Evolution of luminescence properties of natural oxide on silicon and porous silicon

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The main aim of this study is to research the features of luminescence properties of natural silicon oxide layers formed on the polished silicon surface, structural silicon surface and porous silicon films. Luminescence was excited by high energy electron beams — the local cathodoluminescence method. Cathodoluminescence of the samples was studied in 3, 24 and 48 days after preparation.

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1. Introduction

The search for silicon based structures with effective luminescence in visible–UV range has been recently carried out all over the world. Nevertheless there are still a lot of questions concerning the nature of luminescence properties of SiO_2/Si systems. SiO_2/Si systems are different in their luminescent properties in comparison with silicon dioxide and silica. It is connected with the fact that the properties of silicon based structures depend on the quality of silicon–silicon dioxide interface, on the properties of silicon oxide of several monolayers thickness and presence of silicon clusters [1–4].

The main aim of this study is to research the luminescence properties of natural silicon oxide layers formed on the polished silicon surface, structural silicon surface and porous silicon films and its changes in time after storing the samples is the air. Luminescence was excited by high energy electron beams — the local cathodoluminescence method (CL).

It is known that silicon oxides with oxygen deficiency are characterized by luminescence in blue (2.6–2.7 eV) and green (2.0–2.4 eV) ranges of the spectrum. The blue emitting band is connected with two-fold coordinated silicon [5]. In the oxides of several monolayers thickness there was a spectral shift of this band up to 2.8 eV and growth of its full width on the half of maximum (FWHM) [6]. The nature of the green luminescence band has not been completely studied yet. We suggest that it may be connected with such defects as oxygen vacancy and the formation of silicon chain in the silica. In this connection the spectral position of this band may depend on the length of silicon chain. It explains the „red“ shift of the band near the interface silicon–silicon oxide [7]. The various wide of this band in different oxides may be connected with the change in the content of silicon chains of different lengths.

2. Methods and samples preparation

The cathodoluminescence researches were performed at original optical spectrometer attached to electron microprobe analyzer CAMEBAX [8]. Luminescence was excited by electron beam with energy of 1–5 keV and with electron beam current of 10–50 nA. The depth of cathodoluminescence generation at this energy rate changes from 30 to 100 nm. Mathematical processing of cathodoluminescence spectra (spectrum analysis, determination of the spectral position of the maximum of the luminescence band, full width on the half of maximum (FWHM) of the bands and their intensity) was carried out in program Origin 6.1.

The surface of silicon plates was chemically polished in the mixture of hydrofluoric and nitric acids with proportion 1 : 3 (CP-3).

The porous silicon layer was formed by electrochemical method in 30% water mixture of hydrofluoric acid. Current density was 10 mA/cm^2. The time of the process varied from 1 to 30 minutes. Mechanically polished plates of *p*-silicon with resistivity from 1 to 20 Ω cm were used as the initial material.

The structurization of silicon surface was formed by removaling of porous silicon film after increasing of current density to 300 mA/cm^2.

Cathodoluminescence of the samples was studied in 3, 24 and 48 days after preparation.

3. Results and Discussion

3.1. Chemically polished silicon

The spectrum of the luminescence of the natural oxide, which had formed on the polished silicon plate, is represented in Fig. 1. This spectrum did not change in time. It may be characterized by two cathodoluminescnce bands with maximum position 2.75 and 2.1 eV. Besides the „blue“ band with maximum 2.75 eV dominates in the cathodoluminescent spectrum. Thus, this natural silicon oxide is characterized by two types of self defects: two-fold coordinated silicon and oxygen vacancies (silicon chains).

