ISSN 1087-6596, Glass Physics and Chemistry, 2016, Vol. 42, No. 1, pp. 50–58. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © I.V. Petrova, O.A. Shilova, 2016, published in Fizika i Khimiya Stekla.

Study of Rheological Properties of Sol–Gel Systems Based on Tetraethoxysilanes in the Presence of Boric Acid, Gadolinium Nitrate, and Organic Polyols

I. V. Petrova[a] **and O. A. Shilova**[a, b]
[a]*Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, nab. Makarova 2, St. Petersburg, 199034 Russia*
[b]*St. Petersburg State Electrotechnical University (LETI), ul. Prof. Popova 5, St. Petersburg, 197022 Russia*
e-mail: olgashilova@bk.ru

Received November 10, 2014

Abstract—The present work is devoted to studies of the rheological properties of sol–gel systems based on tetraethoxysilane by the falling ball method developed by F. Höppler. The systems under study were modified by organic polyols of linear, branched, and hyperbranched structures and inorganic boron and gadolinium dopants. The parameters of viscosity and strength of the network of the formed organic-inorganic composite, which are important characteristics of sol–gel systems properties, have been presented. The data characterizing the range of permissible concentrations of organic components introduced into a system to improve the synthesized films properties have been demonstrated.

Keywords: structural and dynamic viscosity, rheoviscometer according to Höppler, hybrid and organic-inorganic sol–gel systems, organic polyols, thin glasslike films

DOI: 10.1134/S1087659616010119

INTRODUCTION

Films were among the first objects obtained using the sol–gel method. Their application is still in great demand in microelectronics. Also, their application as a source of a diffusant of one or several dopants (B, P, Sb, As, Tl, Pt, Pd, Sn, V, Mn, Co, Ni, Zn, rare earth and other elements) in silicon and other materials used in electronics on the formation of *p*–*n*-transitions and stop layers is urgent [1–9]. The problem of fabrication of thin glasslike films with high electrophysical parameters on a semiconductor surface is important due to their possible use for various purposes during the manufacture of semiconductor devices and integral circuits.

The method of using thin glasslike films as sources of diffusion into polycrystalline materials has advantages over other methods of polysilicon doping (in processes of film growing, ion implanting, diffusion from a liquid source, etc.) with respect to ecological terms and the simplicity of technological operations. At the same time, the method provides the possibility of reproducibly controlling the parameters of polysilicon layers through variation of the sol compositions and thermal treatment conditions. An important advantage lies in the possibility of carrying out multiple technological processes under controlled conditions. Since films with specified concentrations of dopants serve as diffusion sources, distortions and damage of the crystal lattice of the doped semiconductor become minimal.

Another advantage of the examined method of doping from glasslike films is the possibility of the combined (along with conventional donors and acceptors) introduction (first, into films and, second, into semiconductors) of several dopants, which cannot be done by other methods [2, 5, 10, 11]. For example, nanosized films can be used as sources of diffusion of rare earth elements. In this case, clusters serving as radiation-induced defect sinks are formed in the monocrystalline silicon, which allows avoiding the degradation of the parameters of the semiconductor devices [10, 11].

The use of films as sources of diffusion for creating the dividing *p*- and p^+-stop layers is rather efficient [1–5, 12, 13]. The use of diffusion from silicate glasslike films obtained from sols based on tetraethoxysilane (TEOS) and containing boric acid or other boron compounds [3, 12, 14] as an alternative method results in the formation of highly doped areas in the process of dopant diffusion from such films.

In order to ensure the reproducibility of the parameters of the diffusion layers formed through diffusion from the films, it is necessary for the films to meet specific requirements: homogeneity over thickness, homogeneity over structure without peeling and crystalline inclusions, transparency, integrity without disruptions and cracks, etc. One of the criteria for the fabrication of films meeting the requirements of the microelectronics planar technology is the viscosity of the initial sols.

The available versatility of the methods and designs of the devices for viscosity measurement (viscometers) is the result of the broad range of the viscosity values (from 10^{-5} Pa for gases to 10^{12} Pa for polymers) as the necessity to measure viscosity at low or high temperatures and pressures. In the literature, the miscellaneous unit 'poise' is used to estimate sol ageing, gel formation, and the film-forming capacity ($1\ \mathrm{P} = 0.1$ Pa s).

Three methods of measurement of viscosity of gases and liquids are used the most widely: capillary, falling ball, and coaxial cylinders (rotational). These methods are based on the laws of Poiseuille, Stokes, and fluid flow between coaxial cylinders, respectively [15–18].

Two viscometry methods were used in the present work to study the structuring processes and film-forming properties for our selected objects—the methods of falling ball according to Höppler and of the rotational viscometer with coaxial cylinders. The peculiarities of structuring film-forming silica sols in the presence of organic and inorganic dopants studied by the method of rotational viscometer were described in [19].

The objective of the present work was to study the rheological properties of TEOS-based hybrid borosilicate sols doped with the second inorganic element (gadolinium) and organic modifiers (polyols of linear, branched, and hyperbranched structures) using the Höppler method to improve the technology for the formation of thin glasslike films for microelectronics.

