Optica Applicata, Vol. XXX, No. 4, 2000

Linear extension of porous glasses with modified internal surface in humid environment

SERGEY A. GEVELYUK, IGOR K. DOYCHO, DENNIS E. LISHCHUK, LUDWIG P. PROKOPOVICH, EUGENY D. SAFRONSKY

Odessa State University, Petra Velikogo 2, 270100 Odessa, Ukraine.

EWA RYSIAKIEWICZ-PASEK

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

YAKOV O. ROIZIN

Tower Semiconductor LTD, Migdal Haemek, Israel.

An original interferometric technique for investigating the inflence of humidity on change in linear dimensions of porous silica glasses is developed. The linear dimensions of a specimen are shown to change as a result of competition in the system of compressive capillary forces and expansion forces arising from the swelling of the residual silica gel present in pores. The possibility of selective inhibition of the capillary squeezing forces or the silica gel expansion forces by the pre-treatment of a porous material by a hydrophobized composition (hexamethyldisilazane – HMDS) or by annealing of carbon impregnated inside of pores is shown experimentally.

1. Introduction

A number of our previous papers [1], [2] are devoted to practical application of porous glasses. The porous glasses were obtained by etching of a sodium borate phase from two-phase sodium borosilicate glasses [3]–[5]. The impregnation inside of pores of the various substances promotes further expansion of practical application potential of the specified material. Such a treatment essentially changes the properties of the material, and besides it can be utilized as a research technique for porous glasses. In work [6], the possibility of making optical filters of varying absorption edges by impregnation of carbon into porous glass is shown. Papers [7] and [8] are devoted to further investigation of the influence of impregnated carbon on the properties of porous glasses, in particular, to research on a change in photoluminescence spectra and formation of silicon nanoclusters inside pores after annealing the introduced carbon. The fundamental role the above clusters play in the explanation of photoluminescent properties is emphasised in work [9], in which the comparison of changes in photoluminescence spectra of porous glasses and porous silicon subjected to such carbon treatment is carried out in practice.

The annealing of the impregnated carbon influences on the pore size distribution [10]. This allows us to assume that influence of this treatment on the porous sample linear dimensions dependence on humidity must exist. Such dependences were compared with the similar temperature dependence [11]. The last one is much feeble, and so we neglected it. At the same time the humidity dependence is very sensitive to peculiarities of two-phase glass manufacturing and to post-treatments [12]. This allows us to consider the above measurements as a method of studying the porous glasses structural properties. In works [13], [14] it is also emphasized that the carbon treatment influences not only changes in the photoluminescence spectra of porous glass, but also the dependence of the specific elongation of porous glass on humidity, which confirms the urgency of research undertaken in the present work.

2. Experimental

A set-up consisting of a Michelson interferometer was utilized to study elongation of porous glasses. It included a movable mirror located in the chamber with controlled humidity [9]. Specimens that had received the carbon treatment as well as those hydrophobized in the HMDS were measured using this set-up. The He-Ne laser with the wavelength 633 nm was used as a source of radiation. The humidity changed in ranges from 10% up to 95%. The technique yields direct results and its advantage is rather high precision (0.001%). Besides, it allows us not only to detect general failure of the porous glasses behaviour upon change of humidity, but also to separate the contributions of competing capillary forces and forces connected with the bloating

