Formation of a Conducting Phase in Porous Glasses

I. Doycho, Ya. Lepikh, L. Filevska, E. Rysiakiewicz-Pasek, and V. Grinevych

Abstract A method of embedding a conductive phase into porous glass is proposed for increasing the conductivity of high-resistance samples. The method is based on the processing of samples with carbon-containing substances in special thermodynamic conditions. It is demonstrated that using the method, it is possible to create a reliable ohmic contact to porous substances. This makes it possible to use systems based on porous glass as active elements of resistive sensors. The possibilities of the method are illustrated by the example of the creation of a resistive to humidity sensor, capable of operating in a wide range of temperatures not destroyable for the system.

1 Introduction

Materials often used as active elements of most environmental monitoring sensors are sensitive primarily at their near-surface layers. Therefore, in order to achieve the best sensitivity of the material, it is to be strived the maximum possible unfolding of its surface. This deployment can be achieved by dispersing particles of matter down to nanometer sizes. However, it is difficult to operate successfully with individual particles of the indicated sizes; therefore, they are placed in a certain matrix containing small cavities in the form of through slits. In this case, an ensemble of nanoparticles is formed, consisting of the mentioned small particles of the substance and the matrix itself, in which they are placed. Since the matrix is a part of the ensemble, it must comply with certain restrictions of not affecting the properties of the substance under study. One of the main of such limitations is chemical inertness, that is, the matrix should not enter into chemical interaction with the substance under study and change its (or its own) chemical composition. Secondly, it must

I. Doycho · Ya. Lepikh · L. Filevska (✉)
Odesa I.I. Mechnikov National University, Dvoryanska Str., 2, Odesa 65082, Ukraine
e-mail: lfilevska@gmail.com; liudmyla.filevska@pwr.edu.pl

L. Filevska · E. Rysiakiewicz-Pasek · V. Grinevych
Department of Experimental Physics, Wrocław University of Science and Technology, Wrocław, Poland

O. Fesenko and L. Yatsenko (eds.), *Nanoelectronics, Nanooptics, Nanochemistry and Nanobiotechnology, and Their Applications*, Springer Proceedings in Physics 297,
https://doi.org/10.1007/978-3-031-42708-4_15

have a sufficiently strong skeleton, which will prevent both the aggregation of the nanoparticles of the ensemble and the mechanical destruction of the created system. And finally, if we are interested in the luminescent properties of the particles that make up the ensemble, the matrix should not be luminescent in spectral regions of the substance. These requirements are perfectly met by sparse silicate glass with through cavities of nanometer dimensions. The sizes of interpenetrating slots can vary from a few nanometers to several hundreds of nanometers. In addition, the quartz skeleton of the compound is strong enough, therefore, which limits the size of the formed particles, since they cannot exaggerate the size of the gaps. The columnar structure of the glass makes it possible to influence both the inner surface of the slits and the nanoparticles created inside them. In the most cases, it is convenient to create these nanoparticles by saturating the matrix with solutions of suitable substances. It is possible to extract sparse silicate glass from two-phase soda-borosilicate glass using a not very complicated technology [1].

2 Types of Porous Silicate Glass and the Technology of Their Creation

Two-phase sodium borosilicate glass has a complex chemical formula $SiO_2 \times [Na_2O \times B_2O_3]$. Its components have different furnace temperatures; besides, the sodium-borate component is chemically less stable. Therefore, by choosing the right temperature regime for charge maintenance during phase separation, it is possible to achieve the desired degree of their interweaving. Subsequently, by etching the sodium-borate phase by appropriate chemical treatment, it is possible to obtain a silicate skeleton with a larger or smaller preferred gap size. In this case, the most dispersed quartz particles will precipitate inside the slots in the form of silica gel. Silica gel prevents the aggregation of the elements of the created nanoparticles' ensemble [2]; however, if necessary, it can be eliminated by additional chemical treatment [3, 4]. Types of porous silicate glasses with column structure depending on the thermodynamic conditions of their production and subsequent chemical processing are shown in Table 1.

