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LOW-DIMENSIONAL SYSTEMS

Study of the Formation of Silicon Nanoclusters in Silicon Dioxide during Electron Beam Irradiation

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Abstract—Irradiation of silicon dioxide by an electron beam with a high specific power leads to the formation of silicon nanocrystals in the irradiated region and the formation of a modified region, i.e., a $Si–SiO_2$ nanocomposite. This work is devoted to studying the formation of this nanocomposite and of its luminescence properties.

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1. INTRODUCTION

It is now well known that intrinsic defects are formed in silicon dioxide under irradiation by an electron beam [1]. The properties and the number of these defects depend on the specific power, as well as on the energy and time of exposure of a beam of electrons incident on the sample. It has been shown that, during exposure, first, the concentration of intrinsic defects of silicon dioxide increases; they are nonbridging oxygen and two-coordinated silicon. These defects can be easily identified in the spectra of cathodoluminescence (CL) [2–4]. A long-term exposure to an electron beam with a high specific power can lead to the formation of local regions of nonstoichiometric composition, including the formation of silicon clusters in the irradiated microvolume [5, 6]. In this work, we study a change in the properties of the irradiated microvolume and the process of formation of silicon clusters in the modified region of silicon dioxide, depending on the time of exposure to an electron beam of high specific power. The main method of our study was local cathodoluminescence. This method allows us to record the emission spectra of the microvolume and to observe the change in luminescence characteristics of a modified region directly during the process of exposure of the sample to an electron beam [7]. The structure of the region under exposure was studied by transmission electron microscopy.

2. LUMINESCENCE PROPERTIES OF SiO_2/Si

Several types of intrinsic defects are usually distinguished in amorphous silicon dioxide. Nonbridging oxygen (≡SiO·) is one of the most well studied point defects in glass. This defect is an oxygen atom bound only with one SiO_4 tetrahedron. Nonbridging oxygen is characterized by luminescence into a band with a maximum at 1.9 eV. The characteristic half-width of this band is 0.16 eV, and the decay time is 20 μs (it is insignificantly smaller in films thermally grown on silicon) [2]. This band is determined by transitions between energy states in the atoms of nonbridging oxygen when the O–O bond is formed between the nonbridging oxygen atom and one of three oxygen atoms of the same tetrahedron due to 2*p*-orbital overlapping [2].

Another intrinsic defect in silicon dioxide gives luminescence bands at 4.30 and 2.65 eV [3]. Luminescence band at 2.65 eV is long-lived (decay time is 10 μs). The most probable model for this defect is silicon atom having only two neighboring oxygen atoms, a two-coordinated silicon atom (=Si) [4].

In the green region of spectrum, a band with maximum at 2.2–2.4 eV is observed when the energy of excitation is higher than 7.6 eV [8]. There are several views on the origin of this luminescence. The appearance of this band is related with a lack of oxygen (oxygen vacancies), because this band dominates in silicon dioxide samples with excess of silicon [9]. Luminescence with maximum at 2.2–2.4 eV also takes place due to the change of the structure of the film near silicon–silicon dioxide interface. Exact position of maximum and half-width of this luminescence band depend on geometry of SiO_2Si structure. Another defect causing luminescence in this region of spectrum is related with the presence of the OH group. Luminescence caused by the OH group impurities has a longer lifetime than luminescence related with oxygen vacancies, which makes it possible to distinguish luminescence of these defects.

Bulk silicon crystal is characterized by a weak luminescence. Its radiation is observed in the infrared region of spectrum at 1.1 eV. A relation between the position of maximum of luminescence spectrum and the characteristic size of the structure has been estab-

Table 1. Main characteristics of the CL bands of the SiO_2/Si structure

Position of intensity maximum, eV	Half-width, eV	Decay time	Interpretation
1.15	0.12	–	Bulk crystalline silicon [11]
1.3	0.15	–	Bulk amorphous silicon [12]
1.6–1.8	0.1	–	Silicon nanoclusters [10]
1.9	0.14	25 μs	Nonbridging oxygen [2]
2.1–2.3	0.2	8 μs	Defect =Si–Si= [9]
2.65	0.3	5 ms	Two-coordinated silicon atom =Si: [6]

lished for the luminescence from nanosized silicon. It has been shown that the decrease in silicon cluster diameters leads to a shift of luminescence toward the high-energy region. Bands of luminescence of silicon nanoclusters were observed in the range from 1.4 to 1.8 eV [10].

