes, we believe that water can be present in PS in the form of condensed phase in pores, hydroxyl groups and nearly isolated molecules. Absorption bands in the region of symmetric and asymmetric vibrations of isolated H_2O molecules [4] are shown in Fig. 1b. The IR absorption is lower for the high-frequency component here in contrast to molecular water in such solvents as CCl_4 and CS_2 . Maximum intensity of the 3890 cm^{-1} band, which we assign to the combination tone ($\nu_{OH} + \nu_{Si}$) of O-H vibrations and crystalline silicon optical phonons (520 cm^{-1}), is observed for the sample S_2^{vap} treated in vapour for long time. The presence of such band indicates the possibility of water penetration of silicon crystallites.

The ν_{OH} stretching band profile of the as-prepared sample and the samples oxidized in air and treated in water are shown in Fig. 2. Distinct narrow line at 3749 cm^{-1} of isolated hydroxyl groups O-H is not observed for PS, in contrast to well-studied dispersed silica. The presence of wide vibrational bands of water in the region $2800\text{--}3600\text{ cm}^{-1}$ of stretching mode ν_{OH} as well as the changes in their peak location and shape indicate the variations in both hydrogen bonds (HB) energy and water states in PS [5]. At the initial stages of bonding between water and PS the ν_{OH} band is observed in the higher frequency region compared to the band of bulk distilled water (3390 cm^{-1}) in the samples treated in water ($S_2^{H_2O}$, curve 2 in Fig. 2) and aqueous vapour (S_1^{vap} , curve 1 in Fig. 1a). This indicates the lower HB energy. On the contrary, the ν_{OH} bands in the spectra of as-prepared (S_0) and oxidized (S_2^{air} , $S_3^{H_2O}$, $S_2^{D_2O}$) samples (curves 3–6 in Fig. 2) are shifted into low-frequency region, which points at the greater HB energy.

Existence of at least four discrete water states in PS with typical vibrational bands shown in Fig. 3 has been established using difference spectra (for example, state I is obtained using curves 2 and dotted line in Fig. 2). Stretching band of weakly bonded form of water is located around 3700 cm^{-1} . Absorption band of condensed water lies around 3400 cm^{-1} , while the peaks of two more strongly bonded forms of water are shifted to 2900 and 2300 cm^{-1} .

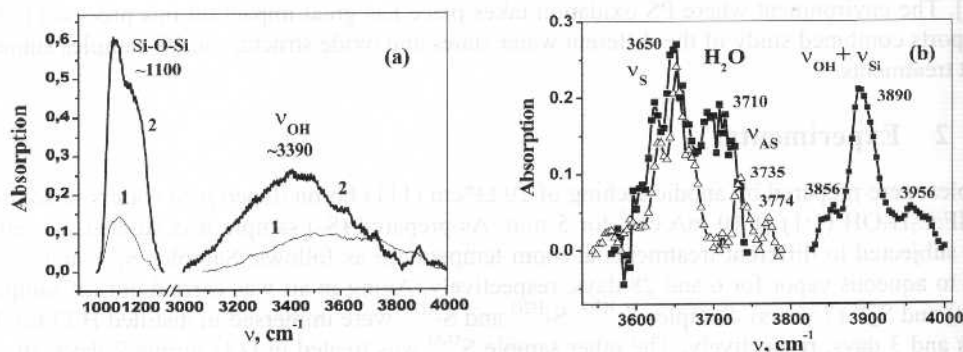


Fig. 1 IR absorption spectra of the samples exposed to saturated aqueous vapour: 1 - weakly oxidized S_1^{vap} and 2 - highly oxidized S_2^{vap} (a). The vibrational modes of molecular water structures in PS oxidized in air (S_2^{air} , triangles) and aqueous vapour (S_2^{vap} , squares), and combination band obtained from normalized spectra are shown (b).

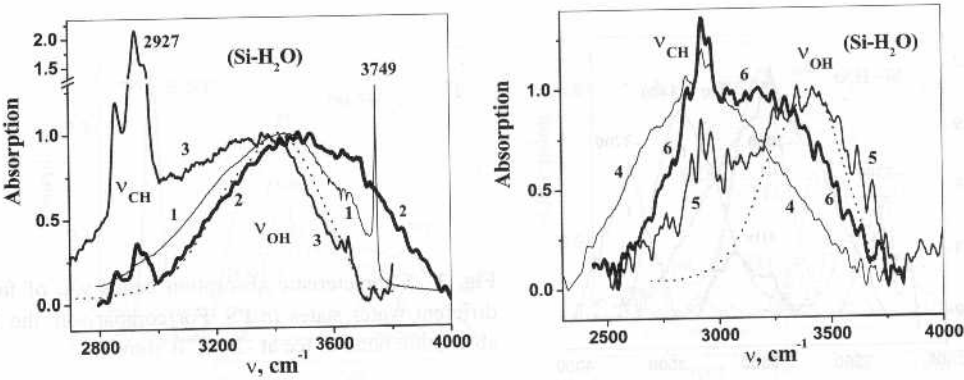


Fig. 2 Comparison of normalized water stretching bands of the samples: 1 - the water in aerosil, 2 - $S_2^{H_2O}$, 3 - S_2^{air} , 4 - S_0 , 5 - $S_3^{H_2O}$ and 6 - S^{D_2O} . For comparison, IR absorption band of distilled water is shown by dotted line.

