

Transformation of Point Defects in Silicon Dioxide during Annealing

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Abstract—In our previous studies, we have demonstrated that annealing of silicon dioxide in the absence of oxygen leads to the formation of silicon clusters near the surface. The mechanism of the formation of silicon clusters by this technique has not been sufficiently investigated. However, it has been found that the rate of the formation of nanoclusters and their sizes depend on the concentration of point defects in the silicon dioxide and on the concentration of impurities, for example, hydroxyl groups. As a continuation of these studies, in the present work we have investigated changes in the concentration of point defects in silicon dioxide films during high-temperature annealing. A new method has been proposed for the evaluation of changes in the concentration of point defects in silicon dioxide films before and after annealing. A model of the transformation of point defects in silicon dioxide into silicon nanoclusters due to the high-temperature annealing has been developed.

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1. INTRODUCTION

In our earlier papers [1, 2], we presented the results demonstrating the process of the formation of silicon nanoclusters under electron beam irradiation of silicon dioxide in a vacuum. It was shown that silicon clusters are formed upon electron beam heating of the irradiated silicon dioxide region, which leads to the release of oxygen and its diffusion toward the surface of the sample. The use of an electron beam for local heating of silicon dioxide made it possible to investigate changes in the cathodoluminescence (CL) spectra of the irradiated region directly during the irradiation. It was demonstrated that, in the irradiated region, initially, the concentration of point defects increases and, then, an oxygen-deficient region is formed. Further, in this region, there is the nucleation of silicon nanoclusters, followed by their growth [2]. It was also shown that the presence of point defects in the structure plays a crucial role in the formation of silicon nanoclusters [3].

In subsequent studies, we have revealed that the high-temperature annealing ($T = 1150^\circ\text{C}$) in a dry nitrogen atmosphere also results in the formation of silicon nanoclusters in the near-surface layer of thermal silicon dioxide [4]. This method of the formation of silicon nanoclusters has not previously been studied. The dynamics of the growth of silicon nanoclusters has been thoroughly investigated during the synthesis in a radio-frequency silane plasma [5], after the chemical synthesis [6], and in the case of using both the plasma enhanced chemical vapor deposition

(PECVD) and inductively coupled plasma chemical vapor deposition (ICP-CVD) methods [7, 8]. The nucleation of nanoclusters in a silicon dioxide film and the dynamics of their growth during annealing have not been investigated in sufficient detail. Moreover, the question about the nucleation of excess silicon for the formation of silicon nanoclusters during annealing of stoichiometric silicon dioxide also remains open. As in the case of the electron beam irradiation of silicon dioxide films, an important role in the formation of silicon clusters during annealing is played by point defects in silicon dioxide. In order to determine changes in the concentration of point defects in silicon dioxide, we have used the original technique. This has made it possible to quantitatively evaluate the concentration of point defects in the silicon dioxide and to investigate the effect of high-temperature annealing in a dry nitrogen atmosphere on their concentration. The investigations have been carried out for thermal silicon dioxide films with different concentrations of OH groups.

2. METHOD FOR THE QUANTITATIVE DETERMINATION OF THE CONCENTRATION OF POINT DEFECTS

In [9], it was proposed to use a method for determining the concentration of luminescence centers from the intensity of the CL bands. This method was tested on bulk samples of amorphous silicon dioxide

[10]. Moreover, it can be applied to silicon dioxide films on silicon.

The concentration of point defects can be evaluated by the following method. The dependence of the CL intensity of luminescence centers on the current density can be represented in the form

$$I = A \frac{LJN\tau_{\text{rad}}^{-1}}{LJ + \tau^{-1}}, \quad (1)$$

where I is the intensity of the luminescence band, A is the coefficient which depends only on the experimental conditions and does not depend on the sample under investigation, L is the CL excitation efficiency, J is the density of the electron beam current, N is the number of luminescence centers, τ is the decay time of the CL band, and τ_{rad} is the radiative lifetime.