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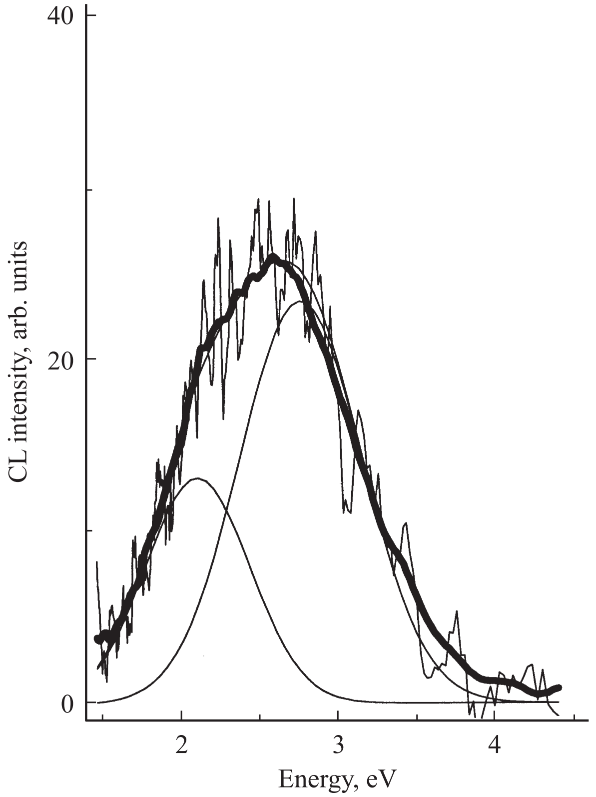

Figure 1. Cathodoluminescence spectrum of natural silicon oxide on the surface of chemical polished silicon.

3.2. Structuralized silicon surface

The structure of structuralized silicon surface was studied by the methods of scanning electron microscopy (Fig. 2). The size of the observed surface imperfections is about a few microns and thickness less than micron decimals.

In Fig. 3 there are cathodoluminescence spectra of structuralized silicon surface in 3 and 24 days after preparation. In three days in cathodoluminescence spectrum of the sample there is one band with FWHM of 0.7 eV and the maximum of intensity at 2.8 eV. In 24 days the spectral position of the maximum of the emission band has a red shift. The intensity of this bands increases twice. No specific changes in cathodoluminescence spectrum were observed during the further storage of the sample in the air.

More intensive cathodoluminescence of the silicon oxide, which had formed on the structuralized silicon surface, is connected with the bigger spesific surface in comparison with the polished silicon. Besides, it has been shown before that natural oxide forms faster on the rugged surface than on the smooth one. Such natural oxide is characterized by being thicker and containing more point defects which also leads to the increase of cathodoluminescence [9]. On the basis of the acquired cathodoluminescence spectra it is possible to suppose that initially on the surface of the structuralized silicon there is oxide which has double coordinated silicon as its main point defect. After storing the sample in the air for a long time the thickness of the oxide grows (cathodoluminescence increases). The observed spectral shift of the luminescent band can be explained

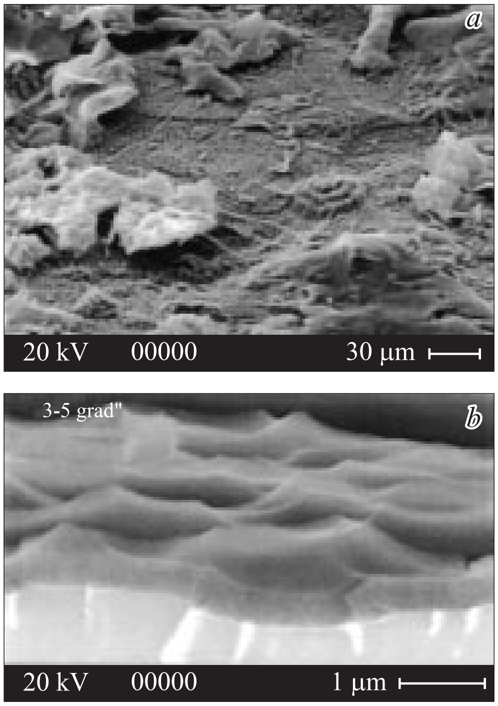

Figure 2. Silicon structuralized surface, *a* — surface, *b* — cross-section of silicon plate with structuralized surface. The picture is obtained on electron scanning microscope.