Comparison of the results obtained by vibrational spectroscopy and gravimetry methods has shown that fundamental absorption band ν_{OH} of water in porous medium is 10-200 times weaker than that of pure distilled water.

3.2 Scenarios of porous silicon oxidation and fractal structure of oxide layer As the samples oxidized, intensity of stretching (1100 cm^{-1} region) and deformation (460 cm^{-1} region) vibration bands of Si-O-Si bonds and SiO_4 tetrahedrons [1] grew differently for the samples subjected to different treatments. We studied the behavior of stretching to deformation absorption band ratio ζ and found that it depends on the duration and the type of PS treatment (Table 1). The value of ζ for the samples aged in air is close to the value of $\zeta_v = 2,62$ for the bulk fused quartz [6]. Higher or lower ζ were found for the samples oxidized in the other media. Moreover, increase of ζ corresponds to the increase in duration of treatment. Considerable variations in the absorption band ratio indicate the difference in the ways of oxidation, probably related to the water states.

Table 1 Absorption values at the maxima of IR bands of stretching (A_{str}) and deformation (A_{def}) vibrational modes of Si-O-Si bonds for the PS samples and their ratio ζ .

	S_0	S_1^{air}	S_2^{air}	$S_1^{H_2O}$	$S_3^{H_2O}$	S^{D_2O}	S_1^{vap}	S_2^{vap}
A_{str}	0.185	0.303	1.618	0.135	0.185	0.331	0.210	0.607
A_{def}	0.085	0.109	0.593	0.079	0.09	0.104	0.119	0.091
ζ	2.18	2.78	2.73	1.71	2.06	3.18	1.78	6.67

Different fine structure (FS) of the bands in the spectra of the samples oxidized in different ways can probably indicate the existence of different states of the oxide layer in PS (Fig. 4). For example, 3 components of the FS of the deformation band and 5 components of the stretching band are observed for samples treated in H_2O ($S_3^{H_2O}$) and aqueous vapour (S_1^{vap}). Besides, the side components for the sample $S_3^{H_2O}$ are located farther from the central one.

For thin oxide layers, we associate the observed fine structure of Si-O-Si bands with fractal structure [7], although longitudinal-transverse (LO-TO) splitting [8] and non-stoichiometry of the oxide layer (low-frequency wing [9]) may contribute to it as well. A previous study [7] demonstrates the possibility of spectrum transformation (splitting, widening and shift) in case individual particles aggregate into fractal clusters. In this paper fractal structure is interpreted as dendrite-like bonded structure consisting of atoms and molecules, which differs from the rest of the material by composition and type of chemical bonds.

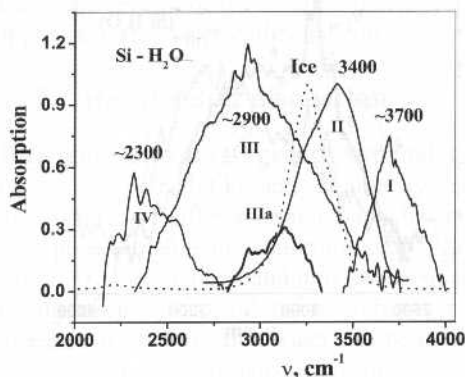


Fig. 3 Characteristic absorption bands ν_{OH} of four different water states in PS. For comparison, the IR absorption band of ice at $-24\text{ }^{\circ}\text{C}$ is shown.

Fractal structure can be formed by the same type $\text{Si}(\text{Si}_x\text{O}_{4-x})$, $x = 0-4$ atomic groups. FS of the bands is caused by different orientation of these groups as well as by different energy of dipole-dipole interaction between them. The central, often most intense component, is determined by collective excitations delocalized on many Si-O-Si bonds, which form quite a dense network. The side components represent more localized excitations on less collectivized bond subsystem.

