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## Spectromicroscopic Studies of Porous Silicon Oxide on Silicon Using Synchrotron Radiation

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### Abstract

This work is dedicated to microscopic synchrotron studies of the morphology, atomic, and electronic structure of an array of submicron-sized pores in a SiO<sub>2</sub> layer on silicon formed with the use of ion-track technology in combination with chemical etching after irradiation. The research method was photoemission electron microscopy using high-intensity synchrotron radiation. The method was used in two modes. The use of chemically selective electron microscopy allowed obtaining morphological information about the studied array of pores. The X-ray spectroscopy mode of the synchrotron radiation of X-rays absorption near-edge fine structure spectroscopy allowed us to obtain information about the specificity of the local surrounding of the given atoms from microscopic regions of nanometer and submicron areas of the obtained microscopic images. The pores had rather sharp boundaries, without a transition layer. The bottom of the pores was a substrate - a crystalline silicon wafer covered with a natural 2-3 nm thick oxide layer. Ion irradiation and chemical etching did not significantly affect the structural and phase characteristics of the porous silicon oxide matrix. There was no significant disordering in the silicon atoms available at the bottom of individual pores. There was no technological contamination. The efficiency of using ion-track technology in combination with chemical etching after irradiation for the formation of isolated pores arrays with close submicron range sizes was shown. The obtained results demonstrated the efficiency of the photoemission electron microscopy method using high-intensity synchrotron radiation for the high accuracy microscopic scale study of a wide range of objects with the composite structure-phase nature of the surface.

**Keywords:** silicon dioxide, submicron pores, atomic and electronic structure, synchrotron radiation, XANES, Photoemission Electron Microscopy, local atomic surrounding.

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## 1. Introduction

Arrays of porous silicon dioxide on silicon can be used as effective matrices in a variety of technological solutions [1–2]. The semiconductor substrate allows the effective control of the porous layer formation itself and various composite structures based on it [3–4]. Such structures (templates) can be used in a wide range of areas from semiconductor magnetic composite devices [5] to optical sensors based on surface-enhanced Raman scattering [6]. Chemical and electrochemical processes of nanostructures synthesis in separate pores and the formation of self-organized particles in the pores require careful selection of the method for the formation of the porous layer and the control of its composition and structure. The ion-track technology of swift heavy ions in combination with subsequent chemical etching is a promising technology for the formation of a porous template [4–6]. Being relatively simple, this method has a number of advantages, for example, the ability to effectively control the density and geometric parameters of pores according to studies [1–6].

The method of scanning electron microscopy is particularly effective in the primary morphology diagnostic of the formed pores arrays. This method has previously been repeatedly demonstrated with high resolution, including for template structures [7]. However, this method is not always sensitive to the phase composition and does not allow the effective study of the structure and the specifics of the local atomic surrounding specificity in the porous layer. Such studies are important considering the developed surface which is accessible to external influences and may also be subjected to internal reconstruction. X-ray and electron spectroscopy is an indispensable tool for accurate and qualitative studies of the physical and chemical state of a porous layer as a morphologically complex object with a pronounced surface and potentially numerous boundaries [8–11]. The use of synchrotron radiation sources in the X-ray spectral range allows increasing the accuracy of experiments for objects of small sizes and low intensities of a useful signal [8, 10]. X-ray photoelectron spectroscopy [10] and XANES – X-ray absorption near edge structure [8–11] are in demand for studying the atomic and electronic structure

of developed surfaces and accessible interfaces between micro- and nanostructured objects.

X-ray and electron spectroscopy experiments are usually conducted independently of microscopic ones, which often complicates the research. In addition, despite the sensitivity to the local atomic surrounding, the area of the surface from which the spectrum is recorded is, at best, hundreds of micrometres [12]. The real microscopic approach in terms of obtaining information about the morphology of small studied objects and their physical and chemical state as well as their atomic and electronic structure in a “micropoint” is implemented in spectromicroscopy methods [13, 14]. Such methods include photoemission electron microscopy (PEEM – PhotoEmission Electron Microscopy), including PEEM with the use of high intensity synchrotron (undulator) radiation in the soft X-ray range. Earlier, we demonstrated the effectiveness of using the PEEM method in the XANES spectrum registration mode for effective studies of the morphology, specificity of the atomic and electronic structure, composition and structure of objects of micron, submicron, and nanometer sizes in a single experiment [14–17]. However, the studies were conducted for structures mainly consisting of different sorts of atoms, e.g. nickel structures in porous silicon dioxide matrix with etched tracks [16, 17].

