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Evolution of point and structural defects in silica glass treated with fine annealing

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The silica glass with a high content of OH groups was synthesized by the high-temperature hydrolysis of $SiCl_4$ in a flame of oxyhydrogen torch and subjected to fine annealing. A combination of the photoluminescence and IR reflection spectroscopy was applied to assess the evolution of the ensemble of structural defects in the bulk and surface layer over the course of annealing carried out at 480°C. The marked decrease of the defect concentration was observed in the bulk at all time expositions in the range 2 to 72 hours.

However, in a thin surface layer, the decrease of the concentration of silanol groups Si−OH formed in the process of synthesis was detected. Decay of these groups results in the silicate network consolidation that led to the forming of the superficial layer characterized by an elevated microhardness.

Keywords: silica glass, fine annealing, photoluminescence, IR transmission.

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1. Introduction

Fine annealing (FA) of an optical glass is used to remove residual stresses in the volume of the material [1–3] by heating products at temperatures from 350 to 650°C [4]. In silica glass, the source of stresses is distortions of the equilibrium structure of the silicate network near its local defects. In addition, in the case of silica glass with a high content of OH groups, heat treatment causes the accumulation of isolated silanol groups ≡Si−OH, the interaction of which leads to the release of free water. This process can vary significantly in volume and on the surface of the products, since the H_2O molecules formed in the surface layer evaporate, and the output of free water from the silicate matrix is limited even at higher (compared to FA) temperatures [5].

In this study, both of these features are considered — the behavior of point defects active in the photoluminescence spectrum (PL) and the role of silanol groups in the modification of the glass surface under the impact of FA.

2. Samples and equipment

Silicon dioxide was synthesized by high-temperature hydrolysis $SiCl_4$ in the flame of an oxygen-hydrogen torch. The SiO_2 obtained by this method contains up to 0.2 wt% of OH groups. Polished plates with a thickness of 9.5 mm were annealed at a temperature of 480°C for a duration of 2, 24 and 72 hours in a chamber electric furnace; the cooling rate was 16°C/h. IR reflection spectra in the bound water band region ($920\,cm^{-1}$) and transmission in the free water band region ($1600\,cm^{-1}$) are recorded using InfraSpek FSM 1201 Fourier spectrometer. The PL spectra were excited by a LED emitting at a wavelength of 370 nm and recorded using an AVANTES — AvaSpec-ULSi2048L-USB2 OEM fiber optic spectrometer.

3. Results

3.1. Microhardness

The microhardness H_V of the Vickers samples was determined before spectroscopic experiments. Measurements at a fixed load on the pyramid showed a decrease in the value of H_V from 7.4 to 6.9 GPa with an increase in the annealing duration (Table 1). However, for annealing with an exposure of 72 h, the opposite trend was noticed — an increase in microhardness during measurements with a lower load on the pyramid (Table 2). The microhardness of samples with a load of 0.2 N (that is, with the lowest depth of indenter insertion) was the highest, whereas the value of H_V decreased with increasing load to 0.5 N and further to 1 N. This result indicates the presence of a compacted layer on the sample surface with a thickness of $\sim 1\,\mu m$, which was estimated based on the depth of the Vickers pyramid indenting (Table 2).

3.2. Photoluminescence

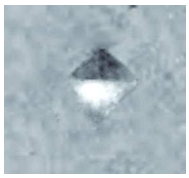
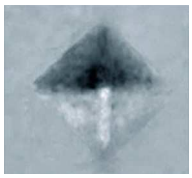
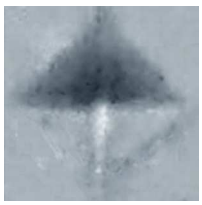
Structurally perfect SiO_2 does not exhibit the PL effect, since it has no direct optical transitions. However, the presence of defects in the structure of the silicate network

Table 1. Microhardness of samples after TO

Duration of annealing, h	H_V, GPa*
0	7.4 ± 0.3
2	7.0 ± 0.2
24	6.8 ± 0.2
72	6.9 ± 0.1

Note. * Pyramid load 1 N.

