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Properties of silica porous glasses with the nanoparticle ensembles of some compounds. Review

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Properties porous silica glasses are systemized in this review. Also the methods of formation of the nanoparticles' ensembles of the substances, which are useful for the microelectronics, are described. Porous silica glasses are perspective due to their chemically resistance, mechanical strength and development of their inner surface. Own electrical resistance is too big for the porous glasses' specimens with standard sizes, that's why ones use them as matrixes for luminescence type of sensors mainly. The luminescent properties' dependence on the molecular structure of investigate substances (such as dyes and metal oxides), as well as on the nanoparticle ensemble technological formation condition is studied. It is revealed to which certain gases dyes of the specified type are sensitive and why it occurs in such manners. It is shown due to which of the described nano-size systems' properties sensitivity is appeared. Besides, one can embed a conductive phase into the pores of glass due to features of its structure. After such treatment one can use the porous glasses as matrix for formation of resistance type sensors.

Keywords: silica porous glass, luminescence, gas sensors, humidity sensors, carbon treatment, ohmic contacts, dyes.

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Introduction

Typically, the luminescent centers of the materials suitable for use as active elements of fluorescent gas sensors are located near the surface. This is understandable, because the changes in the gas composition of the environment primarily affect the near-surface matter layers. Therefore, in order to achieve these changes best registration, it is necessary to strive for the maximum possible development of the substance surface, which is able to be an active element of the gas sensor. This development can be achieved by dispersing the substance to nanometers (or almost molecular level in the case of a molecular crystal), because it is known that the total surface area of many small particles is always much larger than the surface of one large particle of the same volume. It should be emphasized that it is impossible to work fruitfully with nanometer size individual particle, so they should be placed in a system of some test tubes of appropriate size. The role of such a system of nano-sized tubes can be played by a matrix that contains small voids in the through pores form. This forms an ensemble of nanoparticles, consisting of these matter small particles and the matrix in which they are placed. Since the matrix is a part of the ensemble, it must meet certain restrictions, due to which its presence will not affect the test substance gas sensitivity and, moreover, will positively affect its luminescent properties. One of the main such limitations is chemical inertness, i.e. the matrix should not chemically interact with the test substance and change its (or its own) chemical composition. Secondly, it must have a fairly strong skeleton, which will prevent both the nanoparticle ensemble aggregation and the created system mechanical destruction. Finally, it should be non-luminescent (or glow in areas of the spectrum that are not relevant to the test substance). Some authors use polymers [1-2] or gelatin [1, 3] as a matrix. These compounds do not luminesce and are quite chemically inert. Due to their structure peculiarities, they are able to hold the clusters of the substance formed

inside them. However, these clusters can have arbitrary sizes and shapes, and their growth will not be restraining by polymer or gelatin, but on the contrary, they themselves will uncontrollably form the matrix skeleton. Porous silicate glass with nanometer-sized through voids is devoid of this defect. The interpenetrating pores size, can vary from a few nanometers to several hundred nanometers. In addition, compound quartz skeleton is quite durable, and therefore limits the particle size that are formed, because they cannot exceed the pores size. The glass columnar structure allows influencing both the pores inner surface and the nanoparticles created inside them. In most cases, these nanoparticles are conveniently created by saturating the matrix with certain substances solutions. Thus, porous silicate glass perfectly meets the requirements for the matrix, but it does not exist in nature. However, it can be obtained from two-phase sodium-boron-silicate glass by a not very sophisticate technology [4].

I. The porous silicate glass types and their creation technology

Two-phase sodium boron silicate glass has a rather complex chemical formula $SiO_2 \times [Na_2O \times B_2O_3]$. Such glass melting temperature exceeds 750°C. In addition, the melting temperature of the glass silicate component is much higher than the melting temperature of the sodium borate complex, and therefore there exists a temperature at which the glass sodium borate component is in a liquid state, while its silicate component is simply very hot. This state corresponds to a temperature of 650°C. If the burden for two-phase glass melting, which is brought to 750°C, is cooled adiabatically to 650°C, so that the phase separation occurs at the indicated temperature, the sodium borate complex will still melt, forming large bubbles, which will form a silicate skeleton. Due to the melt viscosity, it is kept in such conditions for several hundred hours, until the two phases are completely dissolved in each other, and then slowly cooled to room temperature. The obtained two-phase glass is enough large (up to hundreds of nanometers) areas of interposed silicate and sodium borate phases. These phases, specifically, show unequal chemical resistance, so that a mixture of hydrofluoric, nitric and glacial acids can completely erode the sodium borate phase, with almost no effect on the silicate phase, which leaves a quartz skeleton with through voids in place of etched borate phase. These voids are quite large, however, due to mutual dissolution, rather small, sandy SiO_2 particles got into the sodium borate phase, which after its etching must settle inside the resulting pores. Such settled sandy particles are called residual silica gel. Chemically, they are completely identical to the quartz skeleton and differ from it only in fineness. The resulting glass is conventionally called porous glass type *C*. Such glass is unsuitable for a number of applications, because due to large enough holes it will form test substance particles of significant size, so to achieve significant deployment of its surface will remain impossible.

To form smaller pores in the glass, it is necessary to change slightly the two-phase glass technological modes creating. The burden, for its melt should be adiabatically

cooled to a lower temperature, which is close to the sodium borate phase melting temperature, but some lower than it (about 490°C). If the burden is kept at this temperature for hundreds of hours, it will lead to the formation of sodium-borate phase of relatively small bubbles and, after cooling to room temperature, the phases will separate, resulting in two-phase glass with small (about tens of nanometers) areas of interwoven silicate and sodium borate phases. After etching the unstable sodium borate phase as described above, enough fine-grained silicate glass is formed, which will also contain residual silica gel in the pores. The resulting glass is conventionally called porous glass type A.

The presence of silica gel inside the pores, depending on a particular scientific problem conditions, can be both desirable and harmful. Thus, the presence of silica gel makes the glass more fine-grained, but at the same time reduces the free space for the nanoparticle test substance formation. On the other hand, the presence of silica gel improves the glass adsorption properties, but deteriorates its mechanical properties (due to gel swelling in a humid environment, the sample may deform [5-7]). Although special treatment can improve the glass mechanical properties, but it will not always have a positive effect on its other properties [8]. Within the problem of the surface substance suitable expansion as some sensor active element, the separative ability of silica gel is certainly useful, which prevents the aggregation process of particles formed an ensemble in the pores [1, 9]. However, for cases where the presence of silica gel in the pores is harmful, the lixiviate techniques, have been developed in [10], can be used. In this manner the glass can be depleted with silica gel or this technique quite deprive the glass of this formation. According to this technique, the finished glass is etched in an alkaline etchant based on KOH. This etchant interacts enough quickly with finely divided silica gel and acts much more slowly on solid (at least porous) matrix walls. Due to this, most of the silica gel is removed, while the walls of the matrix skeleton are only slightly etched [4, 11]. The type A glass treated in this way is conventionally called the type B glass, and the type C glass is called the type D glass.