This work presents the results of PEEM studies of the morphology, atomic and electronic structure of an array of submicron pores in a SiO<sub>2</sub> layer on silicon by synchrotron photoemission electron microscopy. The array of submicron pores was obtained using ion-track technology and subsequent chemical etching.

## 2. Experimental

SiO<sub>2</sub> layer with the thickness ~ 500 nm was obtained by thermal oxidation of c-Si crystalline silicon wafers of the KDB 40 (100) type (100) in an O<sub>2</sub> atmosphere (purity 99.9999 vol. %, 1100 °C, 10 hours). The formation of swift heavy ion tracks in the SiO<sub>2</sub> dielectric layer on Si was carried out at the Hahn-Meitner Institute (Berlin, Germany) accelerator by irradiating the silicon dioxide layer with 197Au<sup>+</sup> ions with an energy of 350 MeV. For the formation of pores, latent tracks formed after irradiation of a silicon oxide layer were etched at 20 °C room temperature in a diluted aqueous

solution of hydrofluoric acid (the mass fraction of the acid was 1.35 %). The ion fluence during irradiation was  $1 \cdot 10^8 \text{ cm}^{-2}$ , and the etching time was 80 minutes.

In this work the por-SiO<sub>2</sub>/Si structures were studied by the PEEM method using high-intensity synchrotron (undulator) radiation from the BESSY II Helmholtz-Zentrum-Berlin storage ring (Berlin, Germany). For PEEM studies, a UE56-2 PGM2 radiation beamline was used, and the SurICat beamline was additionally used for XANES measurements of reference spectra in the “standard” (non-microscopic) mode. PEEM studies were performed using the Scienta Omicron Focus PEEM microscope. PEEM data were obtained by recording the electronic yield in the region of silicon L<sub>2,3</sub> X-ray absorption near edge structure (XANES Si L<sub>2,3</sub>). The measurements were carried out at room temperature and the instrumental broadening upon recording the XANES spectra was ~ 0.1 eV.

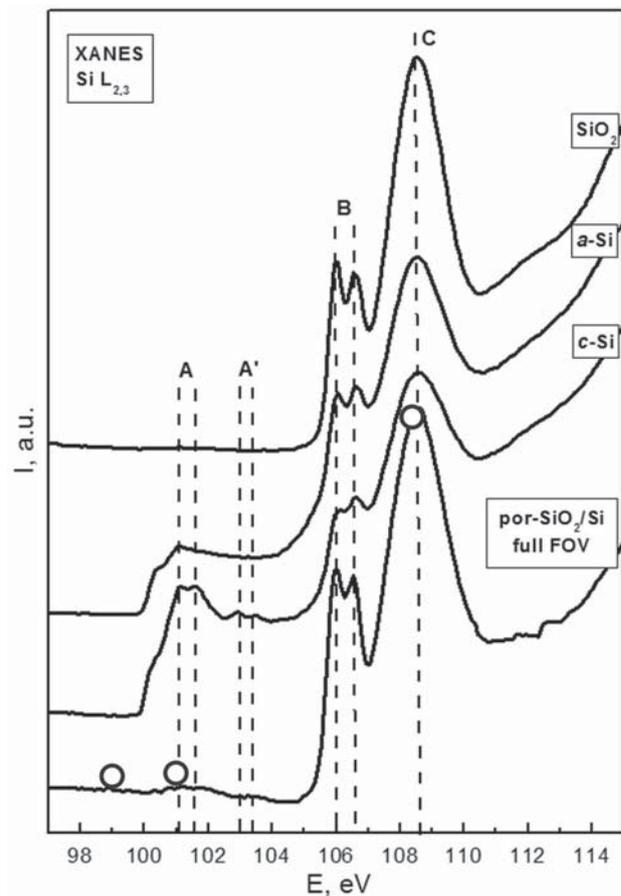
XANES spectra in the “standard” mode were registered using sample compensation (drain) current technique in the mode of the total electron yield (TEY) detection. The vacuum in the working chambers of all synchrotron analytical stations was  $10^{-10}$  Torr. When registering Si L<sub>2,3</sub> XANES spectra, the analysis depth was about 5 nm according to [18]. Standard procedures for calibration and normalization of all spectra obtained using a pure gold foil signal were used. The reference objects were: a source crystalline silicon wafer (c-Si) and an amorphous silicon film (a-Si) on silicon wafer covered by 2 nm layer of natural SiO<sub>2</sub> oxide, as well as thermal SiO<sub>2</sub> film of 20 nm on silicon wafer.