Table 2. Microhardness of the sample after annealing for 72 h

Load on the pyramid, N	Depth embeddings, μm	Prints pyramids Vickers	H_V, GPa
0.2	0.9		8.6 ± 0.4
0.5	1.5		7.9 ± 0.3
1	2.3		6.9 ± 0.1

manifests itself as bands active during external excitation [6]. The PL spectra of the samples before and after FA are shown in Fig. 1. The dominant bands in the spectrum 510 nm and 660 nm belong to neutral oxygen vacancies (neutral oxygen-vacancy, NOV) ≡Si−Si≡ [7] and non-bridging oxygen hole centers (NBOHC) ≡Si−O− [8], respectively. The weak band at 430 nm belongs to the silanol groups Si−OH [9].

FA resulted in the decrease of the intensity of all defect bands to varying degrees. Thus, the applied annealing procedure reduces the degree of structural disorders in it.

3.3. The IR spectroscopy

In contrast to the PL excited in the bulk of the material, IR reflection spectroscopy allows us to observe changes in the structure in the near-surface layer of the sample, the thickness of which in the area of structural bands of glasses

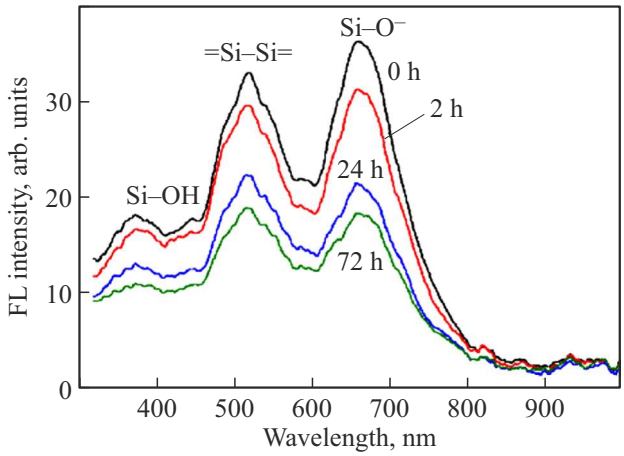


Figure 1. PL spectra of samples before and after the FA. The annealing duration is shown near the spectra.

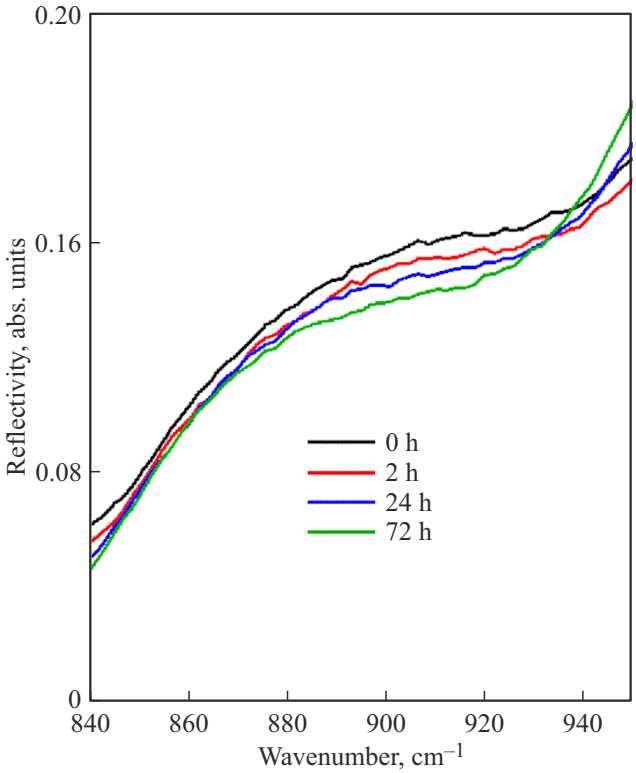


Figure 2. IR-spectrum of reflection in the area of band 920 cm^{-1} before after the FA.

is 1−10 μm. Figure 2 shows the region of the reflection band 920 cm^{-1}, belonging to vibrations in silanol groups. The intensity of the band decreases as the annealing time increases, which indicates the separation of OH groups from silicon atoms when the glass is heated.

