Journal of Engineering Physics and Thermophysics, Vol. 74, No. 2, 2001

INFLUENCE OF TEMPERATURE-TIME PARAMETERS OF HEAT TREATMENT ON THE PROCESS OF PLANARIZATION OF THE SURFACE RELIEF OF MICROELECTRON STRUCTURES

S. P. Zhvavyi, G. D. Ivlev,
V. A. Pilipenko, and V. N. Ponomar'

UDC 621.3.049.77.002

The authors consider the process of fusion of phosphorosilicate and borophosphorosilicate glasses in planarization of the surface of integrated microcircuits under the conditions of both isothermal and pulse heat treatment. An expression for calculating the angle of fusion of the relief step as a function of the concentration of doping impurities in a glass and the time and temperature of heat treatment is obtained.

In the production of integrated microcircuits, much attention is given at present to multilayer metallized structures as one way of developing devices with higher integration levels. In this connection, phosphorosilicate (PhS) and borophosphorosilicate (BPhS) glasses are widely used in microelectron technology [1–6] in order to form interlevel dielectric layers in the manufacture of integrated microcircuits. Smoothing of sharp edges at the boundaries of contact windows and planarization of the surface of PhS or BPhS glass, which is needed for a qualitative deposition of metallization, are achieved in isothermal heat treatment in diffusion furnaces or under the conditions of rapid thermal annealing by intense radiation from halogen lamps. The duration of the isothermal heat treatment is tens of minutes or more, whereas the rapid thermal annealing is usually implemented within the second range of duration. Fusion of PhS and BPhS glasses under the conditions of rapid thermal annealing occurs for the nonstationary temperature $T(t)$ and variable viscosity of the glass $\mu(T)$. The efficiency of planarization of the relief and the smoothing of the side walls of contact windows are characterized by the magnitude of the fusion angle α (Fig. 1), which decreases with rise in the temperature T and with increase in the heat-treatment time t and the concentration of doping impurities in the glasses. Elucidation of the dependence $\alpha = \alpha(t, T)$ based on the simulation of the glass-fusion process is of great importance for optimization of heat-treatment regimes and provides deeper insight into the physics of this process.

The processes of fusion of the PhS and BPhS glasses were investigated in a number of works [1–6] both experimentally and using numerical simulation [5, 6]. Using the experimental data on the fusion of BPhS glass (isothermal annealing, t = 15–60 min) and assuming that the fluidity of glass depends exponentially on the inverse temperature, Vasil'ev et al. [3, 4] obtained an empirical formula that described the dependence of α on the temperature and the percentage of boric and phosphoric anhydrides. They also proposed an empirical expression for describing the time dependence of α during the heat treatment of glass. In [5, 6], the numerical simulation of the processes of fusion of PhS and BPhS glasses was carried out in the approximation of Newtonian viscous flow of a fluid. Whereas in [5] the simulation is based on the equation $A_f = A_0 \exp(-k\sigma h^3 t/\mu\lambda^4)$, where k is the constant, λ is the period of sinusoidal surface oscillation with the initial A_0 and final A_f amplitudes, in [6] a two-dimensional Navier–Stokes equation is solved numerically. The prob-

---

Institute of Electronics, National Academy of Sciences of Belarus, Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 74, No. 2, pp. 127–132, March–April, 2001. Original article submitted May 5, 2000.

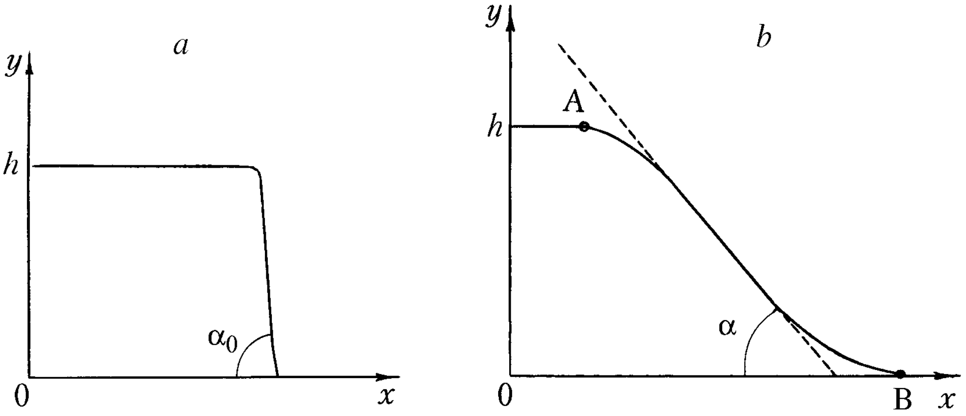

Fig. 1. Schematic of the profile of a glass step before (a) and after (b) fusion.

lem of fusion of the glasses was not solved analytically; for this reason, it is not clear what the functional relation between the quantity α, heat-treatment parameters (t, T), and physical characteristics of the glass (σ, μ) is. Moreover, there is no definite answer to the question of why the fusion process, initiated by a second light heating, is more efficientl than under the conditions of prolonged isothermal annealing in a furnace. The objective of the present work is to elucidate these problems.