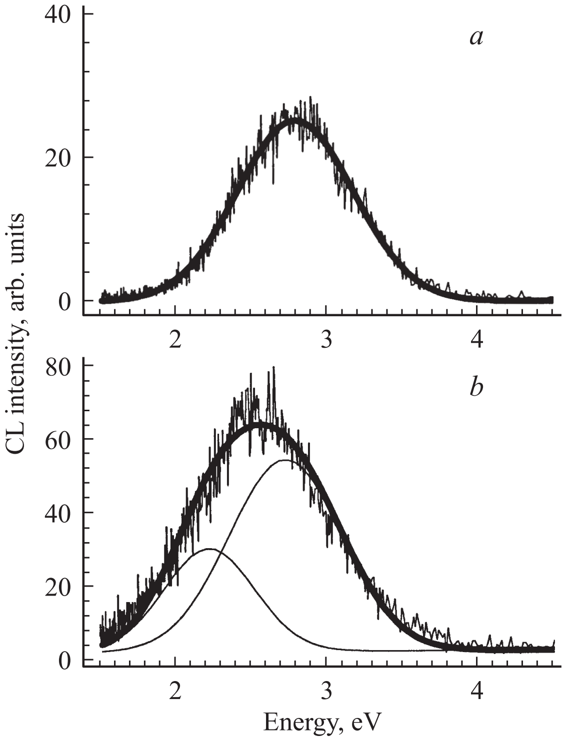

Figure 3. Cathodoluminescence spectrum of natural oxide on the structuralized silicon surface: *a* — in 3 days after preparation, *b* — in 24 days.

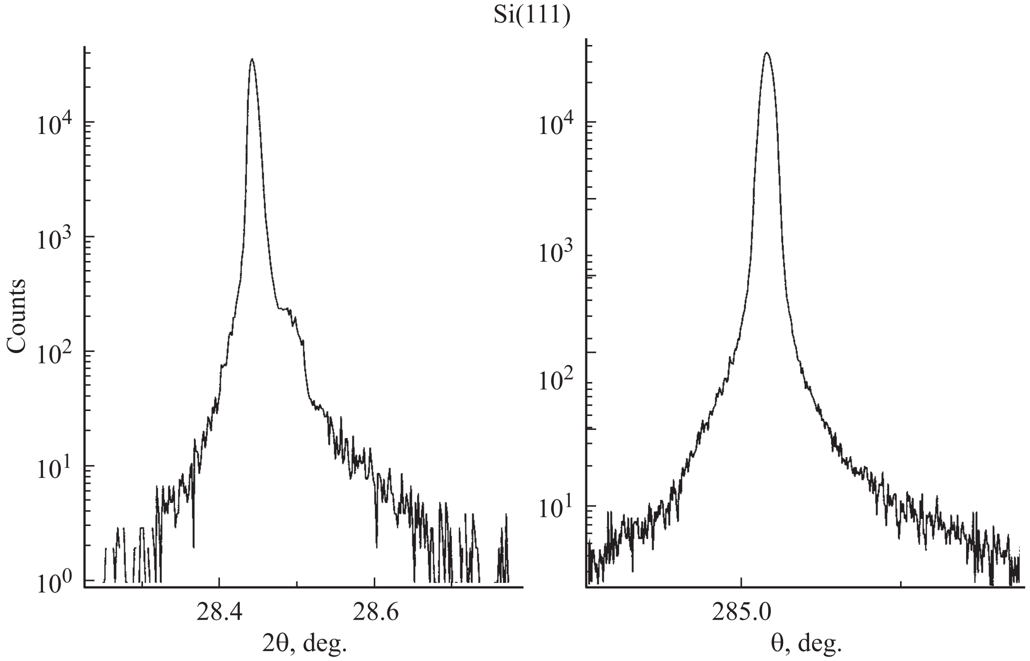

Figure 4. Results of the X-ray diffraction analysis of the porous silicon layer.

by the appearance of the second emission band with the maximum of intensity at 2.1–2.2 eV. This band is related with oxygen vacancies and silicon chains. The increasing of the silicon oxide thickness leads to the appearance of this defect.