Luminescence spectra of SiO_2/Si system are quite complex. They include luminescence from silicon as well as luminescence from nanosized silicon. The radiative properties of such system depend on the luminescence from intrinsic defects in silicon dioxide and in the interface between silicon and silicon dioxide. It is quite difficult to interpret the obtained spectra, because there is band overlapping. The main characteristics of luminescence are given in Table 1.

There are different ways to create silicon nanoclusters in silicon dioxide. One of them is implanting silicon atoms into silicon dioxide and performing annealing at a temperature about 1100°C [10]. Silicon nanocrystals are formed in the bulk of silicon dioxide. Luminescence from silicon dioxide containing silicon nanoclusters changes. The intensity of bands characteristic of silicon dioxide luminescence, decreases, and the bands characteristic of silicon nanoclusters are added to them. In this work, we study one of the methods to prepare systems $SiO_2/Si : Si_{nc}$ and $SiO_2 : Si_{nc}$ and to change the properties of their luminescence during cluster formation.

3. EXPERIMENTAL TECHNIQUE

The modification of silicon dioxide and cathodoluminescence studies were performed using a "Camebax" electron-probe microanalyzer equipped with two optical spectrometers of novel design operating in the IR and visible spectral ranges (1.0–5.5 eV) [6].

Cathodoluminescence spectra in the visible and infrared ranges were measured during a continuous irradiation of the sample. In order to analyze results of cathodoluminescence studies, the spectra were decomposed into spectral bands using Origin software, and we assumed that the bands have Gaussian shapes. This made it possible to determine the wavelength at which Gaussian band has a maximum. The area bounded by the Gaussian curve was treated as intensity of that band.

It has been shown in [1] that the high concentration of the OH groups promotes the formation of point defects in silicon dioxide; therefore, in order to study modification in process, we chose fused silica of type KU with a high concentration of OH groups (1000 ppm). We deposited a thin carbon layer on the surface of the sample (200 Å) which served as a sink for electrons.

The structure of irradiated silicon dioxide was studied by electron microscope EM-420 (Philips). We prepared thermal silicon dioxide films having large amount of the OH groups in order to perform studies by transmission electron microscopy (TEM) in planar geometry. Silicon substrate was ground, and silicon dioxide film was punched by argon beam.

The calculation of heating temperatures of silicon dioxide bulk samples was performed in [1]. We had to perform similar calculations for silicon dioxide films prepared for TEM measurements, because they were studied in this work. In the case studied we can approximate the shape of the region of heat generation by cylinder. The source in the right-hand part of equation serves for uniform generation of heat in the bulk of cylinder with radius r

$$q = \begin{cases} q_0, & \dfrac{\rho^2}{r^2} \le 1 \\ 0, & \dfrac{\rho^2}{r^2} > 1. \end{cases} \quad (1)$$

Here, q is the dissipated energy density and ρ is the radial coordinate.

Thus, the heating temperature has the form

$$T = \frac{q_0 r^2}{2k},$$

where k is the thermal conductivity coefficient.

We show dependence of heating temperature on the current density of electron beam for bulk silicon dioxide and for films prepared for TEM study in Table 2. One can see from this table that heating tem-

Table 2. Dependence of the heating temperature on the current density in the electron beam

Electron probe current density, A/cm^2	Overheating temperature of bulk SiO_2, °C	Overheating temperature of SiO_2 films, °C
0.013	5	10
0.13	50	100
0.63	240	440
1.27	500	900
3.1	1200	–

perature for a thin silicon dioxide film in vacuum exceeds the temperature for bulk silicon dioxide by a factor of approximately two.

Irradiation of glass was performed by an electron beam with 15 keV energy and 400 nA electron current for 40 min. Diameter of irradiated region was 0.5 μm (current density was 5 A/cm^2). In such regime of irradiation, heating of irradiated region by more than 1000°C is possible, which was shown in [1], and it is sufficient for reduction of silicon from silicon dioxide [13]. Subsequent irradiation and study of cathodoluminescence properties was done at 15 keV electron energy and at 0.6 A/cm^2 current density (corresponding to temperature of local heating about 200°C).

Irradiation of samples prepared for TEM studies was performed for 90 min at 5 keV electron energy and at 0.1 A/cm^2 current density (corresponding to heating temperature about 100°C).