Since the flow of a softened glass as that of a very viscous fluid is a complex physical process, in order to solve the problem we restrict ourselves (similarly to [5, 6]) to a model that presupposes the Newtonian viscous flow under the action of a moving force attributed to surface-tension forces. In this case, the Newton equation can be written in the form

$$\mu \frac{\partial v_x}{\partial y} = \frac{\sigma}{r}, \tag{1}$$

where $v_x(y)$ is the flow velocity over the x axis.

The flow of a softened glass is caused by the shearing stress $P_{xx} = -\sigma/r$. By considering the curve AB (Fig. 1) as a half-wave of a sinusoidal function [5] with period $2x$ and amplitude $h/2$, P_{xx} takes the maximum value for the minimum magnitude of the radius of curvature

$$r = \frac{x^2}{2\pi^2 h} = \frac{h}{2\pi^2} \operatorname{ctan}^2 \alpha . \tag{2}$$

By considering further the flow of the fluid with a wedge-shaped profile as the motion of a plane film with a profile of the velocity distribution $v_x = v_x(y)$ of the type of the Poiseuille distribution, the horizontal velocity field for the mean flow velocity U can be represented in the form [7]

$$v_x(y) = \frac{3(2hy - y^2)}{2h^2} U . \tag{3}$$

Having substituted Eq. (3) into Eq. (1), we obtain

$$U = \frac{h\sigma}{3r\mu} . \tag{4}$$

On the other hand, the mean velocity can be written as

$$U = \frac{dx}{dt} = -\frac{h}{\sin^2 \alpha} \frac{d\alpha}{dt} . \tag{5}$$

Having substituted Eqs. (2) and (5) into Eq. (4), we obtain the equation

$$-\frac{\cos^2 \alpha}{\sin^4 \alpha} \frac{d\alpha}{dt} = \frac{2\pi^2}{3} \frac{\sigma}{\mu h} , \tag{6}$$

whose solution will be of the form

$$\mathrm{ctan}^3 \alpha - \mathrm{ctan}^3 \alpha_0 = \frac{2\pi^2}{h} \int_{t_1}^{t_2} \frac{\sigma}{\mu} dt . \tag{7}$$

As follows from Eq. (7), the dependence of the fusion angle on the temperature is determined in terms of $\sigma(T)$ and $\mu(T)$. Since with rise in the temperature the surface-tension forces of the glasses change rather weakly ($d\sigma/dT \sim 0.05$–0.2 erg/(cm^2·K) [8]), it can be considered that σ = const and the dependence of α on T is mainly determined by the behavior of the viscosity of the glass $\mu(T)$. The viscosity of liquid silicate glasses in a wide range of temperatures is described well by the expression [9]

$$\mu (T) = \mu_0 \exp (E/RT) , \tag{8}$$

For the viscosity we also considered another expression [10]:

$$\mu (T) = \mu_0 \exp \left(\frac{E}{RT} + \frac{B}{T - T_0} \right), \tag{9}$$

where B and T_0 are the constants. As the evaluations showed, the quantity $B \sim 200^{\circ}$C, while for $\Delta T = T - T_0 \sim 50$–$200^{\circ}$C ($T_0 = 700^{\circ}$C) the second term is much smaller than the first one ($E \sim 30RT$) and its contribution is manifested only near T_0, i.e., in the range 700–720°C. Therefore, in what follows we disregarded the term $B/(T - T_0)$ in analyzing the fusion process.

From Eq. (7) it follows that cot $\alpha \sim t^{1/m}$, where $m = 3$. In a similar empirical relation [2, 3], from the experimental data for BPhS glass the magnitude of m was 2.4 ± 0.8, which within the limits of a possible error agrees with the value of 3 obtained by us.

In the case of isothermal annealing, from Eq. (7) we obtain

$$\cot^3 \alpha - \cot^3 \alpha_0 = 2\pi^2 \frac{\sigma}{\mu_0 h} t \exp (-E/RT) . \tag{10}$$

If the glass flow occurs under the conditions of rapid heat treatment, then, on the right-hand side of Eq. (7), it is necessary to perform integration over time from the beginning of the fusion process t_1 to its completion t_2, since the temperature of a silicon substrate with integrated-circuit chips changes continuously [11, 12]. A maximum of heating is achieved by the time when the halogen lamps are switched off (Fig. 2), after which the temperature of the substrate decreases. The dynamics of growth and subsequent decrease in T is well approximated by the relation

$$T (t) = \begin{cases} T_{\max} (t/\tau)^{1/2} & \text{for} \quad t \le \tau , \\ T_{\max} \tau/t & \text{for} \quad t > \tau , \end{cases} \tag{11}$$