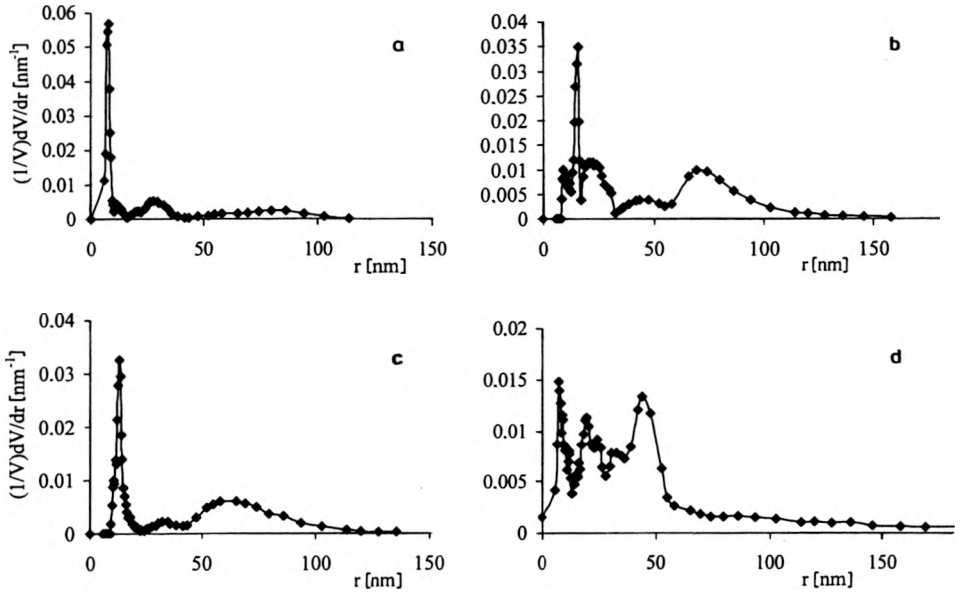

Fig. 1. Pore-size distribution spectra for four types of porous glasses: a — specimen A, b — specimen B, c — specimen C, d — specimen D.

of a high-dispersed secondary silica gel. The main deficiency of the method is duration of measurements, which can continue from ten hours up to several days depending on dominant pore size (till the equilibrium between the atmosphere inside the chamber and the pressure of water vapour inside the sample will have been stabilized). Besides, it is impossible to take measurements when humidity exceeds 95%, as the fogging of the chamber results in a laser beam scattering and disappearance of a fringe pattern.

For research purposes, four types of porous specimens (A, B, C, D) were fabricated from two-phase sodium borosilicate glasses, differing in temperature of phase separation (490 °C for A and B types of glasses, 650 °C for C and D types of glasses) as well as in after-treatment in KOH for removal of high-disperesed secondary silica gel. The B and D types of samples were obtained from glasses types of A and C just by such an after-treatment. The pore-size distribution spectra (Fig. 1) for all 4 types of glasses and also the specific porosity values were obtained by the adsorption-desorption method [2].

3. Results and discussion

Figure 1 shows that the phase separation process at 650 °C results in the formation of larger pores. A comparison of the pore-size distribution spectra for the A and B or C and D types of specimens shows that the removal of high-dispersed secondary silica gel leads to magnification of the pore sizes.

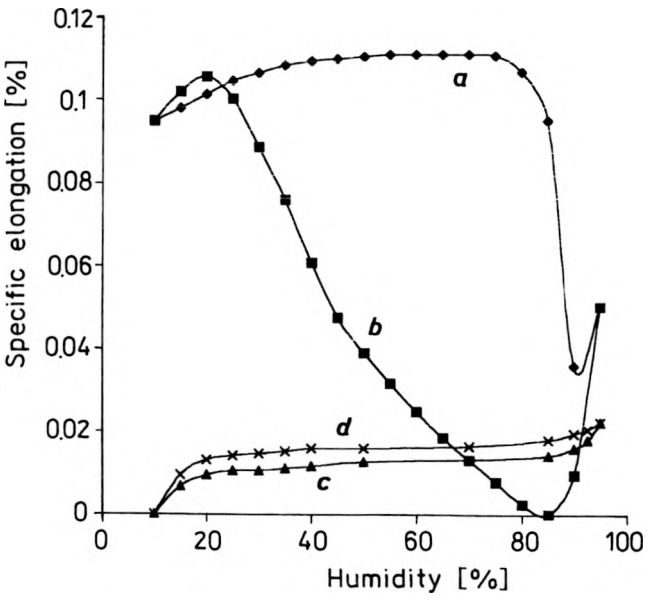

Fig. 2. Specific elongation of A-type of specimens as a function of humidity: *a* — adsorption curve of initial sample, *b* — desorption curve of initial sample, *c* — adsorption curve after HMDS treatment, *d* — desorption curve after HMDS treatment.

Figure 2 presents the adsorption-desorption curves of the specific elongation dependence on the humidity for A-type porous glass samples. A smoothly varying increase of the sample linear dimensions is observed upon the bloating of the high-dispersed secondary silica gel on the surface of pores during adsorption of water vapour (curve *a*). The strong and prompt downsizing of a sample at humidity ranging from 85% up to 95% is explained by the occurrence of the capillary squeezing forces in the small sized pores orifice. The final expansion can be explained by redistribution of water inside the pores, in particular, by the intrinsic capillary effects. This proves to be true also by visual inspection: during humidification the diffuse-transparent sample becomes white and opaque at first, and then it becomes practically transparent upon the achievement of immersion filling at 95% dampness. All changes are repeated in reverse order at desorption (curve *b*). The curves *c* and *d* correspond to similar dependences of the same sample after its treatment by the hydrophobized solution HMDS. It is necessary to pay attention to sharp diminution of sample hygroscopicity that is explained by the increased water-repellent property, which almost completely excluded the meniscus formation. The dependence changes for the opposite one. This indicates prevalence of capillary forces in an initial A-type specimen. Although the expansion over bloating of the high-dispersed secondary silica gel essentially decreases, it does not completely disappear.