SELECTION OF ORGANIC COMPOUNDS FOR THE MODIFICATION OF SOL–GEL SYSTEMS' PROPERTIES

Only sols meeting the stability requirements can be applied in semiconductor technologies. The sol's stability comprises its capacity to preserve mobility for some period of time. The criteria of stability loss include precipitate formation, emergence of a visible boundary of liquids exfoliation, and fluidity loss due to a gradual increase in viscosity and sol transformation into gel [15, 16, 18]. Near the gel formation point, the sol viscosity increases jump-like.

The time period of sols' applicability in the formation of films meeting the microelectronics planar technology requirements is determined by their viscosity, among other parameters [2, 5, 12, 13, 19]. In the case of sols, the film-forming properties do not manifest themselves immediately, but in the course of liquid structuring. Sols with increased viscosity close to transformation into gels are not applicable in the formation of homogeneous thin glasslike films. At the same time, the application of fresh ('not yet ripe') sols is also undesirable. The latter could negatively affect the films' reproducibility. The viscosity value can serve, among other factors, to estimate sols' film-forming properties.

Polyols of linear, branched, and hyperbranched structures of different molecular weights containing different numbers of active functional groups were selected as organic modifying dopants. Due to the presence of end hydroxyl groups, they are capable of interacting with products of TEOS hydrolysis [1, 5, 12, 20–22] through specific interaction with them, yielding the formation of either hydrogen or covalent bonds.

Organic modifiers were added to the base borosilicate solution consisting of TEOS, monoatomic alcohols, and boric acid [6]. The list of introduced additives and their main characteristics are shown in the table.

According to the data in the literature [5, 12, 13, 22, 23], the use of different organic compounds as specific dopants yields significant changes in the chemical processes providing an improvement of the mechanical and physical-chemical properties. Such dopants include modifiers, whose effect significantly changes the material structure and properties at the cost of the introduction of specific substances at virtually identical amounts of the main components.

Glycerol containing two primary and one secondary hydroxyl groups and polyethylene glycol (polyol of a linear structure) containing two end hydroxyl groups were selected as low-molecular organic compounds (see table).

High-molecular dopants were selected based on their capacity to dissolve in the sols' water-alcohol medium and interact with products of TEOS hydrolysis due to the presence of hydroxyl (OH) or urethane (–NH–C–) groups in them. One such dopant (see table) contained both urethane and hydroxyl groups—poly(hydroxyl-oligo-urethane-urea) of a branched structure (POUU). The molecular weight of this triradial oligomer having six end OH-groups is equal to ~4200 g/mol. Aside from POUU, the tetraradial hyperbranched oligomer/(polymer) (HBP) was added into boron-containing sols. The HBP we used as an organic modifier of sol–gel systems comprises hyperbranched aliphatic polyester—polyol. The calculated value of the average molecular weight is ~5100 g/mol. Here, about 64 OH-groups are located around the molecule [12, 22].

An important requirement for organic modifiers is their effect on the properties of sols and on the film formed with their participation. The sols must comprise homogeneous mobile liquids without precipitate and/or exfoliation. It is also necessary that they have the film-forming capacity, i.e., films can be formed from them.

The number of added organic low- and high-molecular dopants was selected due to the necessity to form sol that is homogeneous, stable to gel formation for a few weeks, with no signs of phase separation, and

The main characteristics of modifying organic dopants added to film-forming TEOS-based sols

Modifying dopant, structural formula	Molecular weight, g/mol	Number of OH-groups (end or around molecule)	Amount of added dopant, wt %
Glycerol (GLC)—linear structure $CH_3OH–CH_2OH–CH_3OH$	92	3	0.2
Polyethylene glycol (PEG)—linear oligomer $HO(C_2H_4O)_nH$	300	2	1.1
Poly(hydroxyl-oligo-urethane-urea (POUU)—polyol fo branched structure $CH_2\,O–[RO]_x–[R'O]_y–CONH–R''–CONHCON(CH_2CH_2OH)_2$ I $CH–O–[RO]_x–[R'O]_y–CONH–R''–CONHCON(CH_2CH_2OH)_2$ I $CH_2\,O–[RO]_x–[R'O]_y–CONH–R''–CONHCON(CH_2CH_2OH)_2$ where: $R = CH_2CH(CH_3)$, $R' = CH_2CH_2$; $R'' = 2.4–2.6\text{-}C_6H_3(CH_3)$, $x + y = 19$	4200	6	0.55–2.0
Four-radial poly(ester-polyol) (hyperbranched polymer—HBP): 21 groups O–C(O)– in the repeating unit	$MM_w = 5100$ $MM_n = 2800$	64	0.55–1.1

MM_w is the average weight, MM_n is the average number.

capable of forming films meeting the requirements of the microelectronics' planar technology [1, 5, 10].

SELECTION OF INORGANIC COMPOUNDS FOR SILICON DOPING

Metal salts and alkoxydes are used in the sol–gel technology as precursors for the introduction of metals into the silicate film. In the present work, boric acid (H_3BO_3) and gadolinium water-soluble salt ($Gd(NO_3)_3 \cdot 6H_2O$) were used as dopant-containing inorganic compounds. In order to reveal the effect of each dopant on the properties of sols and films based on theim, several variants of sols with different combinations of elements and their concentrations were prepared.

OBJECTS OF STUDY

Film-forming sols based on the alkoxy-compound (TEOS) hydrolyzed in a water-alcohol medium and containing boron, gadolinium (rare earth element), and both of them at the same time were selected as the objects of study. Besides, borosilicate sols were added with polyols of a linear structure (PEG), as well as POUU and HBP in different concentrations.