Figure 1 shows the results of the structure of all 4 the above noted types glasses investigation using an electron microscope. It is noticeable that of *A* and *B* type glasses are fine-porous ones, while the pores in *C* and *D* type glasses are much larger. Residual silica gel particles in the images corresponding to *A* and *C* glasses look like white spots. In *C* type glass they are larger, in B type glasses they are almost imperceptible (this confirms that the leaching technique leads only to the depletion of glass by silica gel [4, 11]), and in type *D* glasses they do not exist at all.

Figure 2 shows the pore-sizes distribution spectra for all these types of glasses. One can see that two main fractions of pore sizes exist for every type of glass. However, anyone of types contents a small amount of pores with size from about 10 nm to more 100 nm.
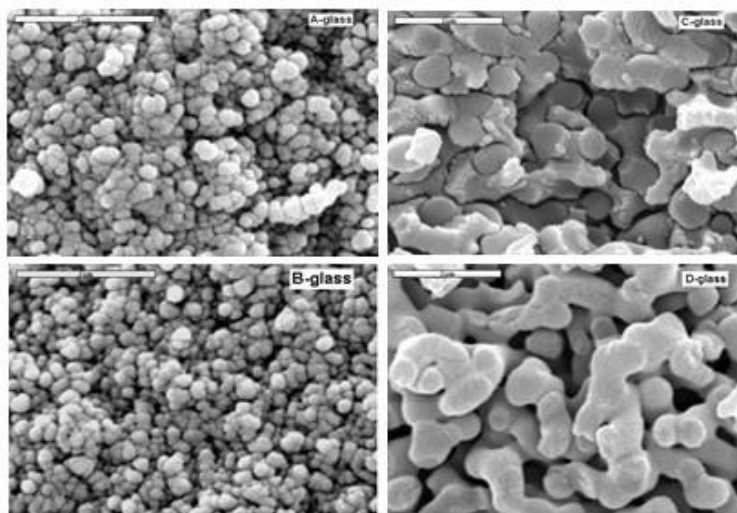
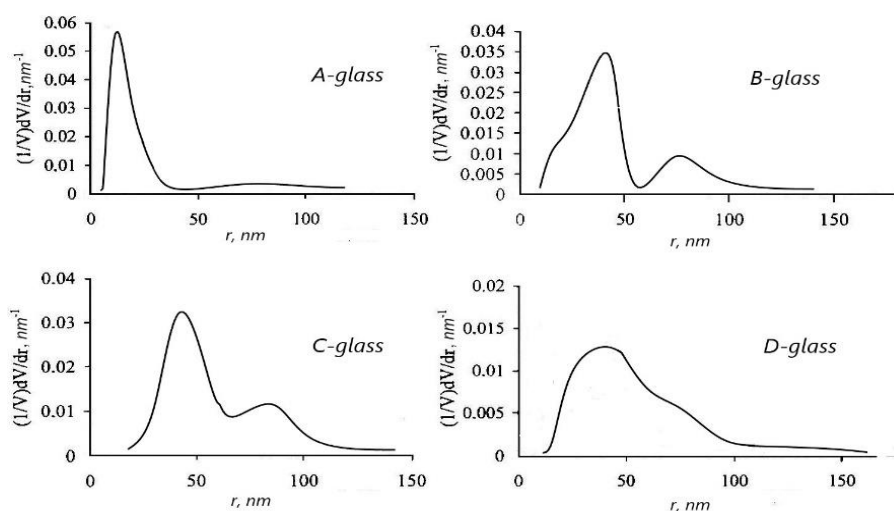**Fig. 1.** Electron microscopic images of structures for four types of porous glass.

Fig. 2. Typical pore-size distribution for four types of porous glass.

II. The structure of the dyes based on the 4-valent tin

It's useful to pay special attention to the dyes based on the 4-valent tin among the materials, which can be used as active elements for the luminescence gas sensors. According to [12], these macromolecular compounds are the most sensitive to the environment gaseous composition. The molecules of this group dye consist of a coordination node with a ligand, which may show different dentition, and a hydrazide fragment with a certain type substituent. It is expedient to consider the dye molecule in this way, because the coordination node is a more stable formation and remains unchanged during chemical transformations, while the substituent composition and its placement in the hydrazide fragment can be changed by simple chemical reactions. Coordination nodes can be of two types: tetradimethylaminobenzaldehyde and dihydroxynaphthaldehyde (denoted by the ligand $\{SnCl_4ON\}$ and $\{SnCl_3O_2N\}$, respectively). Ligand $\{SnCl_4ON\}$ is single-dentate and has a zwitter-ionic structure with a negative charge, which is delocalized in the fragment N=C–O, and ligand $\{SnCl_3O_2N\}$ is double-dentate with a negative charge, which is concentrated in the O-Sn-O area. The structural formulas of both coordination nodes are shown in Figure 3 [13].

The hydrazide fragment in Fig.3 is not indicated. It is a conventional benzene ring with a substituent of nicotinoyl or benzoyl type. In the first case, a certain nitrogen group is built directly into the benzene ring (i.e., one of the benzene ring carbon is actually replaced by nitrogen). This, of course, leads to the appearance of a localized charge near the substitution, which is compensated by the opposite charge in the coordination node; therefore, the corresponding molecule will exhibit the properties of the dipole. In the second case, the hydrogen atom in one of the benzene ring positions is replaced by an amine or hydroxyl group, which is also accompanied by a charge redistribution within the coordination node to maintain the electro-neutrality of the molecule. Isomeric dyes that differ only in the substituent position relative to the hydrazide fragment are called dyes with different tautomeric form. The substituent position in each tautomeric form is indicated by a number. For this all
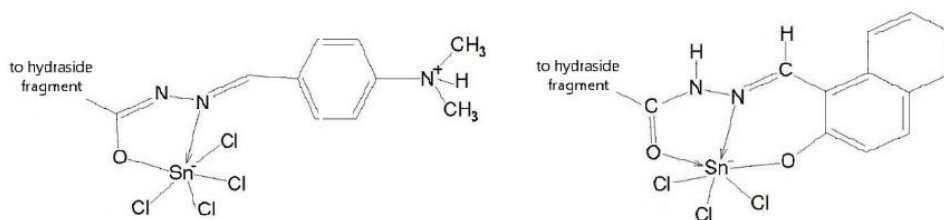
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Fig. 3. Coordination nodes structural formulas of {SnCl$_4$ON} *(left)* and {SnCl$_3$O$_2$N} *(right).*

