

# **Carbon treatment as a method of the surface development of porous glasses**

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A method to develop the structure of the internal pore surface is proposed. The surface of porous silicate glasses is modified by impregnating carbon into the pores and subsequent anneal. The procedure is repeated several times. A technique to control the properties of the pore surface is proposed as well. Analysing the change in the features of photoluminescence spectrum as a result of such treatment in comparison with the pore-size distribution spectra allows us to assume formation of silicon nanoclusters in porous glass and to estimate their sizes. The nonmonotonic change of the surface development with simultaneous stationary increase of photoluminescence intensity is explained by composite pattern of the silicon clusters change during multiple carbon treatments.

## **1. Introduction**

The application area of porous glasses can be expanded owing to controllable change of their properties. One variant of such a change is the impregnation of various substances inside the pores. The impregnated substance can form a padding subsystem with its own properties, reinforced by the development of an internal surface of the porous glass, or to attach new properties to porous glass as a result of interaction with the walls of pores.

In our previous papers [1], [2] we explored changes in optical density, frequency profile of the electrical conductivity of porous glasses saturated with water solution  $\text{AgNO}_3$ , and also with water solutions of glucose of various concentrations. In works [3], [4], we showed that at high-temperature annealing with excess of decomposition point of glucose up to carbon, silicon nanoclusters are formed on the internal surface of pore walls in porous glass. Carbon saturated porous glasses are shown to be a material suitable for hologram recording. In the previous paper [5] we have observed a shift of photoluminescence spectral peak to

the short-waves for porous glasses containing nanoclusters created as a result of carbon treatment. This shift correlated with the changes of the pore size.

The results of the above investigations have prompted us to take up a more detailed study of the effects of carbon treatment in order to change the properties of the porous glass. The purpose of the present work is to observe the influence of consecutively repeated cycles of impregnation and annealing of carbon on the photoluminescent properties and on the development of the internal surface of porous glass.

## 2. Experimental

Porous samples were obtained by etching the sodium-boron phase from a sodium-boron-silicate glass ( $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ). After etching the sample was rinsed with distilled water and dried at 300 °C. The geometrical sizes of specimens equalled  $10 \times 20 \times 0.5 \text{ mm}^3$ . The samples represented microporous glasses with the high content of a high-disperse secondary silicon dioxide gel [6], [7].

The cycle of investigations consisted in recording the photoluminescence spectrum, and determining the fractional porosity of specimens as well as the size-distribution of pores. The sample was subjected to this complex of examinations after each cycle of carbon impregnation. The porosity and spectrum of size-distribution of pores were determined from results of the capacitive measurements of the water vapour adsorption-desorption [8].

The weighting on the torsion scales with the accuracy of  $5 \times 10^{-4} \text{ g}$  allowed determination of porosity. The photoluminescence spectra were recorded at excitation by nitrogen laser with a wavelength of 337 nm, pulse length 10 ns, recurrence rate 50 Hz, mean power 10 mW. The set up consisted of a quartz monochromator SF-4, photoelectric multiplier FEU-79, selective amplifier U2-8 and recorder H-307.

The treatment of specimens was performed on the following procedure. Previously samples were dried on the hot plate at 300 °C. Let us note that at this stage the high adsorption sensitivity of a sample is displayed. Weighting the still hot sample on the torsion scales immediately after drying shows an increase in weight upon cooling due to the imbibition of moisture from ambient atmosphere. In a typical case, weight was observed to change from 260 mg up to 267.5 mg in a few minutes which were necessary for the cooling process (*i.e.*, 7.5 mg of moisture was adsorbed during cooling). The weights of the sample being cooled down were compared at all stages.

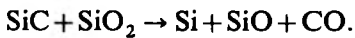
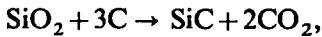
The specimens were soaked into the glucose solution for several hours at the next stage of the experiment. The soaking process was controlled visually. First, the immersion enlightenment was observed that was accompanied by appearance of typical gas bubbles at the surface of the specimen. In the end of the impregnation procedure only fine single bubbles were observed. This was the criterion of smallest voids filling.

The decomposition of the glucose up to carbon was being performed on the hot plate at 250–300 °C for about ten minutes while the sample became deep-brown uniformly over the entire surface. Then the sample was weighted again in order to

determine part of the carbon introduced. Absorption of moisture from the atmosphere decreased significantly at this stage. The specimen weight increased only from 274.5 to 276.5 mg (2 mg of water absorbed before weighting). This is an indication of hydrophilic pore surface transformation into the hydrophobic state by carbon treatment.