If the quantity LJ is much larger than τ^{-1} , the CL intensity reaches the saturation. The CL intensity at the saturation can be expressed as

$$I_{\text{sat}} = AN\tau_{\text{rad}}^{-1}. \quad (2)$$

For the quantitative evaluation of the concentration of point defects in silicon dioxide, it is necessary to determine the coefficient $A(\lambda)$, which depends only on the experimental conditions and does not depend on the sample, the CL saturation intensity, and the lifetime τ . In order to determine the coefficient $A(\lambda)$, it needs to use a reference sample in which luminescence centers will have a maximum of the CL band in the desired spectral range, and the concentration of these centers can be determined by another method. As a reference sample, we chose leucosapphire with Cr^{3+} impurities. The CL spectra of this sample contain a band attributed to the Cr^{3+} ion, with the maximum intensity at 1.8 eV. The chromium concentration was determined using the energy-dispersive X-ray microanalysis. Thus, the coefficient A can be found for the desired spectral range. Since the coefficient A does not depend on the sample, we can determine the concentration of luminescence centers in other samples.

The CL spectra of the silicon dioxide films contained a band with the maximum at 1.9 eV, which is attributed to a point defect (nonbridging oxygen atom). The concentration of these defects can be estimated from the formula

$$N_{\text{ox}} = \frac{I_{\text{ox}}\tau_{\text{ox}}}{I_{\text{Cr}}\tau_{\text{Cr}}} N_{\text{Cr}}, \quad (3)$$

where N_{ox} is the concentration of nonbridging oxygen atoms; N_{Cr} is the concentration of Cr^{3+} ions in leucosapphire; I_{ox} and I_{Cr} are the intensities of the CL bands attributed to the nonbridging oxygen atoms and Cr^{3+} ions at the saturation, respectively; and τ_{ox} and τ_{Cr} are the decay times of the corresponding bands.

In [10], it was shown that the CL band of chromium ions reaches the saturation at a current density of more than 0.015 A/cm². The chromium concentra-

tion was determined using the energy-dispersive X-ray microanalysis: $N = 2.4 \times 10^{19}$ cm⁻³. The decay time of the Cr^{3+} band was found to be 4.3 ms.

3. SAMPLE PREPARATION, EXPERIMENTAL TECHNIQUE, AND RESULTS OF THE INVESTIGATIONS

The samples were prepared as follows. Thermal silicon dioxide films with a thickness ranging from 400 to 450 nm and different concentrations of OH groups were grown on silicon(111) KEF-1.0 substrates. Film 1a was grown in a dry oxygen atmosphere, whereas films 2a and 3a were prepared in wet oxygen atmospheres (with different degrees of humidity). Then, the films were annealed in a dry nitrogen atmosphere at a temperature of 1150°C for 5 h. Both the initial samples (1a, 2a, 3a) and the annealed samples (1b, 2b, 3b) were investigated using the local CL method on a cathodoluminescence station described in [11].

The concentration of point defects was determined according to the technique described above. We measured the CL spectra and decay times of the bands attributed to silicon dioxide films and leucosapphire doped with chromium. The CL spectra are shown in Fig. 1. These spectra were recorded at an electron energy of 5 keV, an electron beam current of 100 nA, and an electron beam diameter of 10 μm. The CL spectra of amorphous silicon dioxide contain bands associated with the luminescence of point defects, or, more specifically, the band at 1.9 eV corresponds to nonbridging oxygen atoms [12], the band at 2.2 eV is assigned to oxygen vacancies [13], and the band at 2.65 eV is attributed to twofold-coordinated silicon atoms [14]. The concentration of nonbridging oxygen atoms (the band with a maximum at 1.9 eV) can be determined using the method described above. In this case, the reference sample was leucosapphire doped with Cr^{3+} . A change in the concentration of twofold-coordinated silicon atoms can also be determined, because the band with a maximum at 2.65 eV reaches the saturation in the range of current densities accessible in our experiments. The concentration of oxygen vacancies (the CL band with a maximum at 2.2 eV) cannot be determined, because the CL band has a lifetime of shorter than 0.1 μs and does not reach saturation in the accessible range of current densities. The decay times of the CL bands of silicon dioxide films are presented in Table 1.