6 carbon atoms in the corresponding benzene ring are numbered, as "1" is a carbon atom having a bond that connects the hydrazide fragment with the coordination node. Other positions are successively denoted by numbers from the natural series from "2" to "6" counterclockwise. Therefore, substitution cannot occur at position "1", because it will destroy the molecule. The results obtained in [4] show that the dye molecules have no intramolecular bonds (at least hydrogen ones), so the tautomeric forms are invariant with respect to the reading direction of carbon atoms in the benzene ring of the hydrazide fragment. Therefore, the dyes in which the substitution took place at position "2" or at position "6" are completely equivalent and have the same photoluminescence spectra. The same is true of dyes with substitutions at positions "3" or "5". A direct consequence of this equivalence is the dye molecule additional rotational symmetry, which leads to additional electron-rotational levels suitable for the radiative transition. Because of this, the dyes luminescence intensity with a substituent in position "4" is the lowest, because there are no additional levels for them. In addition, the interaction of the substituent with the coordination node also increases the luminescence intensity and the stronger the closer is the substituent to the coordination node. Therefore, the dyes luminescence with substitution in position "2" (or "6") is always more intense than when substituted in position "3" (or "5") [14].

The dyes luminescence is a consequence of the radiative transitions between the electron-vibrational sublevels of the first excited and ground singlet dye molecule electronic states. These states system occurs when the molecules are sufficiently mobile relative to each other, which occurs in solutions due to the interaction of the dye molecule (or its part) with the surrounding solvent molecules. The solvent does not affect the energy of the radiation, but, depending on the solvent absorbency, can affect its intensity. As demonstrated in [4, 13], the absorption capacity of the standard organic chemistry solvent dimethylformamide (CH$_3$)$_2$NCO, which is usually abbreviated as DMFA, is the lowest, so it is in it that dyes based on tetravalent tin complexes glow most intensely. But the dye molecules in the solution are separated from the environment by the vessel and, with the exception of those on the surface of the solution, passivate each other. Thus, only a small part of the dye molecules has direct contact with the environment and this should significantly reduce the sensitivity of their luminescence to the composition of the surrounding atmosphere. Thus, the dye in solution is unsuitable for use as an active element in gas sensors.

However, dyes can glow not only in solutions but also in the dry state, if the dye is dispersed in a suitable model environment. As a model medium, it is advisable to use porous silicate glass, in which the average size of the pores is comparable to the size of the dye molecules. When the pores in such glass are saturated with a dye solution in DMFA, it disperses almost to the molecular level, and its nanoparticle glow centers will come into direct contact with the particles of gas contained in the environment, so they can react to changes in its composition. In this case, the presence of residual silica gel inside the pores, which will play the role of separation material between the dye molecules, will allow to get rid of the effect of its molecules mutual matching. From the above it is clear (and confirmed by the results of a number of works [9, 15-19]) that the role of the model medium will be best played by porous *A* type silicate glass. In this case, the glow will occur due to the dye molecules interaction with the model medium inner surface and silica gel particles penetrate between the dye molecules, leading to the formation of aggregations, which are the centers of non-radiative recombination through the source channels. In addition, for more nanoparticle uniform distribution in the pores, majority of the solvent is removed after impregnation with additional low-temperature annealing, and due to its almost absence, the emitted light quanta possible absorption is eliminated. Therefore, the dye nanoparticle ensemble luminescence intensity inside the acceptable type porous matrix always exceeds the photoluminescence intensity of the same dye in the corresponding solution.

We investigated the photoluminescence spectra excited by the ultraviolet laser LCS-DTL-374QT (wavelength λ = 355 nm, power 15 mW) and recorded on a standard setup, which consisted of a quartz monochromator SF-4, a photomultiplier PEM-79 with sensitivity 280÷850 nm, as a photodetector, and a selective amplifier that was synchronized with the excitation laser frequency. The result was transmitted to the computer monitor via an analog-to-digital converter using USB-oscillography software. In order to ensure obtained results comparability in terms of intensity, the installation in each measurement was calibrated with a mineral origin luminophore by type LDP-2mA, which is characterized by constant luminescence and complete degradation absence. The width of the monochromator slot and the enhancement limits were kept constant, therefore, it can be argued that the obtained spectra were comparable in relative units, if the unit luminescence intensity is considered to be the luminophore luminescence.

Analysis of the photoluminescence spectra of dyes based on the 4-valent tin both in DMFA solution and in the form of nanoparticle ensembles in a porous matrix showed that they in all cases have a Gaussian shape with

one maximum and are almost entirely determined by their intensity and its maximum position. As mentioned above, the luminescence intensity of any dye in the form of a nanoparticle ensemble has always exceeded its intensity in solution. The greatest increase in luminescence was observed in the case of the benzoyl type hydroxyl substituent. The spectra remained hyperchromic relative to the dye in solution, whereas in the case of a benzoyl type amine substituent or nicotinoyl substitution there was a spectrum shift in one direction or another. This explains the highest glow intensity for dyes with hydroxyl substitution. For them, the additional energy that arises during the nanoparticle ensemble formation is spent entirely on the luminescence intensity amplifying, while in the case of amine substitution, part of it is spent on the photoluminescence spectrum maximum shifting. The detailed analysis of the luminescence spectra of all tautomeric forms for dyes with both types of coordination nodes and any substituent is given in [4].

III. Concentration dependence of luminescence for the dye nanoparticles ensemble

The dye nanoparticle ensemble luminescence intensity depends on the concentration of the solution used to create the specified ensemble. To identify this dependence regularity, consider how the luminescence intensity of the dye solution in DMFA changes with increasing concentration. There are two competing processes: illumination and light absorption. The first process causes an increase in the luminescence intensity due to an increase in the luminescence center quantity (see, for example, [20]) due to the greater of the dye molecule number in the concentrated solution. This process is almost linear and at low concentrations the luminescence intensity increases from zero to some limit value, which is called the saturating solution limit concentration. After this concentration excess, the second process associated with concentration quenching begins to prevail [20-21]. There are so many molecules in the solution that they begin to merge into aggregations, which are centers of nonradiative recombination through the source channels. The solution luminescence intensity decreases according to the parabolic law. Fig.4 *(left)* shows a model image of the described dependence. It should be noted that according to the Frank-Condom principle, both processes occur simultaneously, and therefore the dye concentration intensity dependence in solution at low concentrations is almost linear, and after excess the concentration limit is almost parabolic.

