UDC 621.315.592

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AN INTERFEROMETRIC METHOD OF INNER SURFACE MORPHOLOGY INVESTIGATION IN POROUS GLASS

A method of inner surface morphology investigation in porous glass using modified Michelson's interferometer is presented. The possibility of residual silica gel detection in pores by interferometric measurements is shown. The method also allows to distinguish the role of compressing and stretching forces in the mechanical deformation of porous samples. The proposed method is convenient to study the effect of additional treatments on the removal of residual silica gel out of porous glasses. Interferometric measurements make it possible to minimize the mechanical deformations of a porous layer on a solid substrate by tuning the layers thickness ratio.

1. INTRODUCTION

Porous glasses are promising as media for fabrication of holographic optical elements [1]. When making specified devices, silica porous glasses having high temperature stability are used. This property profitably distinguishes them from other materials that can be used for manufacturing volumetric holographic elements. However, presence of micropores results in the dependence of the mechanical properties of silica porous glasses on humidity. Change of corresponding samples' linear sizes after water absorption are 2—3 orders higher than for temperature expansion [2]. It is possible to remove or weaken this dependence by additional treatments of the material. The proposed research technique of humidity influence on the linear sizes of porous media suits ideally for monitoring of benefits of these treatments.

Besides traditional applications, ophthalmology (eye prosthetics) may become a potential customer. We have developed the scleral part of a compound eye artificial limb featuring a two-layer structure (a porous layer on solid glass substrate) [3]. The discussed in this paper technique allows us to optimize the thickness ratio between the substrate and the porous layer for minimizing of mechanical deformations when saturating the porous layer with antiseptic agent and its further drying.

Specified in [4] treatments of porous glasses fabricated by different technologies result in essential changes of their photoluminescent properties. Pore-sizes distributions change in parallel [5]. The discussed interferometric method is contactless and allows precision control of porous layer structure.

Thin dielectric layers incorporating nanosize particles (in particular, silicon nanocusters) are employed in modern microelectronics. Porous glass can be also considered as a model substance for studying clusters inside the pores [6]. The shape of these clusters is close to spherical [7]. Similar results were obtained by using the proposed technique in combination with photoluminescent studies [5, 8]. We succeeded to show that secondary silica gel has dominating role in formation of the silicon nanoparticles inside the porous glass.

2. EXPERIMENTAL PROCEDURE

We modified the Michelson's interferometer for studying humidity dependence of the linear sizes of porous specimens (Fig. 1). The mirror of the measuring shoulder was set in direct contact with the sample. The specimen (1) together with the mirror (2) was placed into the isolated chamber (3) and a mix of dry and wet air was passed through it. Humidity of the environment inside the chamber varied from 5 up to 100% using the gas supplying system (4). Humidity in the chamber was varied slowly, and the temperature

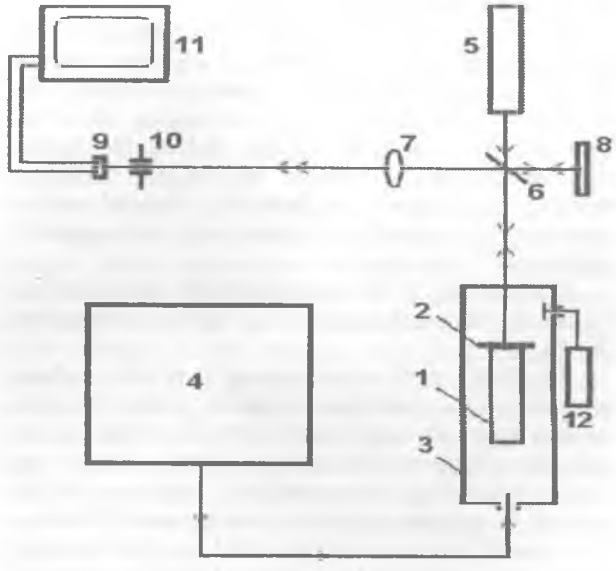

Fig. 1. Block-diagram of the setup for studying humidity dependency of porous glass linear sizes:

1 — specimen; *2* — movable mirror; *3* — isolated chamber; *4* — leak valves system; *5* — light source; *6* — half-transparent mirror; *7* — micro-objective; *8* — reference beam mirror; *9* — photo-detecting system; *10* — slot; *11* — computer; *12* — hygrometer

was kept constant to maintain quasi equilibrium and to maintain the measurements accuracy. The He-Ne laser (5) with the wave length of 632.8 nm was used as the light source. The beam of light is split by the semitransparent mirror (6); the penetrating beam is reflected from the movable mirror (2) and is directed with the mirror (6) on the micro-objective (7). The basic beam is brought there as well with the help of the mirror (8). The photo-detecting system consisting of two half-period biased photodiodes (9) with a slot (10) located in parallel to the interference lines is placed in the plane of the fringe pattern. Change of the linear sizes of the sample leads to the shift of the fringe pattern relative to the slot. The change of the linear sizes of the sample is proportional to the number of passing interference lines. One of the advantages of such a technique consists in the opportunity to ensure full relaxation of the sample at the given humidity (stopping of the fringe pattern motion relative to the photo-detecting system slot). The measurement was taken and the next value of humidity in the chamber was set after the pattern motion stopped. Accuracy of linear dimension measurements depends on the initial size of the sample and for lengths of 15 mm is $\sim 0.01\%$.

Measurements were performed with silica porous glasses of two various types fabricated by etching off the alkali-borate phase from two-phase sodium borosilicate glass. Initial glasses had split on phase separation temperature: 490 °C for A-samples or 650 °C for C-samples. The samples differed by porosity, surface morphology and contents of silica gel [9]. Silica glasses had interconnected pore structure. We measured the humidity dependence of relative elongation along the long side (15 mm) of the rectangular specimens.

Also the humidity dependence of the linear sizes change for porous glasses obtained by sol-gel technology [8, 10] was studied. These glasses have mono dispersive pore-size distribution and no secondary silica gel in the pores. The developed technique allows to clarify a number of features in humidity dependence of mechanical properties caused by this specific structure.

Formation of Si nanoclusters in different types of glasses was done by carbon processing [5, 6].

To study mechanical strength of silica glass, we fabricated two-layer samples with the thin porous layer on solid substrates of various thicknesses. A-type wafers with 0.5 mm, 1 mm, and 2 mm thickness were studied; thickness of the porous layer was constant and equaled 260 μm. We investigated humidity effect on the bending of specified wafers. One edge of the sample was fixed and bending deflection measurement was taken. The mirror of the Michelson's interferometer measuring shoulder was in contact with the porous layer, thus forward deflection corresponded to compression of the porous layer, while backward deflection corresponded to its expansion.

The humidity dependence of the bending deflection was studied in a similar manner for layers of porous silicon formed by anodization of p-type standard silicon wafers with 10 Ω·cm specific resistance, (100) orientation and 200 μm thickness. Anodization was performed in 1:1 ($HF(49\%):C_2H_5OH$) at room temperature and density of a current 10 mA/cm^2. Porous layers of different thickness were created by varying the etch time.

3. RESULTS

Humidity influence on the linear sizes was studied for porous A- and C-glasses. The curves presented at Fig. 2 reflect the influence of two forces: compressing capillary forces, caused by presence of micropores and stretching forces resulting from silica gel swelling.

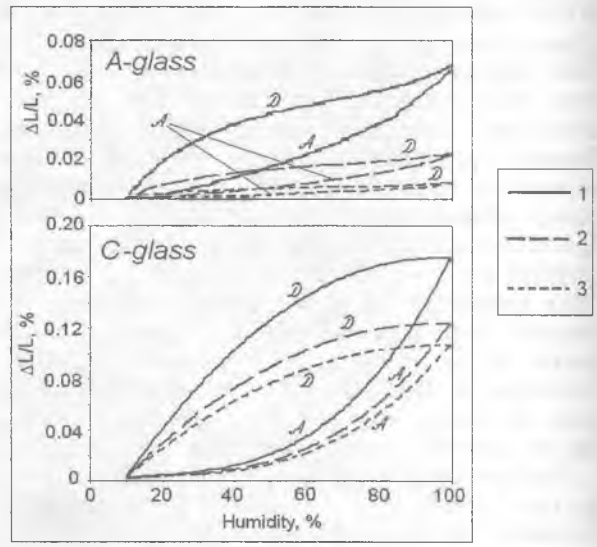

Fig. 2. Humidity dependence of relative elongation of porous silica glasses (*A* — adsorption curve, *D* — desorption curve):

1 — initial glass; *2* — after carbon processing; *3* — after HMDS processing

It is possible to separate the contribution of the swelling silica gel forces by carbon processing of the specimen. The specified treatment results in removal of silica gel out of the pores [4, 5] and simultaneously in its size increase. The forces of silica gel swelling are decreased with simultaneous decrease of capillary forces due to larger pore-sizes.