Compositions of sols under study (calculated as oxides), wt %:

$40B_2O_3 \cdot 60SiO_2$ wt %,
$40B_2O_3 \cdot 60SiO_2$ + 0.5 wt % PEG,
$40B_2O_3 \cdot 60SiO_2$ + 1.1 wt % PEG,
$40B_2O_3 \cdot 60SiO_2$ + 0.5 wt % POUU,
$40B_2O_3 \cdot 60SiO_2$ + 1.1 wt % POUU,
$40B_2O_3 \cdot 60SiO_2$ + 2.0 wt % POUU,
$40B_2O_3 \cdot 60SiO_2$ + 0.5 wt % HBP,
$40B_2O_3 \cdot 60SiO_2$ + 1.1 wt % HBP,
$40B_2O_3 \cdot 60SiO_2$ + 2.0 wt % HBP,
$5Gd_2O_3 \cdot 95SiO_2$ wt %,
$10Gd_2O_3 \cdot 90SiO_2$ wt %,
$40B_2O_3 \cdot 5Gd_2O_3 \cdot 55SiO_2$ wt %,
$40B_2O_3 \cdot 10Gd_2O_3 \cdot 50SiO_2$ wt %.

Dopants were added above 100 wt %.

METHOD OF VISCOSITY DETERMINATION ACCORDING TO HPPLER

The method is used to determine the dynamic and structural viscosities of hybrid and organic-inorganic sols synthesized by the method of sol–gel technology.

The principle of functioning of the viscometer with a falling ball is based on Stokes' law [17, 24]. Determination of the viscosity value is based on measuring the time of the ball falling into the vessel with the sol. For each measurement, a small portion of the sol is placed from the main vessel in that of the viscometer. A ball of the specific diameter was placed inside a calibrated vessel with the solution under study under the effect of different weights on the viscometer's balance arm. The time of the ball falling was measured using a stopwatch. The viscosity measurement limits ranged from 6×10^{-4} to 250 Pa s. The relative error was 1–3%.

Determination of the time of the ball falling in the vessel with the sol under study was carried out for 2 months each 2–4 days during the first 3 weeks and, thereafter, each 4–7 days along with the decrease of fluidity for every solution under study. After 2 months, the following phenomena were observed in sols: opacification, precipitation (homogeneity disruption), and transition into a gel-like state. Viscosity measurements were carried out at 20–25°C. Using the obtained data and the colloid chemistry technique [17, 24], the dynamic and structural viscosities of the sols with the plotting curves depending on the load and the ageing time were calculated [24, 25].

RESULTS OF THE STUDIES OF THE STRUCTURING PROCESSES IN HYBRID BOROSILICATE SOL–GEL SYSTEMS

TEOS-based sols are self-organizing and self-developing systems. Structuring in sols is known to be the result of the processes of particles' adhesion and the emergence of a spatial network emergence yielding the acquisition of a certain mechanical strength and a reduction of the fluidity of the system. Upon attaining some viscosity value, the system transforms into gel [15, 16, 18]. Viscosity is the parameter from which the development of sol structuring can be traced.

Figure 1 shows the curves of the dependence of changes in the dynamic viscosity η (cP) on weight P (g) on the viscometer balance arm. One can see that for all sols the viscosity increases gradually and slowly for approximately 1 month. Besides, thixotropy is characteristic of TEOS-based systems [15–18]. The latter property was manifested for all sol–gel systems under study over the whole observation term. The exception here is related to the behavior of an aged sol with a POUU additive. For instance, one observed a substantial viscosity decrease on the 33th day in the case of sols with a high POUU content (1.1 and 2.0 wt %) after the viscosity measurement performed earlier (on the 27th day) accompanied, as a result of the ball falling, by the destruction of the sol's structural network (Fig. 1f, curve *7*). At the same time, on the 33th day of holding, the ball can be lowered into sols with POUU only at large loads (40 and 50 g). At small loads (20 and 30 g), the ball cannot be lowered. During further tests (on the 40th day), one observed similar sol behavior (Fig. 1f, curve *8*). Here, the viscosity decreased even to a greater degree upon application of the load. These phenomena are characteristic only of sols with POUU: the larger the quantity of POUU the lower the viscosity (Figs. 1e, 1f). As seen from the structural formula (see table), POUU contains, aside from the end OH-groups, urethane groups (–NH–CO–) capable of interact with each other with the formation of strong intermolecular bonds [15–18]. Possibly, this promotes the formation of larger aggregates yielding an increase of the sols' viscosity. However, these aggregates must be bonded to each other only weakly (just through physical bonds), while these bonds destruct irreversibly upon an increase of the load.

Besides, in the case of gel containing 2.0 wt % of POUU, one observes a different (compared to other sols) behavior of the dynamic viscosity curve on the 27th day (Fig. 1f, curve *6*), namely, a noticeable viscosity increase when the applied load is increased through the flow of this system [15–18], i.e., the manifestation of dilatant properties. These results were discussed in part in [12, 19].