3.3. Porous silicon

The structure of porous silicon films was studied by the methods of scanning electron microscopy. The thickness of porous silicon layer is about 1–10 nm.

These structures were studied additionally by X-ray diffraction analysis. Two steps can be observed in the rocking curve of the silicon porous layer (Fig. 4). It is possible to explain this by the appearance of silicon fragments of different crystal lattice parameters in the porous layer, because the process of the porous formation under electrochemical erosion firstly occurs in the crystal defects, which leads to the change of the parameters of the crystal lattice of silicon frame in porous silicon film.

Cathodoluminescence spectra of porous silicon are shown in Fig. 5. In three days after porous silicon had been prepared the film of natural oxide is characterized by two bands with maximum of emission at 2.0 and 2.6 eV. With the increase of the time of the contact of silicon surface with the atmosphere the intensity of the band of maximum 2.6 eV has linear growth. The FWHM and the position of the band do not change. Emission band with maximum 2.0 eV becomes much wider during the time of the storage of the sample. Besides there is a „blue“ shift: spectral maximum position shifts from 1.96 to 2.1 eV. The intensity of this band grows faster than the intensity of the band with 2.8 eV (Fig. 6).

Porous silicon luminescence in the visible range is also caused by the formation of natural oxide on the surface of the silicon walls in porous silicon films. The same two bands

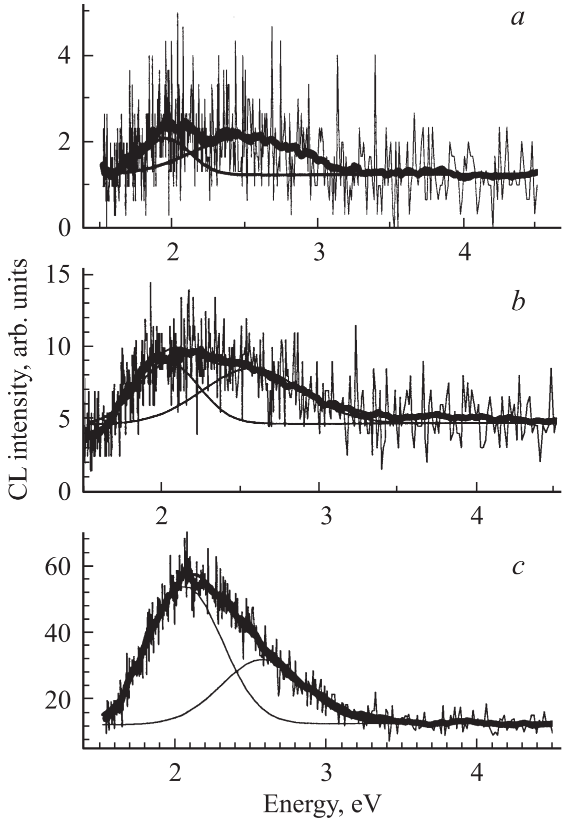

Figure 5. Cathodoluminescence spectra of porous silicon films: *a* — in 3 days after preparation, *b* — in 24 days, *c* — in 48 days.