The XANES method allows obtaining information about the distribution of the local partial density of free electronic states in the conduction band according to [19, 20]. This makes the XANES spectroscopy data extremely sensitive to the specificity of the local atomic surrounding, which has been demonstrated many times before [8–11].

PEEM (XANES) data for the por-SiO<sub>2</sub>/Si structure were recorded using fields of view from 100 to 10 μm. Spectra near the L<sub>2,3</sub> silicon absorption edge from regions up to several hundred nanometres in diameter were considered for obtaining microscopic data on the local atomic and electronic structure.

### 3. Results and discussion

XANES spectra registered in the standard way for a set of reference samples are shown in Fig. 1. These are the top three spectra. It is easy to see the presence of a low-energy absorption edge in the range from 100 to 105 eV of the reference spectra of crystalline silicon and an amorphous silicon film. In the first case, the specified absorption edge was characterized by a fine structure with two groups of A and A' maxima (Fig. 1) corresponding to the spin-orbital splitting of core Si L<sub>2,3</sub> level [21, 22]. A fine structure was not observed for the amorphous film [21, 22] due to the smearing of the density of states in the conduction band. The fine structure of c-Si and



**Fig. 1.** Synchrotron XANES Si L<sub>2,3</sub> spectra of references: crystalline silicon c-Si, amorphous silicon a-Si, silicon dioxide SiO<sub>2</sub>, together with the spectrum extracted from the 10 μm microscopic field of view. Dashed lines highlight the characteristic regions of the spectra fine structure: A and A' for “elementary” silicon; B and C for silicon dioxide. Circles show the quantum energies at which high-resolution images were recorded

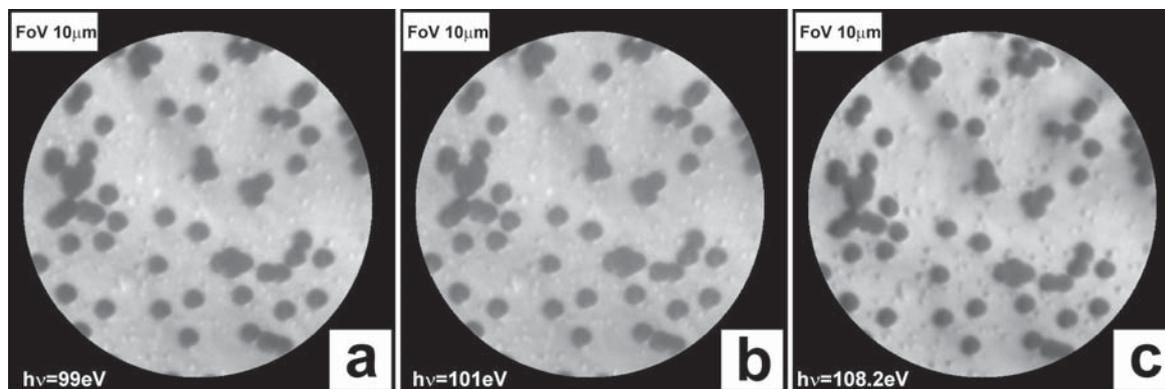
a-Si reference samples was almost equivalent to the SiO<sub>2</sub> reference sample at synchrotron radiation quantum energies exceeding 105 eV (Fig. 1). Sufficiently long-term storage of the crystalline silicon wafer and a structure with a film of amorphous silicon under the laboratory conditions led to the formation of a natural SiO<sub>2</sub> oxide layer with a thickness of ~ 2 nm, the absorption edge from which we observed. For the SiO<sub>2</sub> reference sample the fine structure of this edge was more pronounced (Fig. 1), especially near the first double maximum of 106–106.6 eV (maxima group B) of the molecular orbital  $\sigma^* a_1$  (transitions from  $2p_{1/2,3/2}$  level to 3s state) [23]. The main peak for the SiO<sub>2</sub> reference sample was maximal at  $h\nu \sim 108.6$  eV (molecular orbital  $\sigma^* t_2$ , transition from  $2p_{1/2,3/2}$  level to 3p state), indicated in Fig. 1 as C. It was also more pronounced compared to the natural oxide on c-Si and a-Si. The high intensity of the characteristic maxima of the spectrum of silicon dioxide ( $h\nu > 105$  eV) was obvious since it corresponded to a denser package of the main structural unit of silicon dioxide, the SiO<sub>4</sub> tetrahedron for the thermal oxide film (middle order), compared with a more “loose” layer of natural oxide [23].