When the matrix is saturated with dye solutions of appropriate concentration to create an ensemble of nanoparticles, similar processes occur in the obtained system. However, for the case of a nanoparticle ensemble, there are certain changes in the described dependence. An almost linear curve section at concentrations below the limit is converted to a "piece-linear". Such a "piecewise linear" increase in the dye nanoparticle ensembles photoluminescence intensity in a porous matrix at low saturating solution concentrations may be due to the

inhomogeneity the different sizes pores fraction filling in porous glass during this ensemble formation. At impregnating solution relatively low concentration in the matrix pores there is a relatively small quantity of nanoparticles. They will enter the smallest pores alone, dispersed to an almost molecular level, so they will not aggregate (i.e. no leakage channels will appear). As far as even in fine-grained *A* type glass there is always a certain number of rather large pores, many dye nanoparticles will get into them, but their fusion in aggregation will prevent the surrounding on all sides silica gel particles, and they will settle separately on the pores' walls. The luminescence intensity increases rather slowly with concentration increasing. When the impregnating solution concentration reaches certain "average" values, similar processes continue, but the dye molecules' quantity increases [21]. Therefore, more radiative recombination centers appear inside the pores, and this leads to the luminescence intensity increase acceleration with increasing concentration (see, for example, [4, 21]). The solution limiting concentration in the case of the nanoparticle ensemble remains the same as it was in the solution, and its excess again leads to the absorption processes in the system prevalence. However, due to the solvent practical absence inside the pores of the matrix, this can hardly be explained by the concentration quenching. At such high concentration impregnating solution, small particles in large pores will be so many that they will merge into aggregation at the stage of their formation [22-23], and silica gel particles will not have time to interfere with this process, but will envelop the already existing aggregations (see e.g. [9, 22]). In this case, the largest (about hundreds of nanometers) pores will be filled, in which the silica gel will only partially passivate the dye molecules surface. Solvent residues after annealing will also be concentrated mainly in the specified size pores. Therefore, most of the dye found in large pores will behave as if in solution, i.e. there will be the photoluminescence intensity decrease, which will approach the value typical for the solution. A comparison of the luminescence intensity of the $2NH_3\{SnCl_4ON\}$ dye concentration dependences in DMFA solution and in the form of the nanoparticle ensemble in *A* type porous silicate glass is shown in Fig. 4 and testifies to their complete similarity.
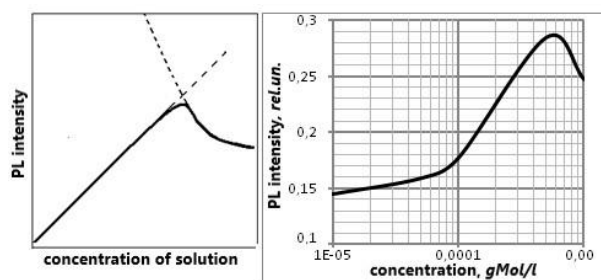

Fig. 4. The $2NH_3\{SnCl_4ON\}$ dye nanoparticle ensemble luminescence concentration intensity dependence in DMFA solution *(left, model curve)* and as a nanoparticle ensemble *(right, experimental curve).*

It can be seen that at solution low concentrations the nanoparticle ensemble glow intensity is insignificant;

then, through the different size pores unequal filling rate (see e.g. [4, 21]), it increases nonlinearly and the corresponding curve slope changes. At a concentration of $0,5 \times 10^{-3}$ gmol/l (the saturating solution limiting concentration), luminescence becomes maximum. When the solution saturating concentration exceeds the limiting one, the photoluminescence intensity decreases, as in the case of the solution.

IV. The dye nanoparticle ensemble gas sensitivity

The luminescence properties of obtained ensemble of nanoparticles of the dyes based on the 4-valent tin complexes can differ sufficiently depending on technological conditions of it formation and on structure of dye molecules. Taking this fact in to account it's useful to observe which species of dyes are sensitive to one of other gas and why it's so for further use of these systems as active elements of gas sensors. One of such sensor important properties is the reproducibility of their properties, which should ensure their reusability. Therefore, it is undesirable to be based on direct chemical interaction of the dye substance with gaseous impurities present in the environment, and should proceed from these dyes molecular structure and the peculiarities of the nano-size system formation based on their chemical composition. The gaseous contaminant presence will be fixed by changing the ensemble photoluminescence intensity, therefore, we will consider such nano-size systems that have the highest initial glow. Therefore, taking into account the above-described properties of dyes and matrices, we will form ensembles of nanoparticles in porous A type silicate glass and use DMFA solutions of dyes with tautomeric form "2".

Nanoparticle ensembles in this sense can be used as active sensor elements not of any gases, but of gases which contain the same chemical elements, as in a dye molecule. Such gases will not chemically interact with the nanoparticle ensemble elements, however, their presence in the atmosphere will create artificial conditions for changing the system luminescent properties. In this case, after entering the unpolluted atmosphere, these artificial conditions will disappear, and the system alone or with the help of simple processing will restore its original glow.

As is clear from the studied dye structure description, their molecule consists mainly from benzene rings assemblage. The rings that make up the coordination node are perfect and therefore chemically quite inert, while in the only ring of the hydrazide fragment there is a substitution of a hydrogen (benzoyl) or carbon (nicotinoyl) atom for a certain amine or hydroxyl complex. Thus, the substituent in the hydrazide fragment is a certain analog of the substitution impurity in the semiconductors, so it can be a luminescently active center. In turn, between the coordination node perfect benzene rings contains a ligand based on Sn and Cl. It is a certain analogue of interstitial impurities in semiconductors and can also be luminescently active and sensitive to some gaseous substances in the environment. Due to its zwitter-ionic structure, the ligand provides a certain charge distribution within the coordination node, and hence the entire dye molecule.

Thus, the dye nanoparticle ensemble based on a tetravalent stannum in a A type porous glass can, by changing its luminescence intensity, detect the gas presence in the environment that can affect the substituent or cause the charge redistribution in the dye molecule. There are two such gases: ammonia, which is very similar in structure and chemical composition to the benzoyl-type amine substituent, and hydrogen chloride vapor, which dissociates perfectly in water, forming negatively charged Cl^- ions. We were able to detect sensitivity namely to these gases in our study.