4. RESULTS

4.1. Modification of Bulk Silicon Dioxide

After irradiation by an electron beam for 30 min with current density 5 A/cm^2 and energy 15 keV, we observed irreversible changes at the sample surface. In optical microscope embedded in the electron probe microanalyzer, we could observe the formation of a "dark" region with 3–5 μm size on the sample surface during irradiation by the electron beam. This region was characterized by a very weak luminescence in the visible region of spectrum (region *1* in Figs. 1, 2). Around the region where electron beam interacted with sample we could observe aureole of a bright blue luminescence (region *2* in Figs. 1, 2). The diameter of this region was 7–10 μm. No changes related with irradiation by an electron beam could be observed in the rest part of the sample (region *3* in Figs. 1, 2) both in optical and electron microscopes and in cathodoluminescence. After several days of storing the sample in air the difference in spectra of regions *2* and *3* disappeared, but changes inside the region where the sample was exposed to electron beam (region *1*) turned out to be irreversible, and the luminescence properties did not change significantly.

Cathodoluminescence spectra at current density 0.6 A/cm^2 (which corresponded to heating temperature 200°C) were studied after irradiation by electron beam with current density 5 A/cm^2 (which corresponded to temperature above 1000°C).

Regions *1* and *3* turned out to be stable, while further change of silicon dioxide took place in region *2*. We show cathodoluminescence spectra in Fig. 3, measured after irradiation by electron beam with low

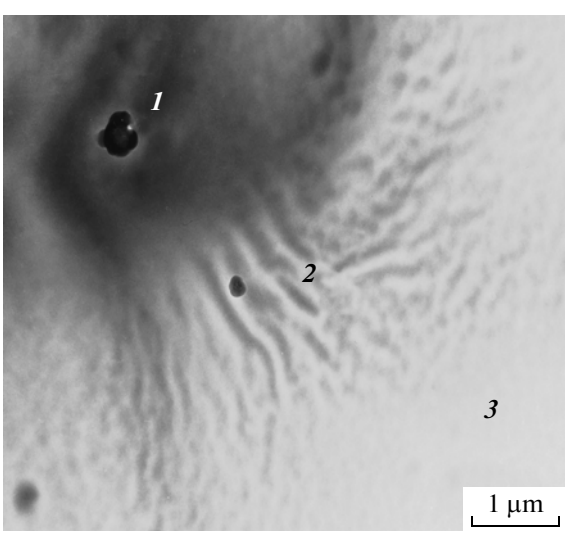

Fig. 1. Bright-field TEM image of silicon dioxide after irradiation by an electron beam: (*1*) region exposed to electron beam, (*2*) region where properties are changed, (*3*) region where silicon dioxide was not changed.

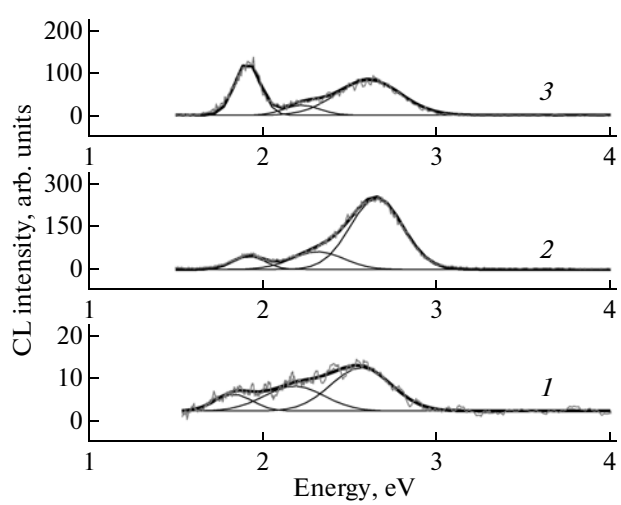

Fig. 2. Cathodoluminescence spectra after exposure to an electron beam. The numbers of spectra correspond to regions *1–3* in Fig. 1.