Figure 2 shows the curves of the changes of the structural viscosity (η') of the above-mentioned sols during their ageing. The highest viscosity characterizes sols with POUU (η' = 7–9 cP), whereas sols with HBP additives (η' = 5–6.5 cP) were the most stable: they preserved homogeneity and mobility for 2 months. After some period of time, in all sols, one observed opacification, which can be induced both by the enlargement of the structural network fragments and by the phase exfoliation of the organic and inorganic components. Thereafter, precipitates were formed in the sols both without organic modifiers and with a POUU dopant. However, the precipitate did not form in the presence of HBP. In this case, HBP (with a wt % of 0.55–1.1) must have the role of a surfactant promoting the increase of the sols' stability to aggregation and sedimentation; i.e., it stabilizes sol–gel systems.

RESULTS OF STUDIES OF STRUCTURING PROCESSES IN SILICATE SOL–GEL SYSTEMS CONTAINING SIMULTANEOUSLY BORON AND GADOLINIUM

Silicate sols with inorganic dopants (boron and gadolinium) added both separately and at the same time were selected as the objects of study.

Figure 3 shows the curves of the dependence of changes in the dynamic viscosity on weights on the viscometer balance arm for silicate sols containing inorganic components (boron and gadolinium). The viscosity for all sols increases gradually and slowly over time during the whole observation period (3 months).

As for hybrid sols, thixotropy is characteristic of the above-mentioned sols as well and manifested over the entire observation term (Fig. 3). However, it turned

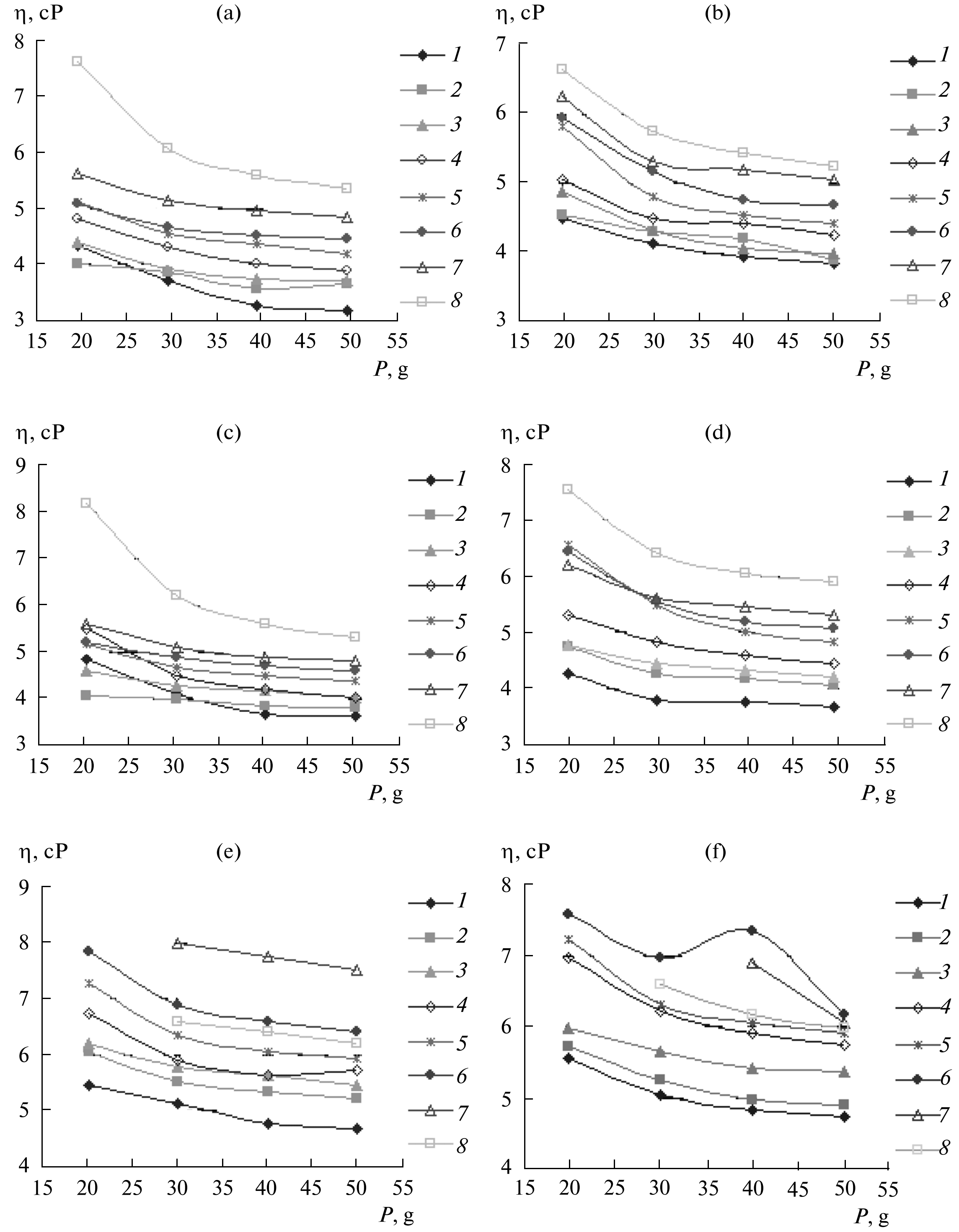

Fig. 1. Curves of the dependence of the dynamic viscosity η on the load *P* applied to the viscometer balance arm for sols: (a) sol without organic modifiers, (b) sol with the addition (doping) of 1.1 wt % PEG, (c) 0.5 wt % HBP, (d) 1.1 wt % HBP, (e) 1.1 wt % POUU, and (f) 2.0 wt % POUU. Periodicity of measurements starting from sol preparation (curves markings): (*1*) 2 days, (*2*) 4 days, (*3*) 8 days, (*4*) 13 days, (*5*) 20 days, (*6*) 27 days, (*7*) 33 days, (*8*) 40 days.