The water absorption–desorption method [5] for each of the indicated types of borehole silicate glass revealed the size distribution of slots. The corresponding

Table 1 Types of porous silicate glasses with column structure

	The low-phase separation temperature in the original glass is 490 °C	The high-phase separation temperature in the original glass is 650 °C
Type of glass after etching of the unstable phase	A	C
Type of glass after tinning	B	D

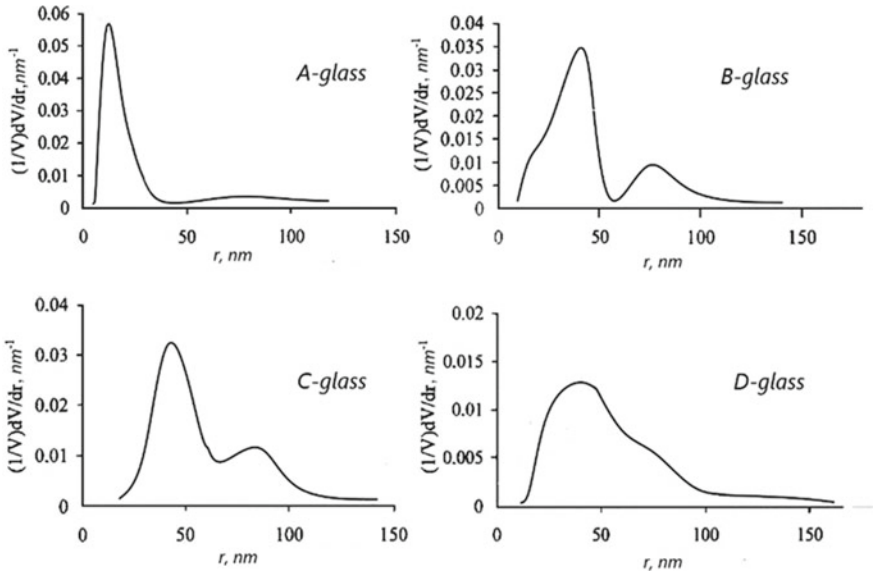

Fig. 1 Size distribution of pores for different types of porous glasses, obtained by the water adsorption/desorption method

graphs are shown in Fig. 1, from which it can be seen that glasses of all types have two preferred phases of the slot sizes. At the same time, glasses of types C and B are most similar in this parameter. In glasses of type D, these phases are almost not traced, and glasses of type A are the most finely spun. The similarity of pores' size distribution for glasses C and B is not of the same nature. In the first case, the spectra have the indicated form due to the silica gel in the slits, and in the second case, due to the etching of the slits in the finely scalded glass of type A. It should be noted that insignificant residues of stack gel remain in the slits of type B glass [1, 4].

3 Carbon Processing

Ensembles of nanoparticles formed in the matrix based on the specified glasses due to rather considerable intrinsic electrical resistance of such systems cause their usage mainly for luminescent-type sensors. At the present work, it is suggested to form inside the pores the nanoparticles' ensemble of a conducting substance for significant reduction of the sample resistance. This method will make it applicable as an active element in resistive-type sensors. Such substance is a carbon, which in the form of graphite exhibits excellent conductive properties, and because of this, the corresponding procedure is called carbon processing [6, 7].

Carbon treatment is able to reduce the electrical resistance of slotted glass samples by several orders of magnitude due to the inclusion of a conductive phase made of

graphite nanoparticles. This increase in conductivity can be beneficial for certain applications of certain types of glasses. In order to subject any type of glass to carbon treatment, it is saturated with a solution of a substance containing carbon. The best in this case is glucose: it is well soluble in water, and when heated to 180 °C, it is easily regenerated simply in the cavities of the matrix to carbon in the form of highly dispersed graphite with the release of water. The process is described by a well-known equation

$$C_6H_{12}O_6 \xrightarrow{(t)} 6C + 6H_2O,$$

which lasts about a day, and its completion can be judged visually by the blackening of the sample.

4 Creation of an Ohmic Contact to Porous Glass

One of the applications of carbon processing is the creation of an ohmic contact to a slotted glass sample [8]. This would make it possible to investigate a possible correlation between the luminescent and electrical properties of nanoscale systems in porous matrices. To achieve the specified goal, the carbon treatment of the system must be partial and is carried out as follows.

