Electronic spectra of porous Si have been investigated in the region $\approx 4$ eV below the Fermi level with specimens subjected to in situ oxygenation and thermal treatments. The measurements were made with a UHV photoelectron spectrometer using "soft" energy ($\hbar \nu = 8.43$ eV) excitation of the photoemission. The significance of DOS to the photoluminescence and its degradation in porous Si is discussed. Fine structure of the photoelectron spectra is found from specimens heated in oxygen at 600 K.
Despite of intensive studies during the past few years the mechanisms of the photoluminescence and its degradation in porous Si are partly unclear. Two main mechanisms proposed for explanation of the photoluminescence are (i) quantum confinement [1] and (ii) chemical modification of the surface [2,3]. The quantum-dot model has been applied to porous Si by assuming escape of carriers through oxide barriers surrounding exciton confinement regions [4]. It is obvious that changes of the atomic structure of the surface will influence on the effective electronic structure of silicon nanocrystals and the carrier dynamics. As shown by secondary ion mass spectroscopy (SIMS) investigations exposure of porous Si to ambient or various other gases results in measurable changes of the chemical composition of the surface [5]. Therefore detailed information about electrophysical parameters (work function $\varphi_T$, dipole component $\delta$ of $\varphi_T$, band bending $V_S$ and spectra of the density of occupied states (DOS)) and their change during reaction of the surface with gaseous molecules is desirable.

In the present paper we report an investigation into electrophysical properties and electronic states near the Fermi level ($E_F$) of porous Si using photoelectron spectroscopy with low energy excitation. Previous measurements of photoelectron spectra in this material have been made with synchrotron [6,7] or x-ray [8] radiation and deal mainly with Si 2p core-level and valence band features or by using a He-I resonance lamp for excitation [9].

Porous Si samples with typical size of $1 \text{ cm}^2$ were prepared by electrochemical anodization of a p-type 5 cm Si(100) wafer for 5 min at current density of 25 mA/cm$^2$ in a 1:1:2 mixture of HF, water and ethanol. The distribution of photoluminescence was unhomogeneous over the surface of the samples: there were large domains with strong red photoluminescence separated from others showing weak yellowish luminescence. An UV photoelectron spectrometer [10] with ultrasoft excitation by Xe line ($h\nu = 8.43\text{eV}$) and an extremely low ($5 \times 10^{-4}$) background radiation for measuring weak signals near the Fermi level was used for the measurements. The excitation light was condensed inside an elliptical spot of $2 \times 3 \text{ mm}$ on the surface of the sample. With this equipment it is possible to determine features of DOS spectra, which are masked under excitation made with more energetic He-I and He-II lines or synchrotron radiation. The spectrometer has the following parameters: the resolution, determined from the Au spectrum, is better than 60 meV and the accuracy referred to the Fermi level is 10 meV. The base pressure of the spectrometer is not worse than $5 \times 10^{-10}$ Torr. The sample was cleaned in situ by heating in vacuum or in an oxygen flow. High-purity oxygen (99.99%) was used in the experiments. Also UV-irradiation was used for in situ desorption of gas contaminants. A special feature is that evolution of the photoelectron spectra during thermo- and photoactivated desorption (adsorption) of oxygen was monitored. The position of $E_F$ was determined through calibration with the photoelectron spectrum of an Au foil cleaned in ultra high vacuum by thermo- or photoactivated desorption of contaminants. The sample could be thermostabilized to within 1 K over the range of 300–700 K (or at liquid nitrogen boiling point) in vacuum or in an atmosphere of ad-
mitted gas at $10^{-8} < P < 10^{-1}$ Torr. The photoelectron spectrometer chamber contained a fused silica window trough which the specimen could be illuminated with a UV-VIS mercury lamp at power density of 0.05 W/cm$^2$ in the region of $h\nu < 5.3$ eV.

The energy diagram and the parameters determined in our experiments are shown in Fig. 1. The value of the band gap of porous Si may vary from sample to sample. Measurements in a diode configuration have given $E_g = 2.2$ eV [11] but larger values were obtained from electron energy loss spectroscopy measurements (2.9 eV) [9] and by spectroscopic scanning tunneling microscopy (2.6 eV) [12]. The Fermi level is located at the midgap region [9]. The displacement of the photoelectron spectrum as a whole means the change of the band bending $V_S$. The value of the work function $\varphi_T$ is obtained from the equation $\varphi_T = h\nu - E_{\text{kin max}}$, where $E_{\text{kin max}}$ is defined directly in the experiment. The shift of the highest binding energy edge of the spectrum (for which $E_{\text{kin}} = 0$) means a change of the dipole component $\delta$ of the work function $\varphi_T$ by $\Delta \varphi_T = \Delta V_S + \Delta \delta$. Thus it is possible to determine the evolution of the electrophysical parameters $\varphi_T$, $\delta$, and $\Delta V_S$ during treatment of the surface. The shape of the spectrum gives the DOS structure.