As can be seen from the right part of Fig. 4, sensitivity to ammonia should be expected from a nanoparticle ensemble based on $2NH_3\{SnCl_4ON\}$, if it is created by A type porous glass impregnation with a solution in DMFA with a concentration of 0.5×10^{-3} gMol/l. In this case, the luminescence intensity achieves the maximum value and the specified concentration exceeding leads to a luminescence weakening. However, the ingress of the sample formed under these conditions into the ammonia medium should lead to an increase in the nitrogen concentration in the pores, which is equivalent to the creation of a nanoparticle ensemble at a saturating solution concentration exceeding the limit. This will reduce the luminescence intensity of the sample [4, 24-25].

To experimentally confirm these considerations, the initial luminescence intensity of the sample $2NH_3\{SnCl_4ON\}$ in the form of a nanoparticle ensemble formed under these conditions was first measured, and then it was immersed in an atmosphere containing ammonia. Measurements were repeated immediately after immersion and after 10 minutes in the specified atmosphere. Then the sample was transferred to a pure atmosphere and kept in it for 24 hours. Next, its luminescence intensity was measured again, immediately and after 10 minutes of low-temperature (at 240°C) annealing. The result in the form of a histogram is shown in Fig. 5. Histograms show that the dye after immersion in the atmosphere containing ammonia sharply and steadily reduces luminescence intensity and it is possible to restore initial intensity only after annealing.

To explain this result, it should be mentioned that the nitrogen inside the coordination node is in an inactive state. Therefore, we can assume that the dye $2NH_3\{SnCl_4ON\}$ initially contains active nitrogen only in the substituent, its amount in the ensemble is determined by the impregnating solution concentration, which is the limit and corresponds to the maximum luminescence. After immersion in ammonia, the amount of active nitrogen in the system increases, and it behaves as if it was formed from a solution with a higher concentration, which corresponds to a lower luminescence intensity (as is well seen in Fig.4). The change durability is probably due to the formation of ammonia-stable bridges within the pores, which is equivalent to the aggregation formation that are leakage channels. Short-term low-temperature annealing breaks these bonds and the system luminescence is practically restored. This model is confirmed by an attempt to perform the same experiment with the $2OH\{SnCl_4ON\}$ dye nanoparticle ensemble. This ensemble shows almost complete insensitivity to ammonia, because the dye on the basis of which it is

formed, initially does not contain active nitrogen, so it does not interact with ammonia [24-25].
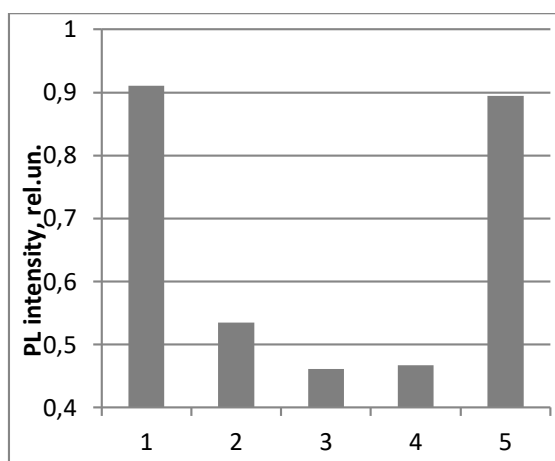

Fig. 5. Sensitivity of the photoluminescence intensity of the $2NH_3\{SnCl_4ON\}$ dye nanoparticle ensemble to ammonia:
1 - initial sample in a pure atmosphere;
2 - in an atmosphere containing ammonia;
3 - for 10 minutes in ammonia;
4 - 1 day after returning to pure atmosphere;
5 - after 10 minutes of low-temperature annealing

Ammonia sensor was patented recently [26] works on described principle.

It should be noted that the hydrazide fragment is resistant to other aggressive media, so it is impossible to detect any other gases that may be present in the environment by their interaction with the hydrazide fragment.

The influence of the environment composition on the ligands in the coordinated nodes may be traced by the changes of glow intensity of dye nanoparticles' ensemble if the atmosphere contents the HCl vapors. Recall that chlorine is contained only in the ligands of dye coordination nodes, moreover in different amounts for different types of forms and choose a dye-based system that it will glow the brightest, so it will be easiest to notice changes in its luminescence. Such system is the dye nanoparticle ensembles with a benzoyl type hydroxyl substituent with a tautomeric form "2". Fig. 6 shows the luminescence spectra of $2OH\{SnCl_3O_2N\}$ *(left)* and $2OH\{SnCl_4ON\}$ *(right)* dyes in a pure atmosphere and in one containing hydrogen chloride vapor. These dyes coordination nodes differ in the ligand dentance hence the charge distribution in the molecule. Ligands are as a whole an electro-neutral molecule placed between the coordination node benzene rings, which in some of its parts carries both a negative and a positive charge, which is localized on non-neighboring atoms. Thus, a specific ligand in the system creates a certain charge balance in it. In the HCl vapors presence in the atmosphere, which are enriched in negative Cl⁻ ions, this balance is disturbed [24-25], which determines the sensitivity of the system to these vapors.

The spectra in Fig. 6. show that the initial luminous intensity of the $2OH\{SnCl_3O_2N\}$ dye exceeds the glow intensity of the $2OH\{SnCl_4ON\}$ dye almost three times, and both are sensitive to the presence of HCl vapors in the atmosphere. However, if the $2OH\{SnCl_4ON\}$ dye reduces the intensity of its luminescence slightly (about 20%), the luminescence of the $2OH\{SnCl_3O_2N\}$ dye decreases significantly and becomes approximately the same as that of the $2OH\{SnCl_4ON\}$ dye in a pure atmosphere.

The study of the glow decrease kinetics of the samples in the atmosphere of HCl vapors showed that the decrease of the luminescence intensity of both nanosize systems occurs abruptly after a short latency period. Measurements were performed at a wavelength corresponding to the maximum of glow (as can be seen from Fig. 6, for $2OH\{SnCl_3O_2N\}$ it is 468 nm, and for $2OH\{SnCl_4ON\}$ it is 510 nm). Fig. 6 shows the corresponding kinetic spectra.

The vertical line on the graph corresponds to the moment when the charge redistribution in the system based on the $2OH\{SnCl_3O_2N\}$ dye begins. It can be seen that to the left of it the decrease in glow intensity for both systems is insignificant and almost the same. But for a system with a two-dentate ligand, it is smoother, and for a system with a one-dentate ligand, it occurs a little earlier and a sharp jump.