out that in silicate systems with 5–10 wt % of Gd dopant a longer period of time was required for the structure's recovery after a mechanical impact than in the case of sols with organic dopants (Fig. 1). As seen from Fig. 3, for all sols of this group, the curves of the dynamic viscosity measured later are located lower

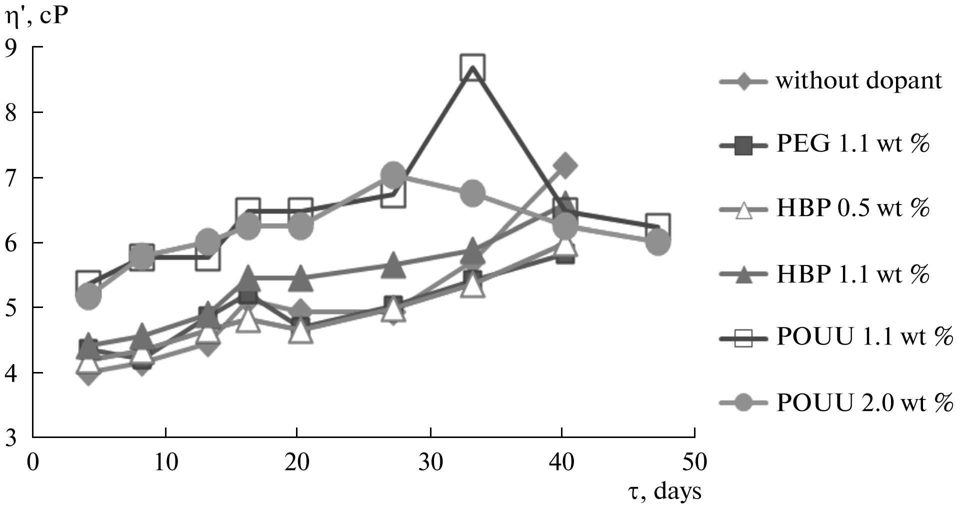

Fig. 2. Curves of the changes of the structural viscosity (η') in the process of ageing (τ) for borosilicate sols: (*1*) without organic dopants, (*2*) with addition of 1.1 wt % PEG, (*3*) 0.5 wt % HBP, (*4*) 1.1 wt % HBP, (*5*) 1.1 wt % POUU, (*6*) 2.0 wt % POUU.