A standard sample of size 10 is immersed with the ends in a glucose solution to a depth of 0.5–1 mm using a clamp-like holder. This creates conditions that almost correspond to the typical problem of diffusion from a steady source. According to Fick's second law, at the stage of driving impurities into the system during time t at a distance x from the interface between the glucose solution and the plate, the glucose concentration C_x will occur

$$C_x = C_0 \mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right).$$

Here, C_0 is the initial concentration of the impregnative solution. The coefficient D is a certain analogue of the diffusion coefficient and is called the impregnation coefficient. It is significantly different from the diffusion coefficient, because, unlike it, it describes the penetration of not individual impurity atoms into the interatomic space of the sample, but the percolation of rather large glucose molecules into the nanoslits of the slotted glass, which are also quite large compared to the interatomic distances (see Fig. 1). The impregnation coefficient depends on the type of glass, more precisely its parameters such as porosity, pore size distribution, the presence of residual silica gel in the pores and its amount, as well as on the temperature at which the impregnation takes place.

The glucose distribution inside the slotted glass plate after it saturates the sample from both ends is schematically shown in Fig. 2. The depth of immersion of the plate

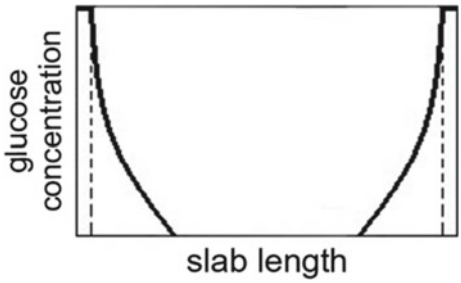

Fig. 2 Glucose distribution inside a slotted glass plate

into the solution is indicated by a dotted line. It is important that both curves do not show the configuration of the permeated glucose profile, but only reflect a decrease in its concentration when moving away from the source of impregnation.

It is noted that error function compliment converges rather slowly when expanded in a series. Therefore, for the analytical estimation of the concentration of permeated glucose at a small distance x from the source, expansion in the McLauren series is usually used, while at large distances, it is better to prefer the asymptotic representation of this function. For almost any specific case, it is enough to save only a few first terms in the corresponding expansions. Up to the first three terms in the first case, we have:

$$C_x \approx C_0\left[1 - \frac{2}{\sqrt{\pi}}\left(\frac{x}{2\sqrt{Dt}} - \frac{x^3}{6\sqrt{(Dt)^3}}\right)\right],$$

and in the second, respectively,

$$C_x \approx C_0\frac{\exp\left(-\left(\frac{x}{2\sqrt{Dt}}\right)^2\right)}{\left(\frac{x}{2\sqrt{Dt}}\right)\sqrt{\pi}}\left[1 - \frac{2Dt}{x^2} + \frac{12(Dt)^2}{x^4}\right].$$

Further, the slotted glass plate, which is saturated with glucose from both opposite ends, is subjected to annealing for the thermal decomposition of the penetrated glucose directly in the slots, during which the resulting graphite is simultaneously dispersed. This process is somewhat analogous to the diffusion from a confined source. If we assume that the concentration of glucose at the ends of the plate at the time of the start of the thermal decomposition procedure corresponds to C_0, and at an arbitrary point x was determined by the above equations and was equal to C_x, then the new concentration of C_{x1} at the moment of time t will be determined by the expression:

$$C_{x1} = C_x \exp\left(\frac{-x^2}{4Dt}\right).$$

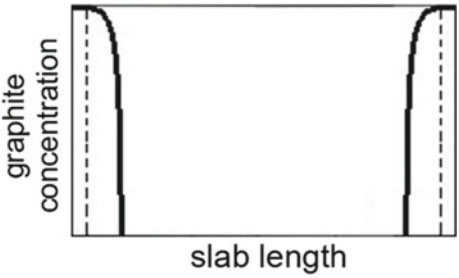

Fig. 3 Distribution of graphite nanoparticles in the formed ensemble

The distribution of graphite nanoparticles in the ensemble formed by the aforementioned heat treatment is shown in Fig. 3. Here, the depicted curves again do not correspond to the configuration of graphite in slotted glass, but only to a decrease in its amount when moving away from the end of the plate.

A comparison of the images in Figs. 2 and 3 shows that the graphite nanoparticles in the formed ensemble, unlike the glucose particles, are concentrated mainly near the ends, and when they are far from them, the specified concentration drops to zero quite quickly. In this way, areas with increased conductivity are formed at the ends of the plate, the presence of which does not affect the properties of the rest of the sample in any way. The indicated conductive sections smoothly transition into the slotted glass itself. Later, after processing the ends of the sample with any conductive paste, an ohmic contact with the slotted glass plate occurs.