The decay of Si−OH groups is accompanied by the interaction of hydroxyl groups with the formation of water molecules. Water evaporates from the surface of the glass, but in the volume of the material, the temperature-stimulated process of decomposition of silanol groups

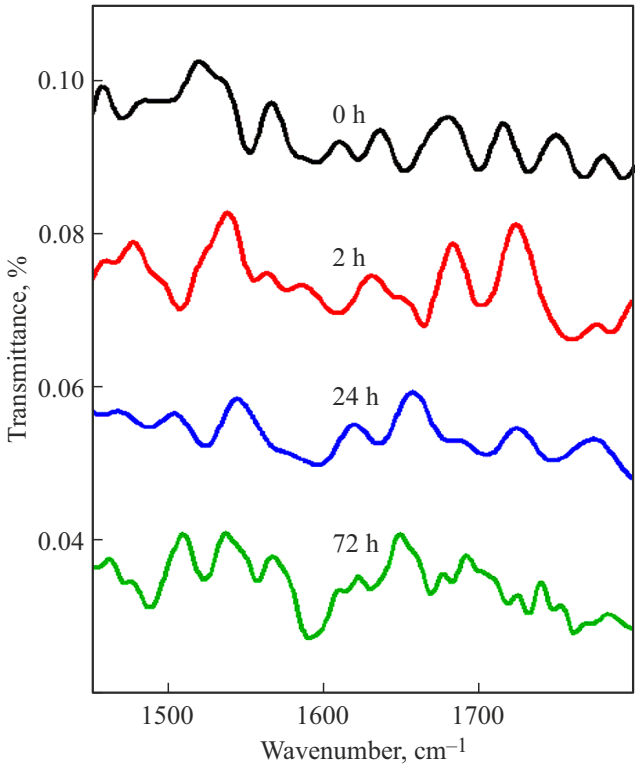


Figure 3. IR spectra of transmittance in the area of band 1600 cm^{-1} before after the FA.

can leave free water. IR spectra of transmittance were recorded in the region of the H_2O deformation vibration band 1600 cm^{-1} to check whether water is manifested in annealed glass and remains in it or it diffuses to the surface.

(The nominal position of this band accepted in the literature — 1630 cm^{-1}. The effect of the shift of the band position towards low wavenumber after high-temperature FA was previously observed in the amorphous SiO_2 [10].)

Fig. 3 shows that before annealing and after annealing with a duration of 2 h, the water band does not appear against the background of the noise track; after annealing for 24 h, a very weak band 1600 cm^{-1} appears; after annealing of 72 h, the clearly visible band manifested itself in the spectrum.

4. Discussion

The presented PL data (Fig. 1) indicate that the FA carried out as it stands (heating at a temperature of 480°C for 2, 24 and 72 h) caused a significant decrease in the concentration of point defects NOV and NBOHC in the volume of samples. This result extends the positive effect of FA to improve the functional properties of silica glass not only in terms of removing residual stresses arising at the stage of its synthesis and mechanical processing, but also by increasing the connectivity of the silicon-oxygen framework.

At the same time, the modification of the surface layer found in the study indicates some changes in microhardness. It was previously shown [11] that the compaction of films of amorphous SiO_2 during heating occurs as a result of the destruction of silanol groups and the departure of free water. It is this mechanism that has manifested itself in the surface layer of glass during FA. The density inhomogeneity across the thickness of the product occurring in some applications may be an undesirable effect.

As mentioned above, there is always a high concentration of bound water in the volume of silica glass synthesized from silicon chloride. When heated, the silanol groups disintegrate to form free molecules H_2O. However, steric obstacles do not allow water to leave the matrix. The accumulation of water reduces the microhardness of the material in volume (Table. 1), but the output of water from the surface layer creates (Table 2) spatial heterogeneity of the object.

5. Conclusion

The spectroscopic study of changes in the structure of silica glass subjected to fine annealing of various durations showed signs of its modification. The concentration of point defects NOV (≡Si−Si≡) and NBOHC (≡Si−O−) in the volume of samples decreased as the annealing duration increased. This is an important positive effect in addition to the relaxation of mechanical stresses in annealed glass. At the same time, after relatively long annealing, the appearance of a compacted layer on the glass surface was observed, which can be considered as a side negative effect of temperature exposure.

Conflict of interest

The authors declare that they have no conflict of interest.

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