The presence of a latent period is probably due to the fact that, unlike the substituent, the ligand is inside the molecule and is shielded on all sides by perfect chemically inert benzene rings. So until the HCl molecules begin to interact with it and change the charge distribution, it takes
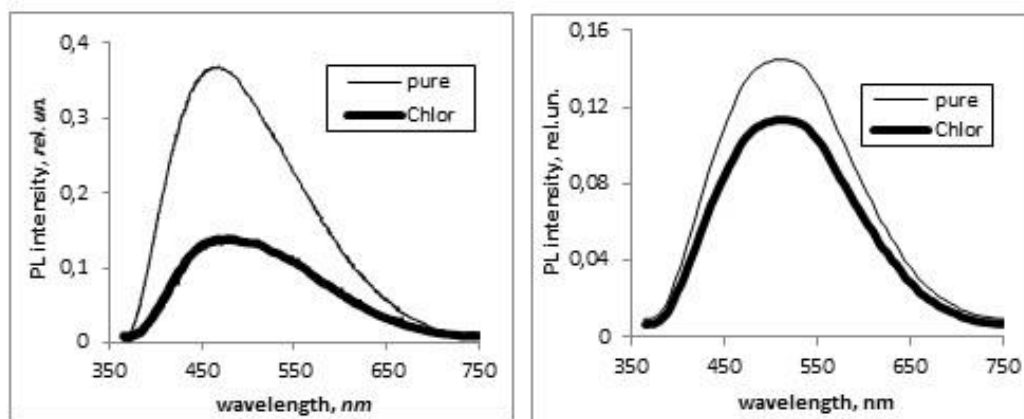

Fig. 6. Luminescence spectra of nanoparticle ensembles of $2OH\{SnCl_3O_2N\}$ *(left)* and $2OH\{SnCl_4ON\}$ *(right)* dyes in a pure atmosphere and in one containing HCl.

minutes. For the 2OH{SnCl₃O₂N} dye with a two-dentant ligand, this time is slightly longer, because the interaction with HCl in this case is to saturate the system with a negative charge to a state that is typical for 2OH{SnCl₄ON} dyes with a single-dentate ligand. After reaching this state, the system begins to glow as a 2OH{SnCl₄ON} dye, i.e. abruptly reduces its luminescence intensity. In the case of a nanoscale system based on the 2OH{SnCl₄ON} dye, no significant charge redistribution occurs, so for it the latency period is less long and the decrease in intensity is insignificant.

It would seem that similar processes should take place in dyes with an amine substituent, but for this type dyes the charge redistribution is mostly compensated by the luminescence maximum shift in one or another direction at a constant intensity. And such a shift can be caused not only by charge redistribution, but also by many other factors [4], so if it occurs, it does not necessarily indicate the appearance of HCl vapor in the atmosphere, and such systems are not suitable for fixing these vapors.

In conclusion, we note that the initial charge distribution for both systems can be restored by the sample heat treatment in the same mode as in the case of 2NH₃{SnCl₄ON} dye nanoparticle ensemble interaction with ammonia. Apparently, this treatment is sufficient to remove foreign gases from any porous system to get rid of their impact.

From the above results, it is cl clear that the role of the HCl vapor sensor active element will be best played by the 2OH{SnCl₄ON} dye nanoparticle ensemble in porous *A* type silicate glass. The sensor of HCl vapor in the environment was discovered on the base of such nanoparticles' ensemble exactly [27].
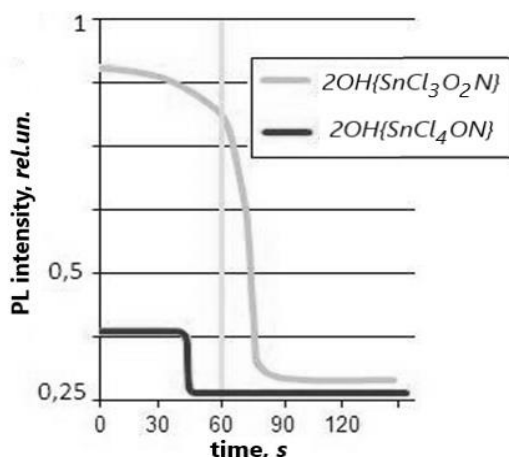

Fig. 7. Photoluminescence intensity reducing kinetics for the dye nanoparticle ensemble of dyes with one-dentant (2OH{SnCl₄ON}) and two-dentant (2OH{SnCl₃O₂N}) ligand in the presence of HCl vapors in the environment.

V. Carbon treatment of the porous glass and it using in sensors

Carbon treatment method [28-29] is an alternative way to get rid of porous glass from silica gel. It is based on the fact that porous glass is almost pure silicon dioxide, and because carbon is similar in chemical properties to

silicon, but is more active, it is able to displace it from the oxide at appropriate temperatures. Silica gel and silicate skeleton, are chemically identical and differ only in dispersion. Thus, under certain conditions, carbon will displace silicon from the oxide, primarily in silica gel, as a more dispersed formation. Carbon treatment consists of two stages: primary and secondary. In the initial stage, anyone type of glass 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 is easily reduced simply in the voids of matrix to carbon in the form of highly dispersed graphite with the release of water. The process is described by a known equation

$$C_6H_{12}O_6 \text{ - (t)} \rightarrow 6C + 6H_2O,$$
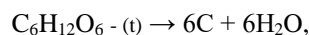
lasts about a day and its completion can be judged visually by the sample blackening. *A* type glass treated in this way is conventionally called *α* type glass, and *C* type glass is called *γ* glass. B and D types of glass, which was lixiviated, are initially removed of silica gel, so these glasses don't require total carbon treatment. However, primary carbon treatment is able to reduce the electrical resistance of pore glass specimens by several orders of magnitude due to the inbuilt of conductive phase consisting of graphite nanoparticles into it. Such a conductivity increasing may be useful for the certain applications of this type of glasses. One designates these glasses after the primary carbon treatment as B_1 and D_1, respectively.

The porous glasses, as every other porous system, are able to soak spontaneously with water vapors due to the atmosphere always contains some amount of humidity. The water vapour reduces the electrical resistance of the system sufficiently, and this fact suggests to use of porous glass as an active element of resistive humidity sensor. It confirms by the fact every type of glass contains some amount of pores of size-range from about 10 to more 100 nm (see Fig.2). Presence such large size-range of pores corresponds to condition of hydrophilicity of system at large humidity range [30]. However, electrical resistance of the porous glasses is too big and it hinders to use a nanosize system on their base in such manner. This resistance can reach some teraohms for the standard size specimens $1 \times 0,5 \times 0,1$ cm³ and its decreasing due to humidity change will be invisible in this background. That's where the primary carbon treatment helps us, that's why it reduce the system resistance by several orders of magnitude due to conductive properties of graphite.