Fig. 2 shows the results of A- and C-glasses additional processing in hydrophobic mixture (HMDS — hexamethyldisilazane) that passivates the inner surface and reduces the pore kinetic diameter.

Similar dependences for glasses obtained by sol-gel technology are presented in Fig. 3. The inset in Fig. 3 shows pore-size distribution curves for this material.

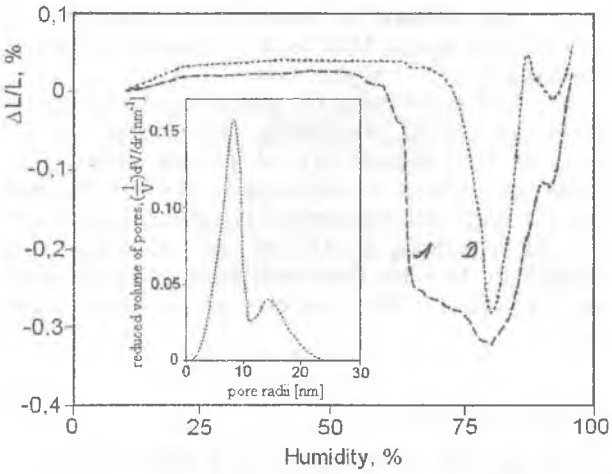

Fig. 3. Humidity dependence of the linear sizes of sol-gel glass during adsorption (*A*) and desorption (*D*). Shown in the inset is the pore-size distribution for the studied specimens

Results atmosphere humidity influence on the bending deflection of the two-layer A-type glass wafers are presented in Fig. 4. These wafers were found preferable for creating of scleral part of the compound eye artificial limb [11].

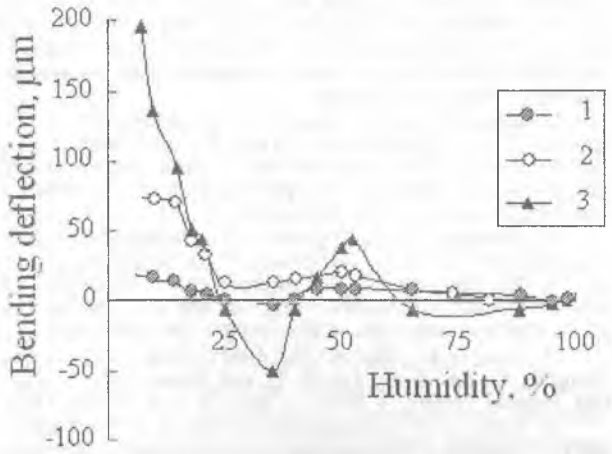

Fig. 4. Humidity dependency of two-layer silica glass bending (A-type). Only the desorption curves are shown:

1 — 2 mm specimen thickness; *2* — 1 mm specimen thickness; *3* — 0.5 mm specimen thickness

Similar researches of humidity dependence of the bending deflection of two-layer specimens were performed for porous silicon on silicon substrates. The two-layer structures were obtained by electrochemical etching [12] for 1, 2, and 3 hours (*a*-, *b*- and *c*-curves on the Fig. 5, respectively).

4. DISCUSSION

Comparison of measurement results of humidity effect on the linear sizes of A-type porous glass samples before and after carbon processing (Fig. 2) shows a decrease of the adsorption-desorption curves slope after carbon processing. We explain this fact by transformation of the most part of secondary silica gel into nanosize silicon clusters. It results in insignificant compression in humidity range from 5 up to 70% compared with essential expansion for the initial sample. We explain these differences by prevalence of capillary compression forces. It is necessary to note, that changes of the relative linear sizes are almost 3 times less for the carbon processing sample, than for the initial one in the whole humidity range. We explain it also by the decrease of silica gel amount in porous glass.