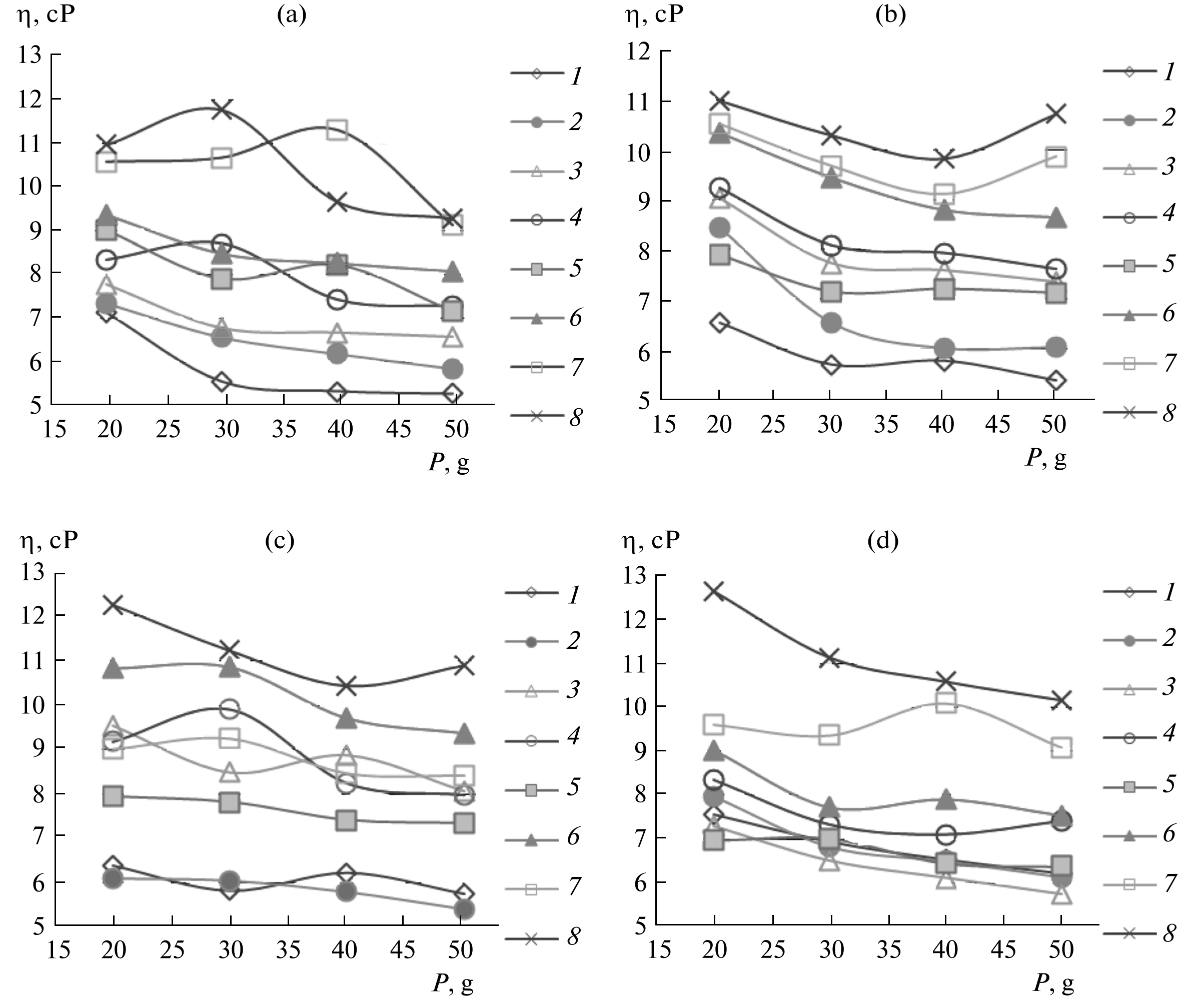

Fig. 3. Curves of the dependence of the dynamic viscosity η on weight *P* on the viscometer balance arm for sols: (a) $5Gd_2O_3$ wt %, (b) $10Gd_2O_3$ wt %, (c) $40B_2O_3 + 5Gd_2O_3$ wt %, and (d) $40B_2O_3 + 10Gd_2O_3$ wt %. Periodicity of measurements starting from sol preparation (curve markings): (*1*) 3 days, (*2*) 6 days, (*3*) 13 days, (*4*) 21 days, (*5*) 39 days, (*6*) 52 days, (*7*) 69 days, (*8*) 88 days.

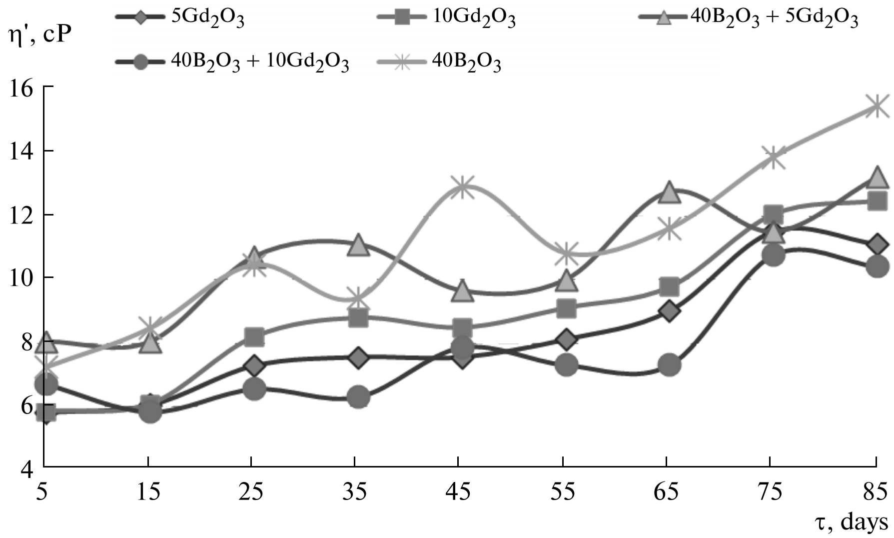

Fig. 4. Curves of changes of the structural viscosity (η') in the process of ageing (τ) for silicate sols containing only Gd as the inorganic component: (a) $5Gd_2O_3$ wt %, (b) $10Gd_2O_3$ wt %, only B: (c) $40B_2O_3$ wt %, combined B and Gd, (d) $40B_2O_3 + 5Gd_2O_3$ wt %, (e) $40B_2O_3 + 10Gd_2O_3$ wt %.

than for the previous measurement (Fig. 3b, curves *4* and *5*). Further, the situation changes into the opposite one, as can be seen from curves *5* and *6* (Fig. 3).

Besides, the dynamic viscosity for sols with inorganic components manifests dilatant properties during the system flow [15–18]. Dilatancy is manifested in all systems from this group of sols. Over the whole period of viscosity measurements, in each case, this property was observed from 3 to 5 times (Fig. 3). Similar results were obtained during the rheological studies of TEOS-based sol–gel systems with a POUU dopant (Figs. 2e, 2f).

Figure 4 shows the curves of the changes in the structural viscosity in silicate sol–gel systems containing boron and gadolinium in the ageing process. One can see that the viscosity of borosilicate sols changes jump-like (for instance, the viscosity of the sol $40B_2O_3 \cdot 55SiO_2 + 5Gd_2O_3$ wt % increases dramatically on the 15th–25th days and falls on the 35th–45th days).

The highest viscosity values are observed for borosilicate sol (without gadolinium). Such behavior is explained by the presence of boric acid easily forming hydrolyzing Si–O–B bonds, which results in the system's instability and affects the structure of borosilicate sols by inducing viscosity fluctuations. Upon addition of the second dopant (gadolinium), the viscosity values decrease slightly, but the curve's jump-like character is preserved. The structural viscosity of silicate sols containing only gadolinium as the inorganic component increases gradually over the whole observation period. The added dopant (gadolinium nitrate) has a much smaller effect on viscosity fluctuations than boric acid in the sol–gel system, which corresponds to the data [10] that larger atoms have a smaller effect on the system's properties, in particular, în structuring processes. Indeed, the Gd atom radius is much larger than that of B: 179×10^{-12} pm and 98×10^{-12} pm, respectively.