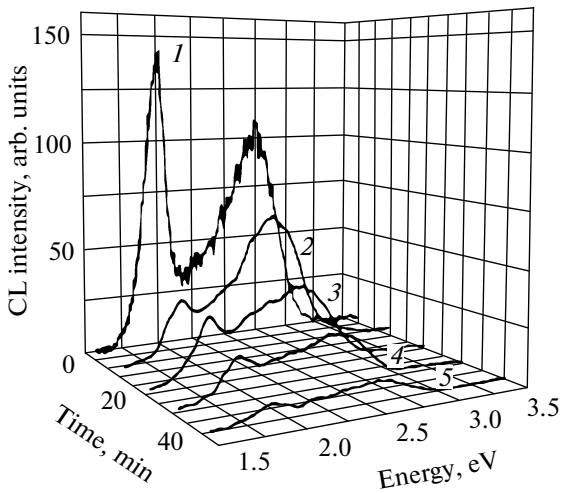

Fig. 3. Cathodoluminescence spectra obtained during exposure to an electron beam. Exposure time: (*1*) 0, (*2*) 10, (*3*) 20, (*4*) 30, and (*5*) 40 min.

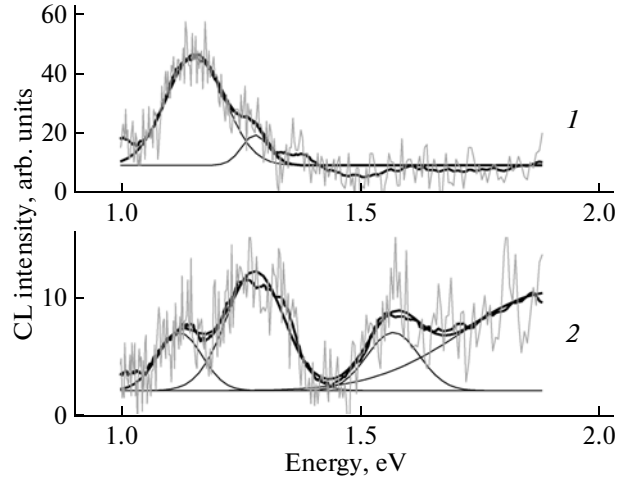

Fig. 4. Cathodoluminescence spectra in the IR range: (*1*) spectrum of crystalline silicon and (*2*) spectrum of silicon dioxide after continuous exposure to an electron beam. Thick lines show the results of smoothing and fitting of spectra by a sum of Gaussian bands.

power density at region *2* of Fig. 1 immediately after the initial change. Each spectrum was measured for 10 min.

The change in cathodoluminescence properties in region *2* during exposure to electron beam with current density 0.6 A/cm^2 gives evidence that there is a large number of broken bonds in this region. One can see from Fig. 3 that the shape of spectrum changes noticeably. According to measurements, cathodoluminescence spectrum stopped changing in 40 min; therefore, the process of change has finished by this moment of time.

Apart from the spectra in the visible range, we measured cathodoluminescence spectra in the infrared region. Figure 4 shows the IR spectrum of a modified region (corresponding to spectrum *5* in Fig. 3) in comparison with the spectrum of crystalline silicon. In the cathodoluminescence spectrum of modified silicon dioxide, we observed additional bands with maxima at 1.1, 1.3, and 1.6 eV.

4.2. Modification of Silicon Dioxide Films

We measured the changes in cathodoluminescence intensity during irradiation of films prepared for TEM. This dependences repeat cathodoluminescence dynamics of bulk silicon dioxide. We measured bright-filed images and microdiffraction images of irradiated regions.

5. DISCUSSION

5.1. Modification of Silicon Dioxide by Electron Beam

We studied CL in the range 1.5–2.0 eV. The change in spectra during exposure to electron beam is shown in Fig. 5. A change in intensity of the bands in IR-region of spectra was observed. The spectra were resolved with bands having maxima at 1.6, 1.7, 1.8, 1.9 eV. Dependences of cathodoluminescence bands intensities on the time of electron beam exposure are shown in Fig. 6.