5 Resistive Humidity Sensor Formed on Porous Glass

The simplest example of the practical use of an ohmic contact obtained in this way is the creation of a resistive humidity sensor on slotted glass [9].

Since the environment always contains a certain amount of moisture, then the slotted glass, like any other porous system, is capable of being saturated with water vapor by itself. The condition of hydrophilicity of the system in a wide range of humidity [10] corresponds to the presence of a wide range of crack sizes in any type of glass. Even in small quantities, their size can vary from about 10 to more than 100 nm (see Fig. 1). Due to the significant reduction of the electrical resistance of the system by water vapor, the use of slotted glass as an active element of a resistive humidity sensor would seem obvious [11, 12], but this is hindered by the very high electrical resistance of these compounds. For samples of standard size, it reaches many teraOhms, and its decrease with increasing environmental humidity even by tens of gigaOhms will remain almost imperceptible against this background. However, the use of carbon treatment not for the ends, but for the entire sample as a whole, can reduce the initial resistance of the obtained system by several orders of magnitude due to the conductive properties of graphite.

It should be noted that not every type of glass is suitable for use as a matrix for the active element of the humidity sensor. For example, type A glass is not suitable, because being saturated with an insufficient amount of glucose, its resistance after annealing will remain high, and excess glucose, turning into graphite nanoparticles after annealing, together with a large amount of residual silica gel, will fill the cracks and make the system insensitive to moisture. When processing type C glass, in addition to the mentioned drawback, it will be difficult to ensure reliable contact with it due to the increased roughness of the surface [13]. And in the case of type D glass, the conductive phase is generally able to shunt the sample. Therefore, type B glass should be considered suitable for use as a humidity sensor matrix. And in fact, it mostly contains quite small cracks with a small amount of silica gel, and it has a typical moderate surface roughness.

As a result of the carbon treatment of type B glass, in addition to the formation of an ensemble of graphite nanoparticles inside the glass, a graphite layer will be formed on its surface, which will provide a fairly reliable ohmic contact. The change in the resistance of the obtained system will be completely correlated with the humidity of the environment.

Figure 4 shows a typical dependence of the resistance of an ensemble of graphite nanoparticles in type B glass on humidity. The ensemble was formed by keeping the glass in a 40% aqueous glucose solution for a day, followed by annealing for two hours at 180 °C. Contacts to such a system were created using silicone paste. Measurements were made at room temperature. It can be seen that the decrease in system resistance when the relative humidity of the environment increases from 10 to 99% reaches three orders of magnitude.

It is notable that similar isotherms can be obtained at any temperature and they will hardly change. This statement applies even to negative temperatures, because at negative temperatures, air humidity is determined by the sublimation of ice. And

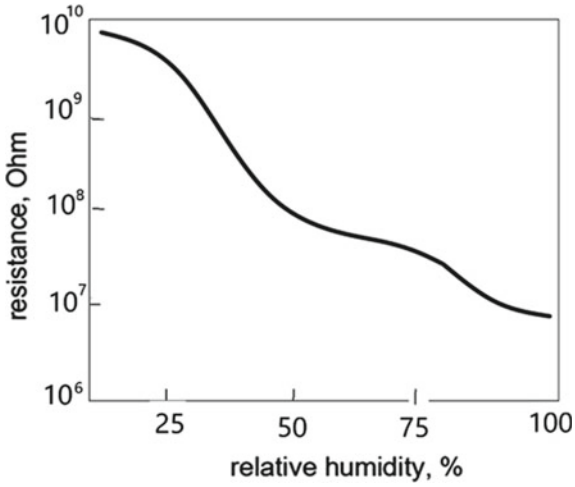

Fig. 4 Resistance–humidity dependence of graphite nanoparticles ensemble in type B glass at room temperature

individual water nanoparticles sorbed by the system are separated from each other by silica gel and graphite nanoparticles, so they are unchanged regardless of the surrounding temperature, and there is no aggregate state for them [13].

6 Conclusion

Carbon treatment leads to the formation of a conductive layer inside slotted glass of any type. This allows significantly reduce the initial electrical resistance of porous standard size glass.

Partial carbon treatment of standard samples of slotted glass allows to create at the ends of the sample an ohmic contact to an ensemble of nanoparticles in said glass for further applications.

A certain type of porous glass, after proper processing, may be used as an active element of a resistive-type humidity sensor, capable of operating at any temperature that does not destroy the system.