It must be noted that not any type of glasses suitable for using as matrix for active element of humidity sensor. So, the A-glass isn't appropriate one that's why the resistance of *α* glass, which was formed after annealing, keeps it high value, if amount of the soaked glucose is too less. At the other hand, excess of soaked glucose together with big amount of residual silica gel will score the pores after annealing and the system will lose it moisture sensibility. In the case of *γ*-glass, in addition, it's difficult to obtain a reliable contact due to high roughness of surface [31]. Inside D_1-glass the conductive phase is able to shunt the specimen. So, namely B_1-type of glasses appropriate to use as matrix for humidity sensor. This

glass contains fine pores mainly and it is depleted with silica gel. Besides its surface haven't high roughness. After formation of graphite nanoparticles' ensemble in B-glass a graphite layer creates on the surface of obtained B_1-glass. A reliable contact may be putting in to this layer with help of conductive paste. The change of the resistance of obtained system will quite correlate with moisture of environment.

Fig.8 shows a typical dependence of resistance of the graphite nanoparticles' ensemble in B_1-glas on moisture. This ensemble was formed by immersion of glass in the 40% water solution of glucose during a day with following anneal by 180°C during 2 hours. Contact for such system was putting in with silicone paste. All measurements was performed at the room temperature. One can see that the reduce of the system resistance by increase of relative moisture of environment from 10% to 99% achieve two order of magnitude.
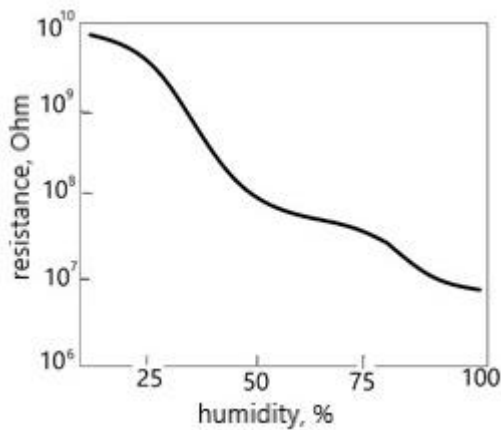

Fig. 8. Resistance dependence of graphite nanoparticles' ensemble in B_1 porous glass on humidity of environment at the room temperature.

It can be note that similar isotherms may be graphed at some temperature and they almost don't change. This statement is true just at negative temperature, because at such temperature the moisture of the air determines by ice sublimation. And besides the separate nanoparticles of water, which was absorbed by system, are divided with silica gel and graphite nanoparticles, that's why temperature of environment is indifferent for them and the state of aggregation doesn't exist for such nanoparticles' ensembles.

Formation of ohmic contact to the pore glass specimen is another application of the primary carbon treatment. It could investigate correlation between luminescence properties of nanosize system in the pore matrix and electrically ones. Primary carbon treatment may be particular to reach such aim.

Using primary carbon treatment a standard specimen deeps with butts $5 \times 0.5 \ mm^2$ into glucose solution on the depth 0.5÷1 mm with the help of clamp-like holder. It creates the conditions, which almost respond to the tusk of diffusion from a constant source. According to the second Fick's low on the step of dopant spin-on into the system there arises concentration of glucose C_x on the distance x during the time t:

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

Here C_0 is initial concentration of soaked solution. Factor D is certain analog of diffusion coefficient, which is called saturation coefficient. It's different from diffusion coefficient sufficiently, that's why in contrast with last one it describes infiltration of enough big glucose molecules into voids of of porous glass. These voids are very big in comparison with interatomic distances (see Fig.2). Corresponding coefficient depends on type of glass, namely on of it porosity, pore-size distribution, presence of residual silica gel and amount of this substance, as well as on temperature of soaking.

Fig.9 shows us schematically the glucose distribution inside wafer of the porous glass after soaking of specimen at both butts with this substance. Depth of immersion of the wafer into solution indicates with dotted line. Let's note that both curves don't show the configuration of profile of soaked glucose, but they image the reduce of it concentration by distance from source of soaking only.

Let's note also that the error function complement convergences too slow by an attempt of series expansion. That's why one usually applies the McLaurin series expansion to estimate analytically of concentration of glucose, which was soaked on a small distance from it source. However, one must use asymptotic mapping of this function for the case of big distances. The first case gives us:

$$C_x = C_0\left[1 - \frac{2}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{(-1)^n\left(\frac{x}{2\sqrt{Dt}}\right)^{2n+1}}{n!(2n+1)}\right],$$

and by the second one

$$C_x = C_0\frac{\exp\left(-\left(\frac{x}{2\sqrt{Dt}}\right)^2\right)}{\left(\frac{x}{2\sqrt{Dt}}\right)\sqrt{\pi}}\left[1 + \sum_{n=1}^{\infty}(-1)^n\frac{(2n)!}{n!\left(\frac{x}{\sqrt{Dt}}\right)^{2n}}\right].$$

Although the convergence of these series is too slow, it's able to keep some first terms only in these cumbersome expression for any specific tusk. So we have for small x:

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

and for big ones:

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

Furthermore, the wafer of porous glass, which was soaked from both butts with glucose according above manner, must be annealed to decompose penetrated glucose in pores thermally. Simultaneously drive-in step of graphite diffusion takes place. It's certain analogue of the tusk about diffusion from a limited source. If the glucose concentration at the butts of the wafer coincided with C_0 before the thermal decomposition, and the concentration in the arbitrary point x determined by above equation and was equal C_x, then new concentration at the time t will determine by expression:

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

Fig.10 shows graphite nanoparticles' distribution in ensemble, which was formed by the above annealing. These curves don't correspond again to graphite configuration in porous glass. They shows just the reduce of graphite amount by drifting apart the butts of wafer.

Comparison of the Fig.9 and Fig.10 shows us that the graphite particles in ensemble in contrast of glucose nanoparticles are concentrated near the butts of wafer mainly. And specified concentration quickly fade away by drifting apart them. Thus, areas with heightened conductivity arise at the butts of wafer. Presence of these areas don't affect to the conductivity of remaining part of specimen anyhow. Treating these areas of the wafer with silicone paste or other one we can form an ohmic contact to the pore glass specimen. Arising conductive areas present an α-glass, which smoothly passes into A-glass (or in case of other types of glass we have a pass B_1 into B or γ into C or D_1 into D).
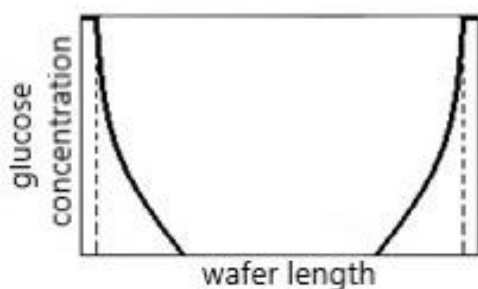

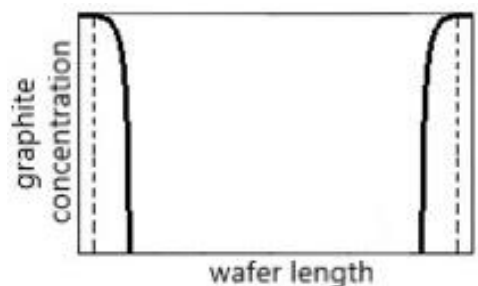**Fig. 9.** Glucose distribution in in the porous glass wafer.