After half an hour electron exposure of sample microvolume cathodoluminescence of intrinsic defects in silicon dioxide decreased (corresponding to bands at 1.90 and 2.65 eV), which was caused by the decrease in silicon dioxide fraction in microvolume (see Fig. 6). It is caused by the formation of regions in the material with a strong deficit of oxygen. Oppositely, the intensities of irradiation from bands with maxima at 1.8, 1.7, and 1.6 eV increased (see Fig. 6). The formation of these bands can be caused by irradiation from nanosized silicon clusters having sizes less than 6 nm [12]. We note that the band with maximum radiation intensity at 1.8 eV obtains its maximal intensity value in 20 min of microvolume modification, while the bands at 1.7 and 1.6 eV obtain their maximum intensity values in 30 min. The intensity of all three bands decreases thereafter. Thus, exposure to electron beam leads to the formation of silicon clusters with an average size of 1–2 nm, which become larger and form clusters of larger sizes (CL-band shifts from 1.8 to 1.6 eV, see Fig. 5). The intensity of radiation from large silicon clusters increases. These silicon clusters can be amorphous or they can have crystalline structure. If their structure is crystalline, then they are characterized by CL-irradiation with maximum at 1.1 eV, the irradiation of amorphous silicon can be observed in the range 1.3–1.4 eV [12]. In our measured spectra we saw bands with intensity maxima at 1.1 and 1.3 eV (Fig. 4). The intensity of the band at 1.3 eV is significantly higher. This gives evidence that predominately large silicon clusters with amorphous

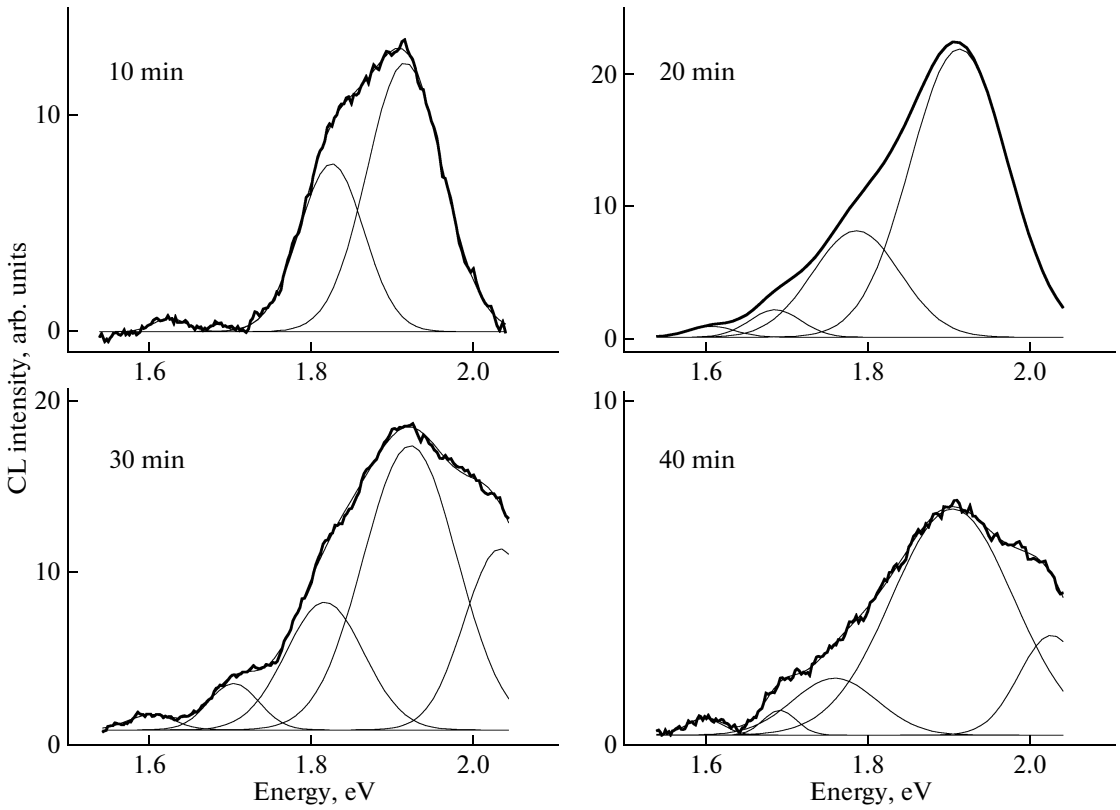

Fig. 5. Cathodoluminescence spectra measured in the IR range during exposure to an electron beam. Exposure time is shown in the figure.

structure are formed after modification. These results were confirmed by TEM data.

In the sample prepared for TEM, we studied four regions: region *1* corresponds to unchanged silicon dioxide; region *2* corresponds to silicon dioxide modified for 15 min; region *3* corresponds to silicon dioxide modified for 30 min and region *4* corresponds to modification time 90 min. We measured the microdiffraction images inside the modified regions and bright-field TEM images (Fig. 7).