The full annealing of carbon was realised on the hot plate at 450–550 °C before complete refining of a sample. Weighting the sample from a hot state (266 mg) to complete cooling (267.5 mg) we see as before the low level of adsorption. For comparison of the results of gravimetric measurements we selected the weight values obtained for steady-state after cooling, bearing in mind the moisture adsorbed from ambient atmosphere.

Basing on the experience of works [3], [9], [10], we selected the carbon annealing temperature to be 450–550 °C. In this temperature range the pores did not collapse and the chemical reaction products were not encapsulated in closed pores:



This soft mode of processing increases the probability to obtain stable silicon nanoclusters. After weighting the photoluminescence spectrum was recorded (Fig. 1), and then the porosity measurements performed. The results are presented in Figs. 2 and 3. Here and below the initial sample is denoted by 0. The numbers along the x-axis are the numbers of carbon treatment cycles (maximum five glucose soaking-anneal procedures).

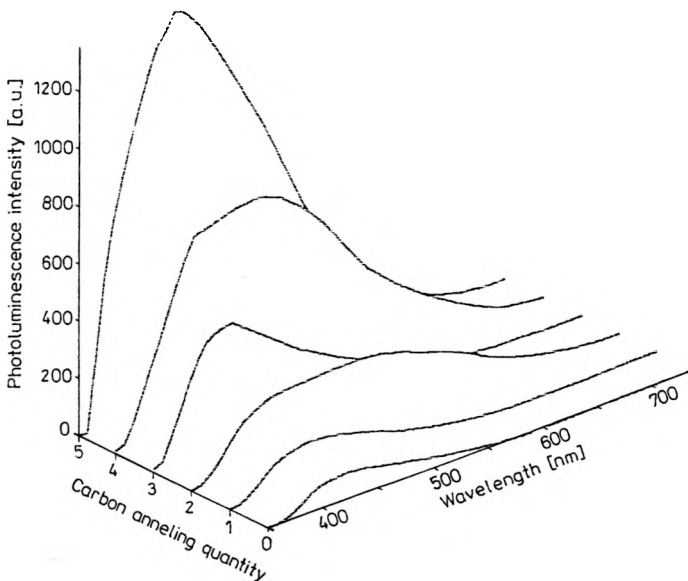


Fig. 1. Photoluminescence spectra after subsequent carbon treatment procedures.

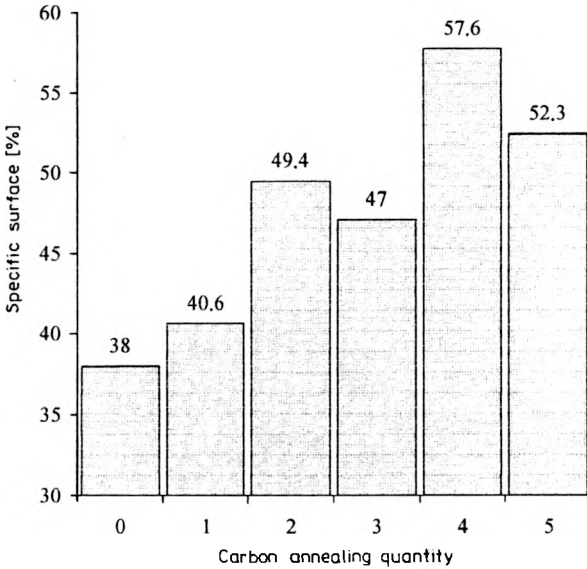


Fig. 2. Specimen surface after a number of carbon treatment procedures.