The fourth curve in Fig. 1 corresponds to the XANES Si L<sub>2,3</sub> spectrum obtained integrally, which was extracted for only 10  $\mu\text{m}$  of the field of view (FoV) of the microscopic image of the surface area (shown in Fig. 2). The following characteristic features of this spectrum can be easily seen. A small “influx” in the region of A and A' maxima indicates a weak X-ray spectral signal from silicon atoms, which are not bound to oxygen atoms and

possibly present in an ordered state (A' “influx”). The oxide part of the spectrum according to the position of the main spectral features (B and C), as well as the distribution of their relative intensities, indicates that the surface layer was mainly silicon dioxide, close to the thermal dioxide based on the package density. This is certain, since the original film was obtained by thermal oxidation. Thus, damage caused by irradiation with gold ions and subsequent chemical etching did not affect, at least “macroscopically”, the nature of the local atomic structure and the electron-energy spectrum of the oxide film.

The electron microscopy images of the studied surface area from which the XANES Si L<sub>2,3</sub> spectrum (shown in Fig. 1) was obtained are shown in Fig. 2. Three images were obtained with high resolution in the X-ray spectral region of synchrotron (undulator) quantum energies preceding the absorption edge of “elementary” silicon (99 eV, the “background” part of the XANES spectrum), after the specified absorption edge (101 eV), and in the region of the main silicon dioxide peak (108.2 eV).

In all three images, the observed picture was practically identical. This result is quite understandable, since images using the PEEM method are formed due to different electronic work function leaving the surface layer of the sample during excitation by quanta of the corresponding energies [13]. In our case, these energies are close, since in addition to the morphology studies, we were interested in the specifics of the local silicon atoms surrounding (see below). According to the X-ray spectral characteristic of the entire



**Fig. 2.** PEEM electron microscopic images of the por-SiO<sub>2</sub>/Si sample surface recorded at different quantum energies of synchrotron (undulator) radiation in three characteristic X-ray spectral regions: a – ( $h\nu = 99$  eV); b – ( $h\nu = 101$  eV) and c – ( $h\nu = 108.2$  eV). The field of view was 10  $\mu\text{m}$

field of view (Fig. 1) for quantum energies before the edge of “elementary” silicon absorption and immediately after this edge (99 and 101 eV, respectively), the increase in intensity was barely noticeable. At the same time, the relative intensity variation for the edge of “elementary” silicon and SiO<sub>2</sub> was quite significant (Fig. 1, lower spectrum). Therefore, the image shown in Fig. 2 (c) is, in our opinion, characterized by higher sharpness. However, it should be noted, that the main features of the surface morphology of the studied area were preserved in all three images.