Fig. 10. Distribution of graphite nanoparticles in the formed ensemble.

It must be noted that the glasses of α- and γ-types are not currently used by themselves: they cannot serve as a matrix to create ensembles of nanoparticles, because their pores are completely filled with carbon. As carbon conducts electricity well, they are actually just constant resistors, with indefinite resistance. However, they give an opportunity to dispose of residual silica gel, if they will anneal additionally, in other words will perform secondary carbon treatment.

This annealing temperature regime corresponds to the silicon displacement from the oxide without simultaneous pores' collapse (i.e. within $300 \div 400$ºC). This produces chemically inert carbon dioxide. This gas is heavier than air and therefore lingers in the pores for a while, preventing oxygen from entering there. As a result, the reduced silicon atoms, which are unable to oxidize, will begin to crystallize into silicon nanocrystallites, which

will settle on the dangle bonds, which will appear on the walls of pores in the "stem" form due to the etching of the silicate skeleton. The completion of the reaction can be fixed visually by restoring of the sample transparency. During secondary carbon treatment, almost all silica gel is converted into silicon clusters, while the leaching technique application leads only to the original glass depletion with silica gel to almost complete sample dissolution, if the leaching lasts long enough [4, 11]. Thus, carbon treatment is an alternative way to remove silica gel from pores. After secondary treatment, α glass is called β-type glass, and γ glass is called δ-type glass. It should be noted that these types of glasses differ in many respects from type B or D glasses, respectively [11]. This is, in particular, due to the change in the matrix structure during carbon treatment (as opposed to leaching): as a result, silicon clusters appear on the slot walls, similar in structure to porous silicon obtained by laser ablation [32]. As a result, extraneous peaks appear in the glass luminescence spectra, which correspond to porous silicon and are located in areas of the spectrum that may be significant for the test substance. Therefore, β and δ type glasses are not usually used as a matrix to create nanoparticle ensembles of, although their absorption properties are applicable to other applications, such as ophthalmic bioprosthetics [33-34].

Conclusion

Photoluminescence of dyes based on tetravalent stannum complexes is possible not only in solutions but also in the dry state, if they are formed in the form of a nanoparticle ensemble inside a fine-porous matrix containing residual silica gel in the porous. Silica gel inhibits the formation of aggregations and this leads to an increase in the glow intensity compared to the solution.

The luminescence intensity of all tautomeric forms of this type dyes increases when the substituent of any nature approaches to the coordination node due to the emergence of additional electron-rotational levels suitable for the radiative transition. This effect does not depend on the coordination node and is true for both solutions and nanoparticles.

When forming an ensemble of the dye nanoparticles in a porous matrix, the increase in the concentration of the impregnating solution first leads to an increase in the intensity of the glow, and after exceeding the concentration limit, photon absorption processes begin to prevail over their radiation, and the luminescence weakens to typical for solution.

There are two types of luminescence centers in the dye molecule: a substituent in the hydrazide fragment, which is analogous to the substitution impurity in the semiconductor, and a ligand in the coordination node, which plays the role of the interstitial impurity. The substituent is responsible for the sensitivity to ammonia and the ligand is responsible for the sensitivity to HCl vapors.

The dye nanoparticle ensemble sensitivity to ammonia shows itself in the luminescence intensity decrease in comparison with photoluminescence in a pure atmosphere, if the dye contains an amine substituent of the

benzoyl type. The effect is probably related to the formation of bridges within the matrix pores, which are the leakage channels.

The dye nanoparticle ensemble sensitivity to HCl vapors shows itself in the switching of the system's luminescence to a lower intensity due to the negative charge redistribution in it under the action of excess chlorine ions if the dye contains a benzoyl-type hydroxyl substituent.

In both cases, in the extraneous gases presence, the attenuation of glow compared to photoluminescence in a pure atmosphere is quite stable, however, the initial intensity can be restored by short-term low-temperature annealing, which provides multiple use of active dyes nanoparticle ensembles as gas sensor active elements.

Through carbon treatment of porous glass, which consists of two steps, one can dispose of the residual silica gel from the pores of glasses. It concerns to the glasses, with contain this substance. Residual silica gel transforms into silicon clusters, which settle on the walls of pores.

Primary carbon treatment leads on creation of the conductive layer inside all the types of porous glasses. It allows to reduce own electrical resistance of standard-size specimens sufficiently. After such treatment these specimens may be used as active element of resistive humidity sensors.

Partial primary carbon treatment of the standard specimens of porous glass allows to form ohmic contacts on the butts of the sample for subsequent applications.

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Властивості кремноземних пористих стекол з ансамблями наночастинок деяких сполук. Огляд

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У цьому огляді систематизовано властивості шпаристих силікатних стекол. Описано методи формування у шпаринах ансамблів наночастинок речовин, що використовуються у мікроелектроніці. Шпаристі силікатні стекла є перспективними в цьому сенсі завдяки власній хімічній стійкості, механічній тривкості та гарній розгорнутості своєї внутрішньої поверхні. Проте, власний електричний опір стандартних зразків цієї речовини є надто великим, і через це у сенсориці її, зазвичай, використовують переважно як матрицю для сенсорів люмінесцентного типу. Досліджено залежність люмінесцентних властивостей системи як від молекулярної будови досліджуваних речовин (на кшталт барвників або оксидів металів), так і від технологічних умов формування ансамблів наночастинок. Виявлено, до яких саме газів є чутливими барвники конкретного типу і чому вони поводять себе саме таким чином. Продемонстровано, завдяки яким властивостям розглянутих нанорозмірних систем виникає зазначена газочутливість. До того ж, завдяки особливостям будови шпаристих силікатних стекол, у їхні шпарини можна вбудовувати провідну фазу шляхом спеціальної обробки. Після зазначеної обробки стекла можуть використовуватися як матриця для формування сенсорів резистивного типу.

Ключові слова: кремноземне пористе скло, люмінесценція, сенсори газу, сенсори вологості, обробка вуглецем, омічні контакти, барвники.