The vibration bands in the region of Si-O-Si modes have been fitted with Gauss components as shown in Figs. 4b, 5. A good correspondence between second derivatives of recorded and calculated spectra proves the correctness of such fitting. FS of Si-O-Si stretching band has been observed for the sample briefly aged in air (Fig. 5a). Abnormal widening of this band is associated with emergence of vibrational states at the Brillouin zone edge ($1245-1350\text{ cm}^{-1}$). The longitudinal-transverse (LO-TO) splitting for SiO_4 tetrahedron stretching modes emerges with the increase in oxide layer thickness. The LO-TO structure for highly oxidized sample S_2^{air} is shown in Fig 5b. IR absorption in LO band region is higher compared to bulk SiO_2 sample. This has been associated with disordered oxide structure [8]. The existence of several bands of TO, LO components and discrete values of LO-TO splitting indicate spatial inhomogeneity of the oxide layer, which supplements the fractal concept of PS oxidation.

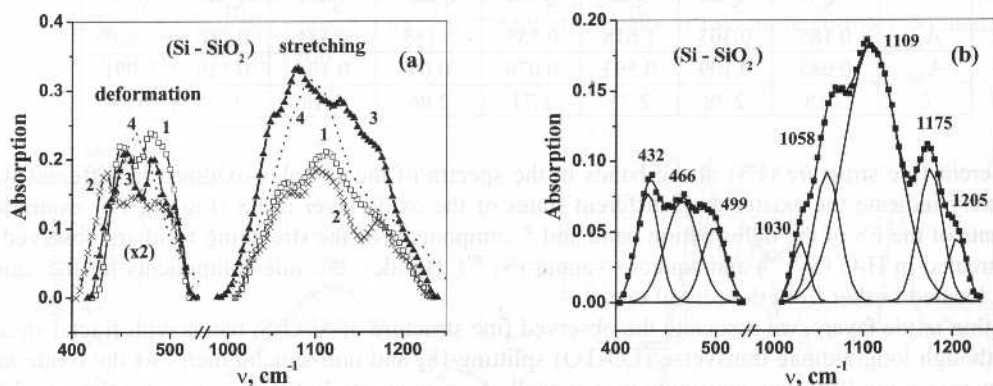


Fig. 4 IR absorption spectra in the region of deformation and stretching Si-O-Si modes for PS samples: 1 - exposed to aqueous vapor (S_1^{vap}), 2 - treated in H_2O ($\text{S}_3^{\text{H}_2\text{O}}$) and 3 - treated D_2O ($\text{S}_3^{\text{D}_2\text{O}}$). Normalized absorption bands for bulk fused quartz (4) are shown by dotted line (a). Fine structure of absorption bands for sample $\text{S}_3^{\text{H}_2\text{O}}$ (b).

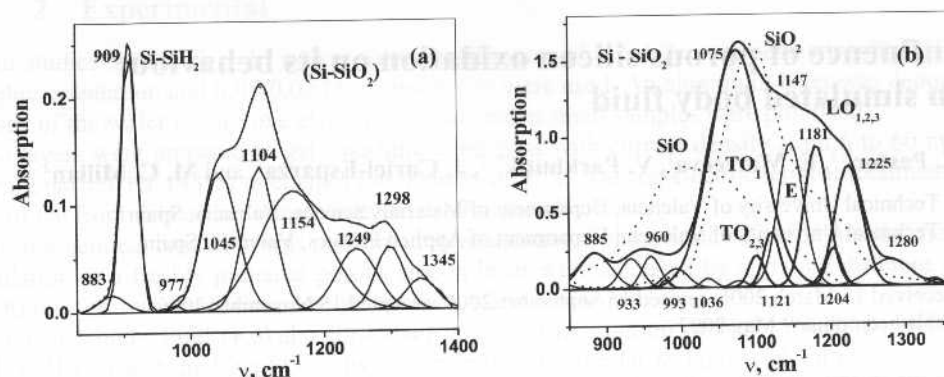


Fig. 5 Fractal structure of vibrational states at Brillouin zone centre and Brillouin zone edge for the sample S_1^{air} (a), as well as three TO and LO components for the sample S_2^{air} (b). For comparison, Fig. 5b shows normalized absorption bands of bulk SiO_2 and SiO (dotted line).

LO-TO splitting is observed in the spectra of the samples oxidized to a great extent in different media. The thickest and the most perfect oxide layer is formed in the samples aged in air for a long time. The samples treated in water contain the least of oxide.

4 Conclusion

IR spectroscopy enables studying oxide layer state on PS surface, including registration of possible oxide non-stoichiometry, as well as identification of different states of adsorbed water. Absorption bands of four discrete water states in PS have been found in difference spectra by vibrational spectroscopy method. They differ by hydrogen bonds energy. Quantity and state of water in PS depends on both environment and exposure time and affects the oxidation process. Existence of oxide layer fractal structure has been shown. Fractal structure variations during PS oxidation under different conditions as well as transformation of fractal structure into nearly bulk SiO_2 structure with increase in oxide layer thickness have been observed.

This paper demonstrates the features of PS as a model object for studying the processes occurring on the surface of a nanoscale material.

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