The evaluation of the concentration of point defects showed that the concentration of nonbridging oxygen atoms in film 1 is equal to 1.5×10^{16} cm⁻³. The results of the evaluation of the changes in the concentration of point defects in the films are presented in Table 2. It was also shown that, after the high-temperature annealing in a dry nitrogen atmosphere for 5 h, the concentration of nonbridging oxygen atoms and twofold-coordinated silicon atoms in film 1 grown

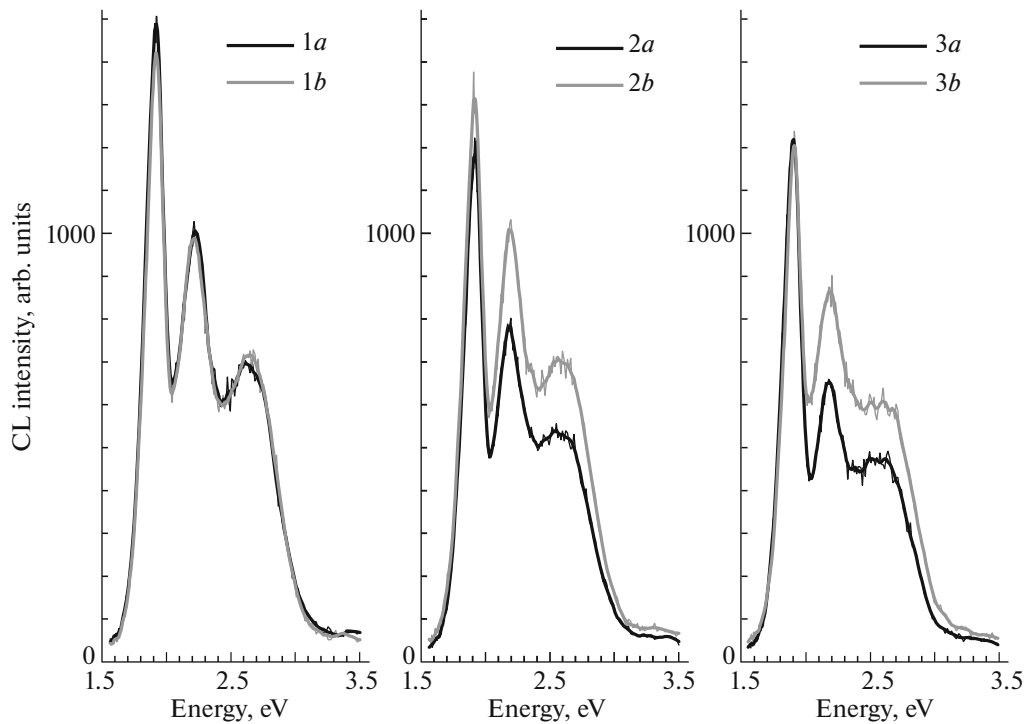


Fig. 1. CL spectra of silicon dioxide films (1a–3a) before and (1b–3b) after the high-temperature annealing in a dry nitrogen atmosphere for 5 h.

in a dry oxygen atmosphere changes by no more than 5%, which corresponds to the measurement error. In film 2 grown in a wet oxygen atmosphere, the concentration of nonbridging oxygen atoms and twofold-

coordinated silicon atoms after the high-temperature annealing for 5 h increases by 10%. In film 3 after the annealing, the concentration of nonbridging oxygen atoms decreases by approximately 10%, whereas the concentration of twofold-coordinated silicon atoms increases by approximately 30%, which indicates the formation of an oxygen-deficient region.