As can be concluded from the photoelectron spectra in Figs. 2 and 3 the strongest feature is the A band with the maximum around 3.2 eV when the specimen is heated in UHV at 600 K. After additional heating in the oxygen atmosphere of $p = 0.5$ Torr the band shows a rigid shift of 0.25 eV toward $E_F$. This shift is due to appearing or increasing of the Shottky barrier $V_S$ (Fig. 2, curves 1,2). The increasing of $V_S$ and change of $\delta$ mean that (i) oxygen adsorption takes place and (ii) the electrons are transferred from the volume of the sample to the adsorbing molecules, forming negatively charged species as $O_2^-$ and $O^-$. The high temperature adsorption of oxygen decreases the intensity of the minor band B while the intensity of the major band A is unchanged (compare curves 1 and 2, Fig. 2). This suggests that the states responsible for B are surface states while the A band is due to bulk-like states. The same effect may be observed due to illumination of the sample (wavelengths longer than 185 nm) in oxygen atmosphere at room temperature (Fig. 2, curve 3). This means that photoactivated adsorption of oxygen takes place. Note that the red luminescence drops drastically after thermo- or phototreatment in oxygen atmosphere. In contrast to this behaviour the short- wavelength luminescence retains its original value.

A sharp reduction in the intensity of the red photoluminescence band of porous Si has been observed after annealing in UHV conditions (1·10$^{-7}$ Torr) at temperatures $> 300$ °C [13,14]. This effect can be ascribed to dangling bonds (trapping centers for nonradiative recombination) created by desorption of hydrogen from the SiH$_2$ surface species. Also UV illumination with an energy exceeding 3 eV may cause hydrogen loss from porous Si in a nonoxidizing ambient [15]. In addition thermally and optically induced oxidation is known to rapidly degrade the photoluminescence intensity [16]. This coincides with re-
results of electron paramagnetic resonance measurements [17] showing formation of disordered dangling bond centers in porous Si annealed thermally in oxygen at temperatures between 420–770 K. We can assign the red luminescence with processes induced by diffusion of photogenerated electrons from bulk to the surface and subsequent recombination on the surface states. The luminescence efficiency is weakened by (i) the Shottky barrier due to charges localized on the thermo- or photoadsorbed oxygen layer and (ii) by formation of dangling bond centers which activate nonradiative transition processes. This conjecture is supported by the observation that the B band of the photoelectron spectrum (see Fig. 2), exhibiting deeper states, is typical to those parts of the specimen which inhibit the red photo-luminescence.

It is noteworthy that some fine structure is observed on the low-energy tail of the photoelectron spectra (see inserts to Figs. 2 and 3). The nature of these states requires additional analysis. Thus in this paper we present for the first time energy structure of porous silicon, described with macroscopic (ϕT, EF, VS, δ) and microscopic (DOS) parameters and their evolution during degradation of photoluminescence of porous silicon.

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Figure captions.

Fig. 1. Energy diagram of porous Si. \( h\nu \) is the excitation energy (8.43 eV), \( \varphi_T \) is the work function, \( \delta \) is the dipole component of \( \varphi_T \); CB and VB are the conduction and the valence bands edges, \( \Delta V_S \) is an additional band bending due to sample treatments, \( D \) is the Debay radius, \( L \) is the sample size, \( E_{\text{kin}} \) is the electron kinetic energy in vacuum, \( x \) is the geometrical coordinate from surface and \( N(\text{DOS}) \) is the DOS magnitude.

Fig. 2. Evolution of the photoelectron spectra of porous Si from the domains of dominating yellow photoluminescence: (1) "as received" sample after vacuum heating at 600 K, (2) after additional heating in \( \text{O}_2 \) at 0.5 Torr at 600 K, (3) sample (1) after phototreatment in \( \text{O}_2 \) at 0.5 Torr, and (4) sample (1) after heating in atmosphere at 600 K.

Fig. 3. Evolution of the photoelectron spectra of PS sample from the domains of dominating red photoluminescence: (1) "as received" sample, (2) after heating in high vacuum at 600K, (3) the same as (2) plus heating in \( \text{O}_2 \) (0.5 Torr) at 600 K and (4) the same as 3 plus heating in atmosphere at 600 K.
fig. 1.
Fig 2.
Fig 3.