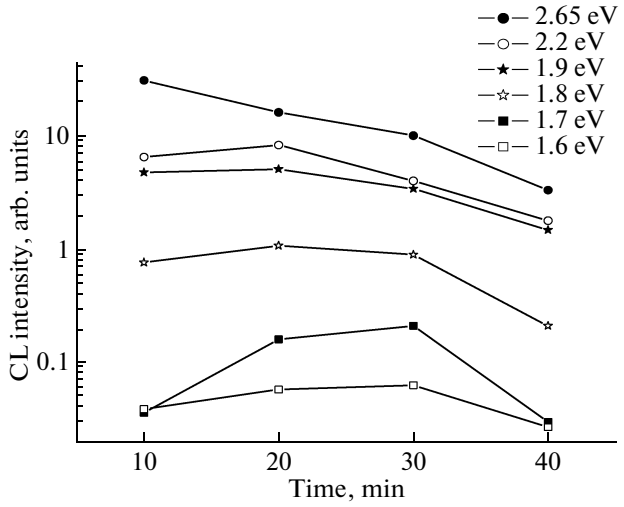

Fig. 6. Change in the intensity of the cathodoluminescence bands under exposure to an electron beam.

One can see from Fig. 7 that no features are observed in bright-field images inside unchanged region (Figs. 7, 9). Microdiffraction from this region is characterized by a broad structureless aureole. This is common for amorphous silicon dioxide films. Modification inside region *2* (Fig. 7b) was performed for 15 min. Contrast region appeared at the sample surface, which can be related with both with changes in density and with surface profile. These waves are related with local heating, taking place during interaction of electron beam with silicon dioxide film. One can see weak concentric circles in microdiffraction image. We speculate that this modification step corresponds to beginning of formation of silicon nanocrystals. In 30 min after the beginning of modification density waves become more distinct (Fig. 7c). One can see well-defined concentric circles in microdiffraction image, which gives evidence that crystalline fine-dispersed phase is present in the sample.

We show image of the region modified for 90 min in Fig. 1. Dark region in the sample is the region where silicon dioxide was exposed to electron beam. We do not observe any concentric circles in microdiffraction

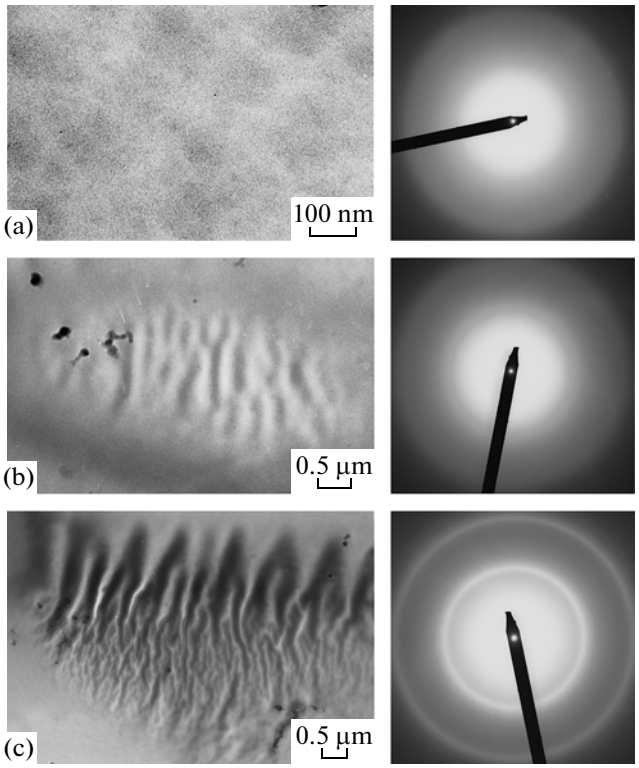

Fig. 7. Bright-field TEM images and microdiffraction patterns obtained in (a) unirradiated silicon dioxide and (b, c) silicon dioxide exposed to an electron beam for (b) 15 and (c) 30 min.

image inside this region. This might be explained by the formation of inclusions of amorphous silicon with sufficiently large sizes. Density waves can be observed around the modified region similar to waves in Figs. 7b and 7c. Microdiffraction, which is characteristic of silicon nanoclusters, is observed in density waves.