All the sols studied in the present work are homogeneous in structure and composition, while the unstable behavior of their viscosity within terms of up to 30–35 days does not hamper the formation of structurally homogeneous films without surface defects—diffusion sources [3, 4, 6, 13].

Interestingly, the rheological characteristics of the borosilicate sol containing 10 wt % Gd_2O_3 are substantially different from those of the sol containing 5 wt % Gd_2O_3. The latter is characterized by a more gradual increase of the dynamic viscosity and a higher structural viscosity value. As was also demonstrated in [3, 6, 12, 14], using the methods of optical microscopy, secondary mass-spectrometry, and those of the study of the electrophysical parameters, the optimal amount of doped gadolinium was ~5 wt % Gd_2O_3. Addition of larger amounts of Gd_2O_3 yields the emergence of undesirable phenomenon such as the increase of the variation of the thickness of the formed film over the plate surface area. However, in most cases, one can weaken or even eliminate these phenomena by thermal treatment (annealing).

CONCLUSIONS

The results of the studies of the rheological properties of sol–gel systems based on TEOS, boric acid, and gadolinium salt, with the addition of small amounts (0.5–2.0 wt %) of organic modifying dopants—polyols of linear, branched, and hyperbranched structures—are presented. The objective of these studies consisted in improving the process of the formation of hybrid organic-inorganic boron-containing films in order to make them meet the requirements relevant to such films—sources of diffusion of boron and gadolinium in the microelectronics planar technology.

The best dopants are polyols of the branched POUU and HBP structures. The optimal concentration of these dopants (~1 wt %) has been determined. At the exceeding of some critical concentrations of the dopant (more than ~2 wt %), one observes the loss of strength of the structural network of the inorganic polymer due to the embedding of the organic fragments into it.

All the studied sol–gel systems manifested thixotropy over the whole observation period (more than 2 months). The exception here is concerned with sols aged for 30 days and more with the POUU dopant and those with a higher HBP concentration (≥2.0 wt %).

Studies of the effect of organic modifying dopants on the rheological properties of sol–gel systems demonstrated that the highest viscosity was characteristic of borosilicate sols with POUU (η' = 7–9 cP). This is related to the branched structure of the POUU molecule containing, apart from end OH-groups, urethane groups (–NH–CO–), which tend to interact with each other with the formation of strong intermolecular bonds.

The character of the changes in the viscosity of borosilicate sols with HBO doping in amounts of ≥2.0 wt % is not strictly regular, while the dilatant properties are clearly manifested—the increase of viscosity upon an increase of the applied load. The dilatancy phenomena must be induced by the mechanical activation of the structuring processes occurring in these sol–gel systems. The effects related to the manifestation of the dilatant properties are observed in sols with POUU, and the higher the POUU concentration the stronger this phenomenon.

The most stable sols were borosilicate sols with doping additives of the hyperbranched polymer (η' = 5–6.5 cP) added in amounts of 0.5–1.1 wt %: they preserved homogeneity and mobility for almost 2 months. In the presence of a hyperbranched polymer, during the sol transition into gel, the precipitate was not formed (unlike other sols), which indicates the manifestation of sensitizing properties of this dopant. Thus, a hyperbranched polymer in the above concentration promotes the increase of sol stability against aggregation and sedimentation; i.e., it has a stabilizing effect on sol–gel systems.

With respect to sols containing 5–10 wt % Gd_2O_3, they comprise systems homogeneous in structure and composition and can be used in the formation of quality films for the same period of 2 months, just like hybrid sols.