The surface contained an array of spherical objects with close diameter values of ~ 300 nm. Presumably, these objects are voids or pores, which follows from the lower signal intensity from these areas (dark shades), and the fact that the etching mode assumed reaching the wafer. The edges of the pores were sharp, which indicates an extremely small difference in pore width at the base and at the top, as well as an almost unchanged surface morphology around the pore, even due to a noticeable “etching” of the SiO<sub>2</sub> film surface. Mainly separated pores were formed. However, individual cases of the merging of 2–4 pores and the formation of voids of several micrometres in size can be noted. This distribution was not accidental and it was a consequence of the selected etching mode (etching reagent composition, etching time) and the inhomogeneous distribution of <sup>197</sup>Au<sup>+</sup> ions. However, with the fluence used, despite the arbitrary nature of the distribution of latent tracks, etching of the irradiated silicon dioxide film practically did not lead to pore fusion.

Finally, a separate formations of random location with sizes less than 100 nm were observed on residual, non-etched SiO<sub>2</sub> surface areas. This distribution pattern may indicate that the observed features correspond to the intrinsic defects of the original thermal SiO<sub>2</sub> film. Such defects were characterized by sizes smaller than the latent ion track and therefore were less susceptible to etching.

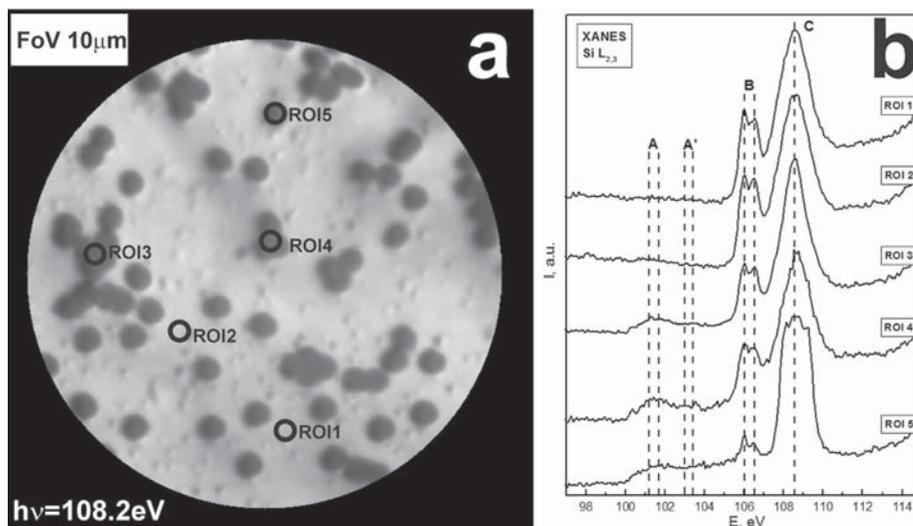
Before proceeding to the real “micropoint” spectra, extracted from surface regions of interest (ROI) of submicron sizes, the following should be noted. We used the PEEM method in the XANES Si L<sub>2,3</sub> spectroscopy mode for morphology studies with simultaneous reference to the analysis of

the local surrounding of silicon atoms in the “micropoint”. Here, the registration of the XANES spectrum using the PEEM method involves the accumulation of a set of images for each specified quantum energy value in the detecting spectral range. In our case, this range was 95–115 eV, at 0.1 eV increment step. Extraction of the XANES spectrum from the image ROI area (desired surface part) occurs by recalculating the relative intensity of the signal from the desired ROI from the entire sequence of the registered microscopic images stack in a single scale.

A set of characteristic individual surface areas not exceeding a diameter of 250 nm each is shown in Fig. 3a. In the same figure (Fig. 3b), we present the XANES Si L<sub>2,3</sub> spectra extracted from each of the designated ROI. The first two sections, ROI1 and ROI2, respectively, were selected outside the pores and provide an idea about the surface property of the residual, non-etched thermal SiO<sub>2</sub> film. ROI3 is a surface region selected in the centre of a massive surface part of several merged pores. ROI4 corresponds to the centre of a three merged pores region with the common external boundary. Finally, ROI5 represents the inner part of a single pore.