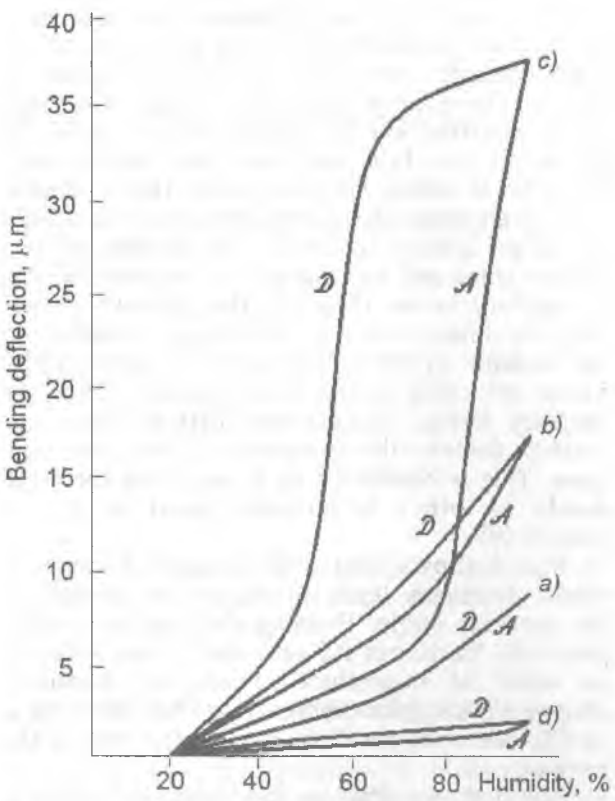

Fig. 5. Humidity dependencies of porous silicon on Si substrate samples bending:

a — anodization during 1 hour; *b* — anodization during 2 hours; *c* — anodization during 3 hours, *d* — anodization during 3 hours and subsequent HMDS processing

C-glasses are produced from a glass with larger phase separation temperature. Therefore, the pore sizes are one order of magnitude larger in them compared with A-samples (and the specific surface is one order of magnitude less, accordingly). Thus, there should be much less secondary silica gel in the finest pores of initial C-sample, than in the A-sample one. This fact is also confirmed by significantly smaller difference between humidity dependences of the linear sizes before and after carbon processing for these glasses (Fig. 2).

HMDS processing passivates the internal surface of the porous glass and suppresses the process of linear sizes change by reducing the kinetic pore diameter. It is well illustrated for A-glasses by Fig. 2. However, HMDS processing almost does not change the curves received after

carbon processing for C-glasses (corresponding curve don't presented on the Fig. 2 since it almost coincides with the curve 3 for C-glasses). This confirms once again, that large pores, not giving contribution to capillary forces, prevail in glasses of this type and also, that there is less silica gel in them, compared with the A-glasses.

The analysis of the appropriate dependences for sol-gel glasses confirms the absence of secondary silica gel and shows the dominating role of capillary forces (Fig. 3). The diagram shows, that the linear sizes of the sol-gel samples do not depend on humidity practically up to 70%. Sharp reduction of the sample sizes, caused by capillary forces, is observed further. Thus, our method detects the presence of two pore fractions. This is confirmed by porous size measurements by other techniques (inset in Fig. 3 shows) [9].

Fig. 4 shows that little change of the substrate thickness leads to significant change of the bending angle. Bending deflections of samples with thickness 0.5 mm and 2 mm differ in an order of magnitude. Thus, the humidity change in the measurement chamber from 98% to 7% does not result in any destruction of the sample.

Fig. 5 shows, that for the increase of etching time (and, accordingly, thickness of the porous layer), the hydro-sensibility of the sample increases too. Similar dependences were measured after processing of the most hydro-sensitive sample (etched for 3 hours) in hydrophobic mixture (HMDS). It is possible to conclude from results of these measurements (Fig. 5, *d*-curve) that the role of capillary compression forces is exclusive during the change of humidity for porous silicon and that hydrophilic impurity (like secondary silica gel) is practically absent in the porous silicon layer. Hydrophobisation of the pore surface prohibits from formation of capillary crosspieces in porous silicon. Fig. 5,˜d shows that the dependence on humidity disappears. Thus, the forces of capillary compression were the dominant cause of the deflection at increased humidity; while the silica gel swelling forces were absent (the deflection to the other side would be otherwise observed). We remind that the mirror of the Michelson's interferometer measuring shoulder is in contact with a porous layer.

5. CONCLUSION

The proposed above technique allows to detect secondary silica gel in porous glass from high accuracy linear dimensions measurements in atmosphere with different humidity. This technique also allows to separate contributions of competitive forces that lead to mechanical deformations.

Special processing (in particular, low-temperature anneal of previously introduced carbon) reduces hydrosensibility of porous glass. This treatment allows to distinguish the effects connected with fine-dispersing secondary silica gel.

The proposed technique can be used as a diagnostic tool for detection even of small silica gel impurities after various silica glass treatments.

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