We have measured bright-field TEM image of silicon nanocrystals and their size distributions (Figs. 8, 9). It can be seen that 4 nm nanocrystals are most abundant. Thus, when CL bands intensity reaches maximum as a result of modification (Fig. 6) and distinct concentric circles appear in microdiffraction pattern, silicon nanoclusters are formed inside silicon dioxide. The average silicon nanocluster size is 4 nm according to TEM results. In 40–50 min after the beginning of modification amorphous silicon forms inside silicon dioxide.

The identification of the obtained microdiffraction patterns gives the following set of interplanar spacings: 2.08 ± 0.02, 1.24, and 1.08 Å. The ration of these values does not allow us to relate them with cubic structure. Tetragonal lattice with structure of type β-Sn is considered as one of the possible phases in strained silicon in work [14]. In this case we should have the following set (the probability of reflection is given in brackets): d_{201} = 2.698 Å (100%), d_{320} = 2.075 Å (80%), other values are less significant. In the measured diffraction patterns the ring with highest intensity is related with d_{320}, but intensive amorphous aureole is observed in the place where a ring related with d_{201} should be present, therefore we should assume that silicon clusters have tetragonal structure as a working hypothesis.

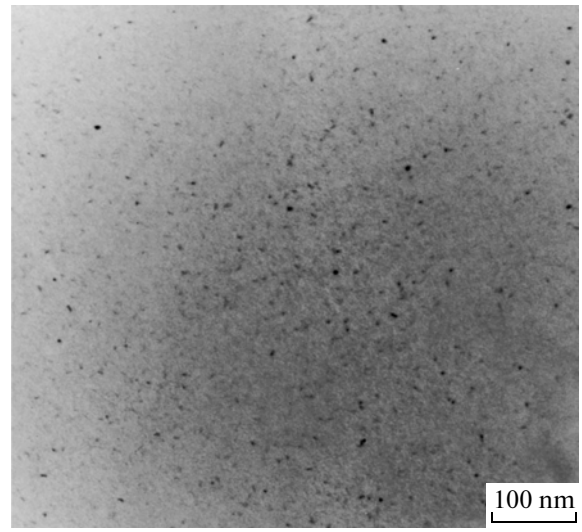

Fig. 8. Bright-field TEM image of silicon clusters in silicon dioxide exposed to an electron beam for 30 min.

5.2. Factors Responsible for the Formation of Silicon Nanoclusters in Silicon Dioxide Exposed to an Electron Beam

From the obtained results, one can see that silicon nanocrystals are formed inside silicon dioxide exposed to electron beam. One of possible causes of silicon nanocrystals formation can be heating of modified microvolume. It has been shown in [1] that heating temperature under these experimental conditions can exceed 1000°C. At such high heating temperature,

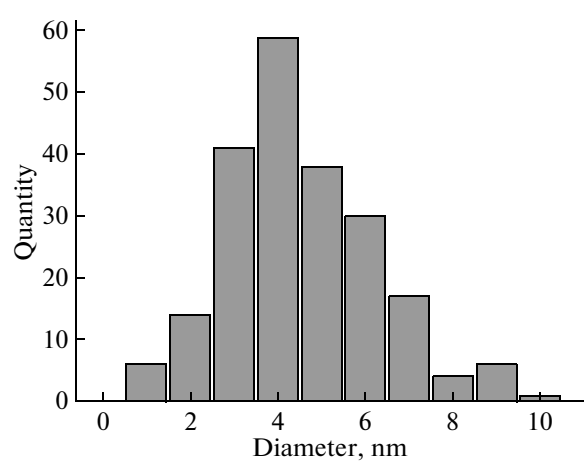

Fig. 9. Size distribution of silicon nanoclusters.

first, the breaking of silicon–oxygen bonds takes place followed by oxygen atoms diffusion in vacuum through the surface, which results in the formation of a nonstoichiometric region, where silicon nanoclusters are formed at this heating temperature. When the OH groups are present formation of regions with oxygen deficit takes place faster due to the fact that initial concentration of point defects in silicon dioxide is higher.

6. CONCLUSIONS

In this work, we have shown that silicon nanoclusters are formed inside silicon dioxide exposed to electron beam. We have studied the spatial distribution of defects formed during modification and their stability. We have studied cathodoluminescence properties of modified silicon dioxide regions and their dynamics. Our TEM results confirm the formation of silicon nanocrystals in silicon dioxide and the regions of amorphous silicon during further modification.

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