The character of the main features distribution of the ROI1 and ROI2 spectra suggests their complete coincidence, as well as their similarity to the reference spectrum of the SiO<sub>2</sub> thermal film. Thus, the surface of the film that was not affected by the collision with the ion and subsequent chemical etching did not undergo noticeable transformations with respect to the local surrounding of Si atoms. The relatively weak signal characteristic of all ROIs was particularly noticeable on the pre-edge background and it was a result of the low spectrum extraction area dimensions (~ 250 nm).

XANES Si L<sub>2,3</sub> spectra extracted from the ROI3–ROI5 sections differed from the fine structure of the ROI1 and ROI2 spectra. In the quantum energies range above ~ 100 eV, a pronounced absorption edge was observed, indicating the presence of silicon atoms not bound with oxygen atoms. The fine structure was indistinguishable due to the low intensity, however, the flatter shape of A–A’ regions was closer to the c-Si reference. This result confirms that pores in silicon dioxide were formed down to the wafer, the corresponding



**Fig. 3.** a – PEEM image of the studied surface area with a field of view of 10 microns, registered at the energy of synchrotron (undulator) radiation quanta  $h\nu = 108.2$  eV with designated spectra extraction ROI with a diameter of  $\sim 250$  nm. b – Synchrotron XANES Si  $L_{2,3}$  spectra of individual submicron surface regions from the ROI indicated on the microscopic image. The characteristic fine structure maxima identical to the XANES Si  $L_{2,3}$  spectra of the reference samples are shown

area of which provides such X-ray spectral signal. The presence of B and C features indicates a natural oxidation of the silicon surface at the bottom of the pores. The shape of the observed features in the “oxide” region corresponds to the reference spectra for ROI3 and ROI4. In the case of ROI5, the maxima were deformed, possibly due to a noticeable local redistribution of the potential within the area near the pore that had a pronounced surface relief. This redistribution of the surface potential, obviously, affects the signal statistics, causing deviations in the form of the registered (extracted) absorption edge fine structure. Nevertheless, all the main features peculiar to “elementary” silicon and its dioxide were observed. The ratio of the relative intensities of these edges, according to data [18], and the dip in the energy region between the features B and C, suggest the natural origin of the oxide layer with thickness  $\sim 2\text{--}3$  nm on the surface of the bottom of individual pores. Thus, even individual  $\text{SiO}_2$  pores in their array in the por- $\text{SiO}_2/\text{Si}$  structure had sharp vertical boundaries separating the silicon oxide walls from the bottom of the silicon wafer pore. We did not find any traces of transition layers or other transformations of the physical and chemical state of the studied structure of the array of spherical pores formed in a layer of thermal silicon dioxide on a c-Si wafer.

#### 4. Conclusions

For the first time, in a single experiment, the morphology and atomic and electronic structure of porous silicon oxide on silicon formed by irradiating the  $\text{SiO}_2$  film with  $197\text{Au}^+$  ions with an energy of 350 MeV and its subsequent chemical etching were studied. The PEEM method with the use of high-intensity synchrotron (undulator) radiation in two complementary modes: physico-chemically selective electron microscopy and spectroscopy of the X-ray absorption near edge fine structure with high lateral and energy resolution was used for studies.

It was shown that the pores formed in the por- $\text{SiO}_2/\text{Si}$  structure had rather sharp and almost vertical borders, without a transition layer. At the bottom of the pores was a substrate – a crystalline silicon wafer covered by a natural oxide with a thickness of  $\sim 2\text{--}3$  nm. Despite the conducted ion irradiation and subsequent chemical etching the porous silicon oxide matrix did not undergo noticeable structural-phase transformations. Significant disordering and technological contamination were not revealed for the silicon wafer atoms at the bottom of the pores. Thus, ion-track technology in combination with irradiation followed by chemical etching is effective for obtaining arrays of the isolated submicron range pores of identical sizes. Por-

SiO<sub>2</sub>/Si structures can be used as a convenient matrix for further controlled functionalization of the developed surface.

The extremely high efficiency of the PEEM photoemission electron microscopy method for study of a wide range of the objects characterized by composite structural-phase state of the surface layer with high accuracy and on a microscopic scale was demonstrated.

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### Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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