References

1. I.K. Doycho, Study of the photoluminescent properties of nanoparticles ensembles of dyes, ed. by V.A. Smyntyna, in *Non Equilibrious Processes in the Sensor Structures* (ONU (Odesa Mechnikov National University), Odesa, 2015), pp. 120–170
2. O.V. Tyurin, Y.M. Bercov, S.O. Zhukov, T.F. Levitskaya, S.A. Gevelyuk, I.K. Doycho, E. Rysiakiewicz-Pasek, Dye aggregation in porous glass. Opt. Appl. **40**(2), 311–321 (2010)
3. O.V. Mazurin, G.P. Roskova, V.I. Averianov, V. AntropovaT, *Biphasic glasses: structure, properties, applications* (NAUKA, Leningrad, 1991)
4. I.K. Doycho, V.S. Grinevych, L.M. Filevska, Porous silica glasses as a model medium for the formation of nanoparticles ensembles: review, in *Advanced Nanomaterials for Detection of CBRN, NATO Science for Peace and Security Series A: Chemistry and Biology*, pp. 283–294 (2020). https://doi.org/10.1007/978-94-024-2030-2_21
5. M.M. Dubinin, Kapilyarnye yavleniya i informatsiya o poristoy strukture adsorbentov, Izvestiya AN SSSR, ser. Khimicheskaya **1**, 101–125 (1978) (M.M. Dubinin, Capillary phenomena and information about the porous structure of adsorbents, Ed. of the USSR: Izvestiya of the Sov. Union Acad. of Sc. Chemical series Chemical **1**, 101–125 (1978))
6. S.A. Gevelyuk, I.K. Doycho, L.P. Prokopovich, E. Rysiakiewicz-Pasek, K. Marczuk, The influence of anneal of incorporated carbon on the photoluminescence properties of porous glass and porous silicon, ed. by L. Stoch, in *Polish Ceramic Bulletin 19, Ceramics 57, Porous and Special Glasses (Proceedings of the 4-th International Seminar PGL'98)* (Polish Ceramic Society, Krakow, 1998), pp. 59–64
7. S.A. Gevelyuk, I.K. Doycho, L.P. Prokopovich, E. Rysiakiewicz-Pasek, E.D. Safronsky, Influence of carbon multiple treatments on the photoelectrical properties of porous glasses. Radiat. Eff. Defects Solids **158**, 427–432 (2003). https://doi.org/10.1080/1042015022000037292
8. I.K. Doycho, Ya.I. Lepikh, Sposib vygotovlennya omichnogo kontaktu do shparystogo skla: MPK H01L21/28; B82B3/HO1L21/02 Zayavnyk ta patentovolodar Odesky Natsionalny universytet imeni I.I. Mechnukova.-N A2022 02802, zayavl. 25.07.2022 (Method for making ohmic contact to porous glass MPK H01L21/28 B82B3/00 HO1L21/02; Applicant and the Patent owner Odesa I.I. Mechnykov National university, Ukraine)

9. Ya.I. Lepikh, I.K. Doycho, Sensor vologosti na shparystomu skli: MPK G01N27/00/zayavnyk ta patentovolodar Odeski natsionalny universytet imeni I.I,Mechnykova. №: A2022 02804, zayavl. 25.07.2022 (Ya.I. Lepikh, I.K. Doycho, The humidity sensor on the porous glass: MPKG01N27/00 Applicant and The Patent Owner: Odesa I.I. Mechnykov National University, Ukraine, №: A2022 02804, app l. 25.07.2022)
10. H. Grange, J.-S. Danel, B. Desloges, V. Jousseaume, US patent 8739622 B2, Jun 3, 2014, G01N27/00
11. S.A. Gevelyuk, I.K. Doycho, E. Rysiakiewicz-Pasek, K. Marczuk, Relative changes of porous glass dimensions in humid ambiance. J. Porous Mater. **7**, 465–467 (2000)
12. S.A. Gevelyuk, I.K. Doycho, D.V. Lishchuk, L.P. Prokopovich, E.D. Safronsky, E. Rysiakiewicz-Pasek, Ya.O. Roizin, Linear extension of porous glasses with modified internal surface in humid environment, Optica Applicata **30**(4), 605–611 (2000)
13. E.D. Safronsky, Y.O. Roizin, E. Rysiakiewicz-Pasek, Application of porous glasses in oftalmic prostetic repair. J. Porous Mater. **11**, 21–29 (2004)