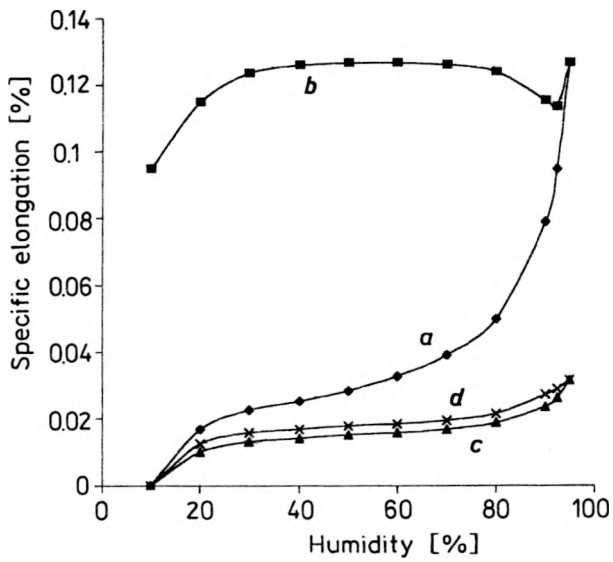

Fig. 3. Same as in Fig 4, but for B-type of specimens.

The initial B-type sample behaves differently (Fig. 3). The pores that are bigger in size do not provide now any appreciable capillary squeezing forces, but there is still sufficient amount of secondary silica gel, therefore the forces of tension become dominant. The absence of competing squeezing forces leads to a destruction

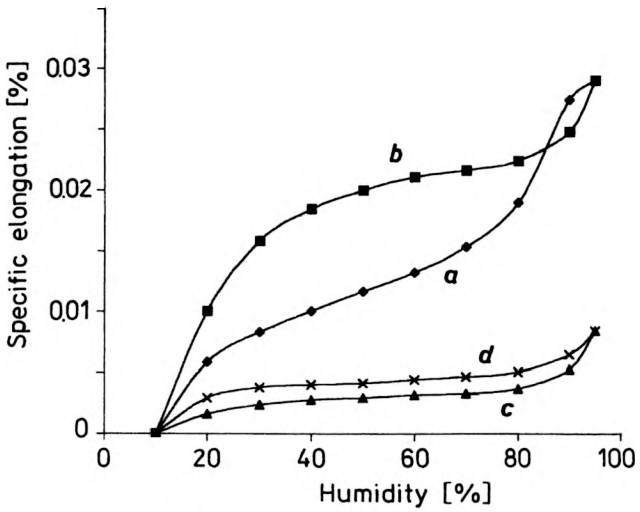

Fig. 4. Same as in Fig. 3, but for C-type of specimens.

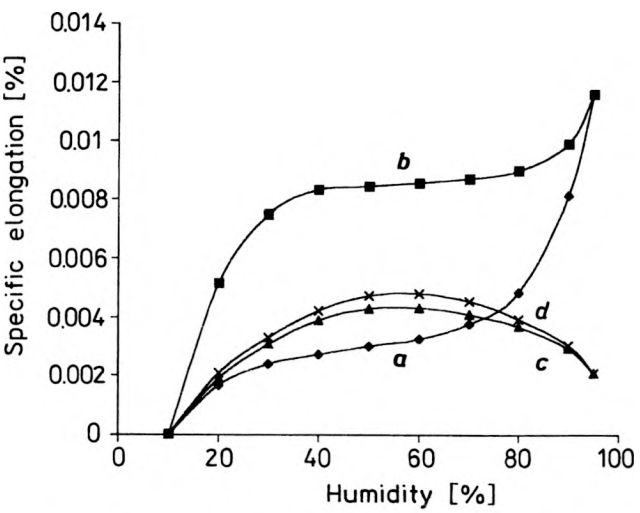

Fig. 5. Same as in Fig. 4, but for D-type of specimens.

of a sample, which is confirmed by non-reproductivity of its initial sizes upon termination of an adsorption-desorption cycle. The treatment by HMDS leads to the same effect as in the case of sample A.

The C-type samples (Fig. 4) and, especially, D-type ones (Fig. 5) reveal an absence of capillary squeezing forces and considerably smaller sensitivity to moisture, which, apparently, may be explained by significantly lower content of the secondary silica gel in them.