REFERENCES

1. *Khimicheskie metody polucheniya keramicheskikh i polimernykh nanomaterialov iz zhidkoi fazy: Uchebnoe posobie* (Chemical Methods for the Preparation of Ceramic and Polymer Nanomaterials from the Liquid Phase: A Textbook), Luchinin, V.V. and Shilova, O.A., Eds., St. Petersburg: St. Petersburg State Electrotechnical University "LETI," 2013.
2. Shilova, O.A., Synthesis and structure features of composite silicate and hybrid TEOS derived thin films doped by inorganic and organic additives, *J. Sol–Gel Sci. Technol.,* 2013, vol. 68, no. 3, pp. 387–410.
3. Smirnova, I.V., Shilova, O.A., and Bubnov, Yu.Z., Investigation of the parameters of layers prepared through diffusion of boron and gadolinium from silicate and hybrid films into silicon wafers, *Glass Phys. Chem.,* 2009, vol. 35, no. 1, pp. 102–111.
4. Smirnova, I.V., Shilova, O.A., Moshnikov, V.A., and Gamarts, A.E., Features of simultaneous diffusion of boron and gadolinium in silicon from nanoscale hybrid organicinorganic films, *Semiconductors,* 2009, vol. 43, no. 10, pp. 1394–1399.
5. Shilova, O.A., Silicate nanosized films prepared by the sol–gel method for use in planar technology for fabricating semiconductor gas sensors, *Glass Phys. Chem.,* 2005, vol. 31, no. 2, pp. 201–218.
6. Petrova, I.V., The sol–gel technology of silicate and hybrid films—sources of the diffusion of boron and gadolinium into silicon, *Molodoi Uchenyi,* 2014, no. 10, pp. 46–53.
7. Maksimov, A.I., Moshnikov, V.A., Tairov, Yu.M., and Shilova, O.A., *Osnovy zol'–gel' tekhnologii nanokompozitov* (Fundamentals of the Sol–Gel Technology of Nanocomposites), St. Petersburg: Tekhnomedia, 2007.
8. Petrovskaya, T.S., Kozik, V.V., and Borilo, L.P., Formation of thin films in the silico-phosphate system, *Izv. Tomsk. Politekh. Univ.,* 2010, vol. 316, no. 3, pp. 23–27.
9. Petrovskaya, T.S., Borilo, L.P., and Kozik, V.V., Physical and chemical processes in the formation of thin films in the P_2O_5–SiO_2 system, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.,* 2010, vol. 53, no. 8, pp. 120–125.
10. Novikov, V.V., *Teoreticheskie osnovy mikroelektroniki. Uchebnoe posobie dlya radiotekhnicheskikh spetsial'nykh VUZov* (Theoretical Foundations of Microelectronics: A Textbook for Specialized Radiotechnical Universities), Moscow: Vysshaya Shkola, 1972.
11. Emtsev, V.V. and Mashovets, T.V., *Primesi i tochechnye defekty v poluprovodnikakh* (Impurities and Point Defects in Semiconductors), Moscow: Radio i Svyaz', 1981.
12. Smirnova, I.V., Shilova, O.A., Moshnikov, V.A., Panov, M.F., Shevchenko, V.V., and Klimenko, N.S., Investigation of the physicochemical properties, structure, and composition of nanosized borosilicate films prepared by the sol–gel method, *Glass Phys. Chem.,* 2006, vol. 32, no. 4, pp. 460–470.
13. Smirnova, I.V., Development of gadolinium and borosilicate nanoscale films formed by the sol–gel technology, *Extended Abstract of Cand. Sci. Dissertation,* St. Petersburg, 2007.

14. Smirnova, I.V., Shilova, O.A., Efimenko, L.P., Pugachev, K.E., Moshnikov, V.A., and Bubnov, Yu.Z., Investigation into the surface morphology of nanosized silicate and hybrid films by optical and atomic-force microscopy, *Glass Phys. Chem.,* 2007, vol. 33, no. 4, pp. 306–314.
15. Shchukin, E.D., Pertsov, A.V., and Amelina, E.A., *Kolloidnaya khimiya* (Colloid Chemistry), 3rd ed. revised with additions, Moscow: Vysshaya Shkola, 2004.
16. Ur'ev, N.B. and Ivanov, Ya.P., *Strukturoobrazovanie i reologiya neorganicheskikh dispersnykh sistem i materialov* (Structure Formation and Rheology of Inorganic Dispersion Systems and Materials), Sofia: Bulgarian Academy of Sciences, 1991.
17. Matveev, A.N., *Molekulyarnaya fizika: Uchebnoe posobie dlya studentov vuzov* (The Molecular Physics: A Textbook for Students of Universities), Moscow: OOO "Izdatel'stvo Oniks," 2006.
18. Frolov, Yu.G., *Kurs kolloidnoi khimii. Poverkhnostnye yavleniya i dispersnye sistemy* (A Course of Colloid Chemistry: Surface Phenomena and Disperse Systems), Moscow: Khimiya, 1989.
19. Smirnova, I.V., Movchan, T.G., and Shilova, O.A., Specific features of structuring of film-forming silica sols in the presence of boric acid and four-arm polyol with hyperbranched structure, *Russ. J. Appl. Chem.,* 2010, vol. 83, no. 12, pp. 2128–2134.
20. Sviderskii, V.A., Voronkov, M.G., and Klimenko, V.S., Hydrolytic polycondensation of tetraethoxysilane with metal salts and oxides in sol–gel process, *Russ. J. Appl. Chem.,* 1997, vol. 70, no. 10, pp. 1615–1619.
21. Novoselova, N.A., Li, N.M., Sorokina, V.V., and Anokhina, L.V., Specific features of the film-formation of the products of hydrolysis of TEOS, *Prikl. Khim.,* 1982, no. 8, pp. 1862–1863.
22. Shilova, O.A., Tarasyuk, E.V., Shevchenko, V.V., Klimenko, N.S., Movchan, T.G., Hashkovsky, S.V., and Shilov, V.V., The influence of low- and high-molecular hydroxyl-containing additives on the stability of sol–gel tetraethoxysilane-based systems and on the structure of hybrid organic–inorganic coatings, *Glass Phys. Chem.,* 2003, vol. 29, no. 4, pp. 378–389.
23. Taranenko, E.V. and Kandyrin, L.B., Rheological properties and rheokinetics of curing of modified thermoset oligomers, *Vestn. Mosk. Inst. Tonkoi Khim. Tekhnol. im. M. V. Lomonosova,* 2008, vol. 3, no. 1, pp. 82–88.
24. Zhukov, I.I., *Kolloidnaya khimiya* (Colloid Chemistry), Leningrad: Zhdanov Leningrad State University, 1949.
25. Khamova, T.V., Shilova, O.A., and Golikova, E.V., Investigation of the structuring in the sol–gel systems based on tetraethoxysilane, *Glass Phys. Chem.,* 2006, vol. 32, no. 4, pp. 448–459.

Translated by D. Marinin