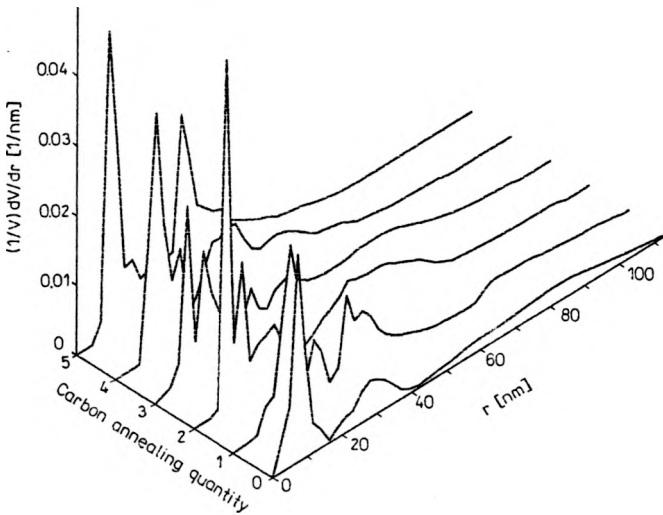


Fig. 3. Pore-size distribution after a number of carbon treatment procedures.

### 3. Results and discussion

Figure 1 shows diagrams of the photoluminescence spectra of a sample after each cycle of carbon annealing. Two peaks (420 and 500 nm), present either simultaneously or alternately in all the spectra, are distinct. Figure 2 shows the change of specific surface determined from results of the water vapour adsorption-desorption measurement. Note that in our experiment no removal of mass after each cycle of carbon

annealing was observed, and that is why, in reality, we should speak about an internal surface development ( $\Delta V/V$ ) rather than about fractional porosity ( $\Delta m/m$ ). With sample weight being invariant a nonmonotonic increase of the internal surface development was observed. This happens in course of the nonlinear but monotonous photoluminescence intensity increase. The spectrum changes periodically due to redistribution of intensity between the two mentioned bands.

In work [9] we observed a similar evolution of the photoluminescence spectrum at various temperatures and time of carbon annealing in porous glasses. This confirms our assumptions about formation of the next fraction of the silicon nanoparticles during each consecutive annealing of carbon with simultaneous after-oxidation of the silicon clusters formed in the previous cycle.

Also the changes in a pore-size distribution spectrum are not monotonic (Fig. 3) However, the nonmonotonous pore surface development accompanied by photoluminescence intensity monotonous increase can be explained by scaling effects. This is due to changes in pore sizes that effect formation of silicon clusters at the walls of these pores during carbon anenaling. Thus, as the silicon clusters, changing their sizes during the subsequent cycles of carbon annealing, remain inside pores, the free space between them also varies. It explains oscillating behaviour of the pore size distributions but with stable increase of the share of the large pores. Photoluminescence intensity increases after subsequent carbon treatment procedures (Fig. 4). This supports the assumption of the silicon cluster number increase. The intensity redistribution of two maxima in the photoluminescence spectrum also confirms the fact that the silicon nanoclusters undergoing alternations in their sizes are sources of luminescence.

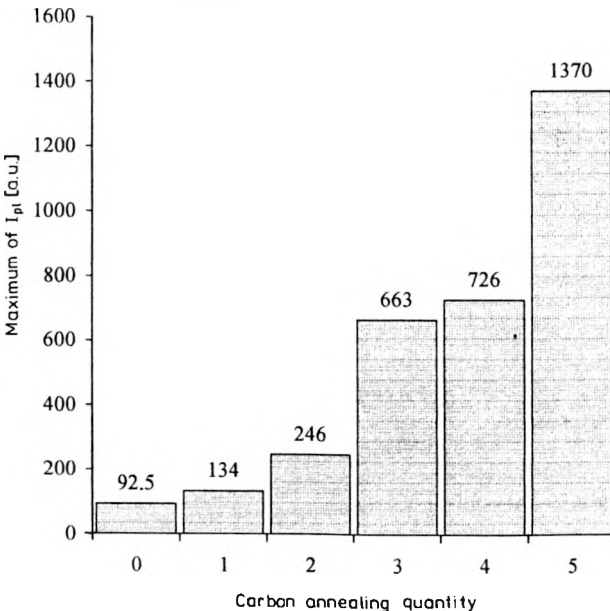


Fig. 4. Photoluminescence peak intensity vs. the number of carbon treatment procedures.

## 4. Conclusions

The proposed carbon processing technique can be used for the development of the internal pore surface in silica porous glasses. Positions of photoluminescence spectra peak can be controllably by repeating the carbon processing cycles.

The discussed method is also a convenient tool to study the influence of the glass manufacturing prehistory at the stage of phase separation on the porous structure.

*Acknowledgments* – This work was financially supported by the Polish Committee for Scientific Research (KBN), under grant No. 7T08D 00419.

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*Received September 18, 2000*