The carbon treatment effect on the specific elongation dependence humidity was pronounced mostly for A-type specimens. This is supposed to be due to the greatest

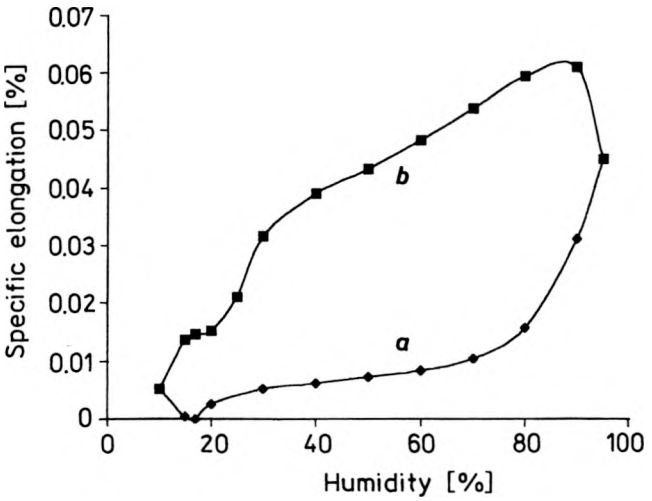

Fig. 6. Specific elongation of A-type of specimens after carbon treatment as a function of humidity: *a* — adsorption curve, *b* — desorption curve.

content of the secondary silica gel and the prevalence of the small-size pores. The carbon annealing leaded to the almost complete disappearance of the squeezing forces and to the increase of the sample wetting ability (Fig. 6). We explain this behaviour by the formation of silica particles that lead to the increase of the porous glass active interior surface with the pronounced hydrophilic.

4. Conclusions

The results of researches demonstrate that the proposed technique is efficient in the studies of porous glasses that underwent different post-fabrication treatments. Procedures which allow us to change porous glass absorption were developed. We can increase the interior surface and water absorption by creating silicon clusters inside the pores and to suppress absorption by HMDS treatment.

Acknowledgments — This work was financially supported by the State Committe for Scientific Research (KBN), Poland, under grant No. 7T08D 00419.

References

[1] ALEXEEV-POPOV A.V., ROIZIN YA.O., RYSIAKIEWICZ-PASEK E., *et al.*, Opt. Mater. **2** (1993), 249.
[2] SAFRONSKY E.D., ROIZIN YA. O., RYSIAKIEWICZ-PASEK E., Opt. Mater. **5** (1996), 217.
[3] MACEDO P.B., SANTANA M., SIMONS J., Patent U.S.A. No. 4188196, 1980.
[4] JANOWSKI F., HEYER W., *Porous Glasses*, VEB Deutcher Verlag für Grundstoffindustrie, Leipzig 1982.
[5] MAZURIN O.V., *Multicomponent Glasses*, Nauka, Leningrad 1991.
[6] RYSIAKIEWICZ-PASEK E., ROIZIN YA.O., MARCZUK K., *et al.*, Molecular Crys. Liquid Cryst. **230** (1993), 197.

[7] ROIZIN YA. O., ALEXEEV-POPOV A. V., GEVELYUK S. A., *et al.*, Phys. Chem. Glasses **37** (1996), 196.
[8] ROIZIN AA. O., KORLYAKOV A. B., GEVELYUK S. A., Proc. MRS, 1994. p. 346.
[9] GEVELYUK A. A., DOYCHO I. K., PROKOPOVICH L. P., *et al.*, Polish Ceramic Bull. **19**, Ceramics **57** (1998), 59.
[10] GEVELYUK S. A., DOYCHO I. K., KOVALENKO M. P., *et al.*, *The influence of humidity on the linear dimensions of porous sol-gel and silica glasses*, J. Porous Materials, in press.
[11] ROIZIN YA. O., GEVELYUK S. A., PROKOPOVICH L. P., *et* l., J. Porous Mater. **4** (1997), 151.
[12] Gevelyuk S. A., DOYCHO I. K., RYSIAKIEWICZ-PASEK E., *et al.*, J. Porous Mat. **7** (2000), 465.
[13] SAVIN D. P., GEVELYUK S. A., ROIZIN YA. O., *et al.*, Appl. Phys. Lett. **72** (1998), 3005.
[14] MAMYSHKIN A. I., MOSHNIKOV V. A., ILJIN A. YU, Fiz. Tekh. Poluprovodn. **32** (1998), 356.

Received September 18, 2000