Table 1. Decay times of CL bands in silicon dioxide films

Film	Decay time of the CL band with the maximum at 1.9 eV, μs	Decay time of the CL band with the maximum at 2.65 eV, ms
1a	10	4.2
1b	10	4.4
2a	10	4.5
2b	10	4.5
3a	9.3	4
3b	9.3	4.3

Table 2. Concentration ratio of luminescence centers in the annealed and initial films

	Concentration ratio of the 1.9 eV luminescence centers in the annealed and initial films	Concentration ratio of the 2.65 eV luminescence centers in the annealed and initial films
1b/1a	0.95	1.04
2b/2a	1.10	1.13
3b/3a	0.91	1.31

As was shown in [1, 3], the electron beam irradiation of silicon dioxide leads first to an increase in the concentration of point defects in the irradiated region and then to the formation of an oxygen-deficient region. The results of the evaluation of the concentration of point defects demonstrate that, after the high-temperature annealing in a dry nitrogen atmosphere for 5 h, film 1 (with a low concentration of OH groups) remains stable. In film 2 (with a high concentration of OH groups), the concentration of point defects after the annealing increases, while in film 3 (with the highest concentration of OH groups), the annealing results in the formation of an oxygen-deficient region. This suggests that film 3 most significantly changes after the annealing under the chosen conditions.

4. MODEL OF THE TRANSFORMATION OF POINT DEFECTS

According to the data available in the literature [15], there is only a small dissociation of silicon dioxide at temperatures below 1400°C. This indicates that the annealing carried out at a temperature of 1050°C is

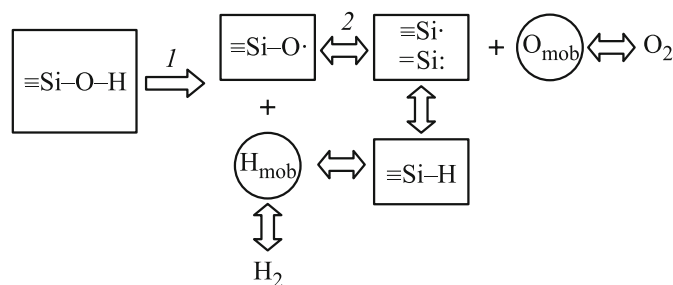
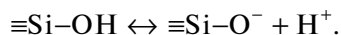


Fig. 2. Schematic diagram of the transformation of point defects in silicon dioxide: (1) the dissociation of Si–OH groups and (2) the formation of an oxygen vacancy and a twofold-coordinated silicon atom.

not sufficient to break silicon–oxygen bonds and to form point defects. This assumption is confirmed by the fact that the high-temperature annealing does not lead to a change in the structure of the film with a low concentration of OH groups. Nevertheless, significant changes occur in the films with a high concentration of OH groups. Accordingly, it can be assumed that the formation of free oxygen and then silicon precipitates occurs precisely at point defects of the silicon dioxide. As was shown in [16] during the investigation and visualization of redox reactions in porous silicon, the dissociation of Si–OH groups is also possible. In this case, the reaction is reversible:



The schematic diagram of possible processes of transformation of point defects is shown in Fig. 2. As can be seen from this figure, the dissociation of Si–OH groups results in the formation of nonbridging oxygen atoms (the CL band with a maximum at 1.9 eV). A further dissociation can also lead to the formation of an oxygen vacancy (the CL band with a maximum at 2.2 eV) and a twofold-coordinated silicon atom (the CL band with a maximum at 2.65 eV). This diagram explains the increase in the concentration of point defects, as well as the subsequent decrease in the concentration of nonbridging oxygen atoms and increase in the concentration of twofold-coordinated silicon atoms.

5. CONCLUSIONS

In this study, we proposed and used a new method for the quantitative determination of the concentration of point defects. Silicon dioxide films with different concentrations of OH groups were studied before and after the high-temperature annealing in a dry nitrogen atmosphere for 5 h. It was shown that, in silicon dioxide samples with a low concentration of hydroxyl groups (film 1), there is no significant change in the concentration of point defects during the high-temperature annealing, whereas in the films with a high concentration of OH groups (films 2 and 3), the concentration of point defects substantially

changes after the annealing in a nitrogen atmosphere. Apparently, the high concentration of impurities, in particular, OH groups, is a necessary condition for the formation of a nanocomposite region. We also proposed a model of the transformation of point defects in silicon dioxide during the high-temperature annealing.

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