

Visible and infrared luminescence of porous silica glasses

A. V. ALEXEEV-POPOV, S. A. GEVELUK, A. V. KARPOV, YA. A. ROIZIN

Noncrystalline Electronics Systems Department, Odessa State University, Odessa, Ukraine.

E. RYSIAKIEWICZ-PASEK

Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland.

We have studied luminescence of silica porous glasses excited by the UV laser. Two wide peaks with maxima at about 540 and 740 nm were observed. They did not change after thermal treatment at 200° C and thus were not attributed to the capillar water. After the treatment in hexamethyldisilazane the peak at 740 nm completely vanished. We argue that this peak is due to the water molecules, chemically bonded on the surface of voids and that visible luminescence is connected with silicon enriched regions (silicon clusters).

1. Introduction

Porous silica glasses are promising materials for different applications. They are widely used as microporous filters and absorbents with easily changed parameters [1], [2]. The most interesting application is, probably, the possibility of phase hologram recording in porous glasses filled with different photosensitive substances.

Many interesting physical phenomena were registered in porous glasses [3], [4]. These materials have a pronounced luminescence both in visible and infrared spectral regions. The physical origin of this luminescence is not clear enough. The peculiarities of luminescence spectra are in many ways similar to those of porous silicon [5]. From this point of view, porous silica glasses can be considered as the model media with the developed fractal structure incorporating low-disperse silicon particles. In this paper we discuss the observed effects of surface treatments on the luminescence spectra with the aim to reveal the nature of luminescence processes.

2. Experiments

2.1. Preparation of porous glasses

Porous glasses employed in our experiments were fabricated by etching of borosilicate glasses ($\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$) in acid solutions. Two types of samples were investigated. Samples of the first group were made of sodium borosilicate glasses not subjected to thermal treatments. Phase separation initially existed in these glasses.

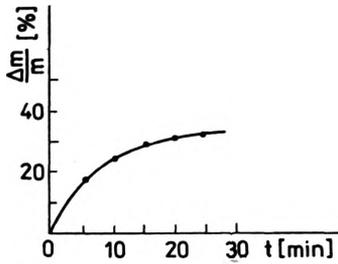


Fig. 1. Mass decrease of porous glasses as a function of the etching time

Second group of samples was thermally treated at 650°C for 22 hours before etching to enhance phase separation. The samples were etched in 0.5 N HCl at $50-60^{\circ}\text{C}$ for different periods of time (5–50 minutes) to remove the borate phase, then bathed in distilled water and dried at 140°C for 30 minutes. The decrease of mass dependence upon the etching time is shown in Fig. 1. All specimens were rectangular wafers ($10 \times 15 \times 0.5 \text{ mm}^3$) with nonpolished external surfaces. Their dimensions did not change after the etching procedure.

2.2. Structural investigations

Size distribution of voids was determined from desorption isotherms using modified Robert's theory [1]. The experimental setup consisted of a standard direct read-out analytic balance placed into the vacuum chamber. The pressure of alcohol and toluene vapours which had been used in these experiments was set in the range from 0.1 torr up to the saturation value at room temperature. The samples in vacuum chamber had been exposed to toluene vapours before the measurements in order to force out residual water absorbed on the walls of voids and the system was pumped out again. This procedure was repeated several times. The employed technique made it possible to reveal small voids (micro- and mesovoids according to the classification given in [1]). Voids with larger dimensions were observed using a scanning electron microscope. Both the surfaces of porous glasses and splits of porous glass wafers were studied, particularly fractal dimensions were calculated. Typical size distribution of voids for microporous samples is shown in Fig. 2.

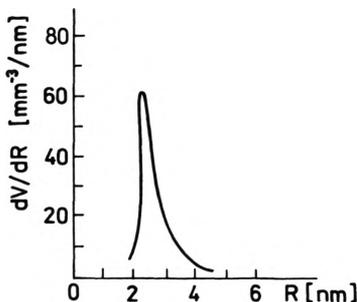


Fig. 2. Size distribution of voids for a microporous glass sample

2.3. Luminescence investigations

Photoluminescence spectra measurements were carried out by He-Cd or N₂ laser excitation. The wavelengths of the excitation light were 440 and 330 nm, average power density 0.4 and 0.25 W/cm². PL spectra were measured with SF-4 spectrometer. Since photoluminescence was very weak, we could not observe fine details of the spectra — resolution of our setup was about 30 nm. We have not found any significant difference between spectra, obtained with He-Cd and N₂ lasers. A typical spectrum for microporous glass samples, etched during 15 min, is shown in Fig. 3.

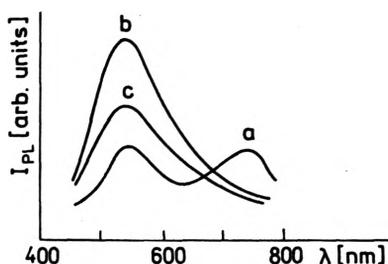


Fig. 3. Porous glass luminescence spectra. *a* — at 300 K, *b* — at 77 K (in liquid nitrogen), *c* — at 300 K (after nitrogen treatment)

Spectra for other etching times have the same shape with two wide bands with maxima at 540 and 740 nm, but differ significantly in intensity. Dependence of the peak intensity upon the etching time has a maximum at 15 min, and then decreases abruptly. Spectra for macroporous glasses are quite similar, but are an order of magnitude weaker. Then we measured PL of the sample drowned in liquid nitrogen (curve *b*, in Fig. 3). The intensity of IR band drops almost to zero, and the intensity of visible band increased about 5 times. Thus for the sample drowned in liquid nitrogen the PL spectrum consists of only one broad band with the maximum at about 540 nm. After slow heating back to 300 K in nitrogen ambient the intensity of visible luminescence decreased, but still was about 1.5 times higher than before cooling (curve *c*, Fig. 3). The IR band did not restore in the nitrogen ambient, but after being exposed to air for some time the shape and intensity of the spectrum became the same as before cooling.