	Number of days after preparation	Emission band at 2.0–2.2 eV			Emission band at 2.5–2.8 eV		
		Spectral position, eV	FWHM, eV	Intensity, arb. units	Spectral position, eV	FWHM, eV	Intensity, arb. units
Chemically polished silicon	3, 24, 48	2.1	0.7	10	2.75	0.8	20
Structuralized silicon surface	3	–	–	–	2.8	0.75	22
	24, 48	2.2	0.6	21	2.7	0.75	48
Porous silicon	3	1.95	0.3	0.3	2.5	0.7	0.8
	24	2.0	0.4	2	2.6	0.6	3
	48	2.1	0.5	25	2.6	0.5	13

with luminescence maximum of 2.0 and 2.6 eV appear in cathodoluminescence spectra of porous silicon. The band with maximum 2.0 eV is originally (already in three days after the sample was prepared) more intensive than the blue one with maximum 2.6 eV. During the storage of the sample in the air for a long time the intensity of the band with 2.6 eV has linear growth, and the intensity of the band with 2.0 eV grows significantly faster. This change in the intensity of the bands under the samples oxidation in the air is similar to the process, which can be observed in the oxide formed on the structuralized silicon surface. The „blue" shift of the band (from 1.95 to 2.1 eV) with maximum 2.0 eV and the increase of its FWHM are connected with the decrease of the length of silicon chains in the oxide during the oxidation of the sample. The spectral position of the maximum of the luminescence bands, FWHM of the bands and their intensity are given in Table.

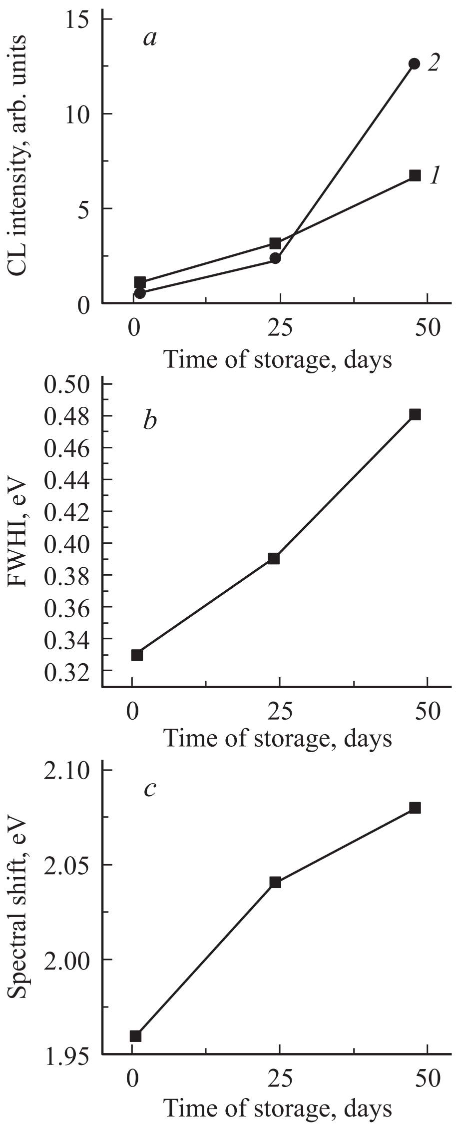

Figure 6. The change of cathodoluminescence bands characteristics in the time of storage of the sample on the air: *a* — intensity of band at *1* — 2.7, *2* — 2.2 eV, *b* — FWHM of the band at 2.2 eV, *c* — spectral shift of the band at 2.2 eV.

4. Conclusion

According to the acquired results it is possible to make the following conclusion:

1. In natural oxide there are two types of self defects in cathodoluminescence spectra: two-fold coordinated silicon and oxygen vacancies (silicon chains). Change of cathodoluminescence spectra of natural oxide in time reflects the evolution of natural silicon oxide during the storage. Besides, initially the silicon oxide contains mostly the first type defects (two-fold coordinated silicon). The band related with silicon chains in cathodoluminescence spectra appear later.

2. The spectra specific character of natural oxide formed on porous silicon is caused by the fact that formation of silicon chains under oxidation of thin (1–10 nm) silicon frame fragments is more probable. The long process of natural oxide formation on porous silicon is related to the fact that the approach of the oxidant (air) is more difficult because of the special characteristics of the structure of outer surface of the porous layer.

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