To determine whether the luminescence is connected with capillar water in the volume of the voids, some samples were subjected to thermal treatment at 150–200°C, but that did not change either the shape or the intensity of the luminescence spectrum.

To determine the influence of chemisorbed and physisorbed water, the samples were annealed at 500°C. This treatment is known to eliminate chemisorbed water [1]. The effect was the same as after nitrogen treatment — visible luminescence increased, then after exposure to ambient air the spectrum restored its initial shape.

To confirm the influence of chemisorption and physisorption of water on the surface of voids, the samples were treated in hexamethyldisilazane (HMDS). It is known [3] that HMDS can effectively reduce the number of surface silanol groups,

substituting them by apolar methyl groups



After that the physisorption of water molecules



became impossible. The resulting change of luminescence spectra is shown in Fig. 4. The effect is very similar to the previous case. The infrared band almost completely vanished after HMDS treatment, while the visible band intensity increased about 1.5–2 times. This effect does not vanish after keeping the samples at room ambient, which is consistent with the known data about stable hydrophobic effect of HMDS treatment.

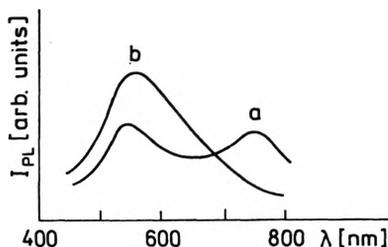


Fig. 4. Luminescence of porous glass at 300 K. *a* – initial, *b* – after treatment in HMDS

Both visible and infrared luminescence completely vanished after thermal treatment at 800°C for 10 min and was not restored.

3. Discussion

3.1. Infrared luminescence

It is known [1] that water in porous glasses can be in three different forms: chemisorbed water (silanol groups), physisorbed water (mostly connected with silanol groups) and free (capillar) water in the volume of voids. Since PL spectra did not change after thermal treatment at 200°C, though that treatment should significantly decrease the amount of capillar water, we argue that PL is not connected with capillar (free) water. HMDS treatment is known to eliminate most of silanol groups and, respectively, the water molecules physisorbed on these groups. Filling of the sample with liquid nitrogen pushes out the physisorbed water, not the silanol groups. We can thus conclude that infrared photoluminescence of porous glasses is connected with water molecules, physisorbed on the silanol groups on the surfaces of voids. This explanation is consistent with the observed nonmonotonous dependence of PL intensity upon the etching time. It is known [1] that in the last stages of the etching process slow increase of the volume occupied by voids takes place (see Fig. 1). This is due to the disappearance of smallest (subnanometer) voids. This corresponds to the decrease of the total surface of voids. Since PL centres

(silanol groups with physisorbed water) are mostly localized on the surface of voids, long etching times should decrease the PL intensity.

3.2. Visible luminescence

The origin of visible (green) band on photoluminescence is not quite clear yet. The dependence of intensity upon the etching time is the same as for the IR luminescence. We can thus conclude that it is not connected with luminescence centres in the volume of the SiO_2 matrix but rather with surface traps. We can also assume that centres leading to the visible luminescence are localized in the vicinity of IR centres. This follows from the fact that the intensity of visible luminescence increases when IR luminescence decrease is observed. It is known that silanol groups, which are responsible for IR luminescence, are formed from siloxane (SiOSi) groups on the surface. We can assume that visible luminescence is connected with the places in the SiO_2 matrix with local excess of silicon (silicon clusters). Annealing at 800°C leads to the oxidation of these clusters, so that the luminescence vanishes. It is known that silicon particles in SiO_2 matrix give rise to luminescence in the near infrared range, while the position of the PL band maximum depends upon the size of the particles [4]. Decreasing of the sizes shifts the peak from the infrared region to the visible one. Similar behaviour is known for the luminescence spectra of porous silicon [5]. In this case etching shifts the peak of luminescence to the visible region too. We argue that there is a deep analogy between above-mentioned materials and our porous glasses. In our case visible luminescence is due to silicon clusters existing in the SiO_2 matrix, while the IR luminescence can be attributed to the water molecules bounded with silanol groups located in the vicinity of these clusters.

Acknowledgements – The authors would like to thank Professor V. M. Belous for valuable discussion, and Dr S. Zhukov for his assistance in luminescence measurements.

This work was partially supported under the Research Project KBN 75201 078 06.

References

- [1] ZHDANOV S. P., *J. Mend. Chem. Soc.* **34** (1989), 298.
- [2] JANOWSKI E., HEYER W., *Porous Glasses*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1982.
- [3] OLTHIUS W., BERGVELD P., *On the charge storage and decay mechanism in silicon dioxide*, [In] *Proc. 7th Intern. Symposium on Electrets*, Berlin 1991, p. 16.
- [4] OSAKA YU., TSUNETOMO K., TOYOMURA F., MYOREN H., KOHNO K., *Jpn. J. Appl. Phys.* **31** (1992), L365.
- [5] KOMPAN M. E., LAIKKO R., *Sov. Solid State Phys.* **35** (1993), 365.

Received June 6, 1994