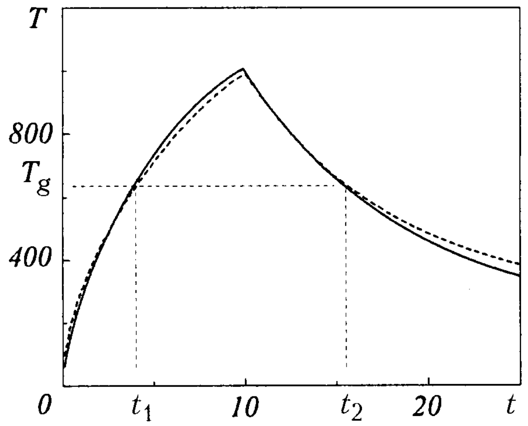

Fig. 2. Time dependence of the glass temperature in rapid thermal annealing. t, sec.

where τ is the time of heating, i.e., the duration of the light pulse. Figure 2 presents the time dependence of the glass temperature in the pulse heat treatment of duration $\tau = 10$ sec [12]. The same figure shows as a dashed line dependence (11). It is obvious that the dependence selected agrees rather well with the experimental one.

As is known, glass becomes plastic on heating and is softened at a temperature above the softening (transformation) temperature T_f. For this temperature the viscosity of the glass is $\mu(T_f) = 10^{13}–10^{14}$ P and with increase in the temperature it decreases sharply. In the case of cooling, the softened glass is vitrified for $T \le T_g(\mu T_g) = 10^{13}–10^{14}$ P. Consequently, the limits of integration in Eq. (7) must be as follows (Fig. 2):

$$t_1 = \left(\frac{T_f}{T_{max}}\right)^2 \tau, \quad t_2 = \frac{T_{max}}{T_g}\tau . \tag{12}$$

In pulse fusion of the glass, the rate of change in its temperature $W = dT/dt$ reaches values of ~100 K/sec; therefore, here account must be taken of the dependence of the temperature of softening (vitrification) on the rate of heating (cooling). For this, we used the relation [13]

$$\frac{1}{T_{f,g}} = C_1 - C_2 \log (W) , \tag{13}$$

where C_1 is the constant depending on the glass composition; for this constant we took the value

$$C_1 = \frac{1}{T_f^0} - 4.62 \cdot 10^{-5}\ \mathrm{K}^{-1} ,$$

which corresponds to the softening temperature T_f^0 measured experimentally on heating the specimens at a rate of 0.05 K/sec; $C_2 = 3.55 \cdot 10^{-5}\ \mathrm{K}^{-1}$.

The values of the vitrification temperature and softening temperature generally differ and, in addition, the constants C_1 and C_2 in Eq. (13) for T_g depend on the vitrification temperature through the activation energy [13], which for the softened glass is nonlinearly temperature dependent. However, for the problem considered this difference (~10 K) is of no considerable importance; therefore, in what follows we will assume that $T_f = T_g$.

In [1, 4, 14], it was shown that the same degree of planarization can be obtained for a temperature 20°C lower provided that the concentration of phosphor in the glass is increased by 1%, while with a 1% change in the concentration of boron the temperature of fusion decreases by 40–50°C. Since the temperature

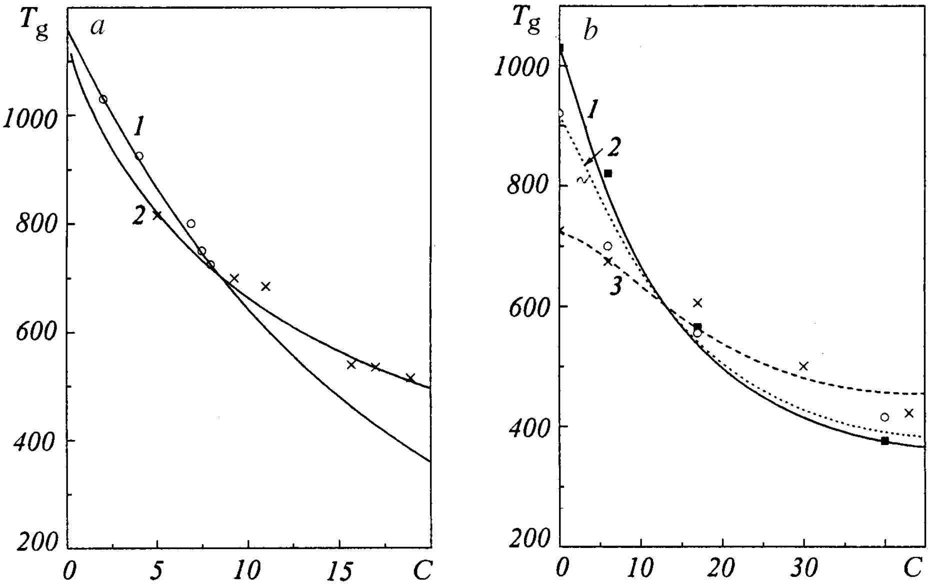

Fig. 3. Dependence of the softening temperature of PhS and BPhS glasses (a) on the concentration of P_2O_5 (1) and B_2O_3 (2); of BPhS glass (b) on the concentration of B_2O_3 with a concentration of P_2O_5 of 2 (1), 4 (2), and 8 mole % (3). T_g, K.

and the concentration of the impurity are the basic factors that affect the fusion of the glass, the determination of the optimum regimes of heat treatment requires knowledge of the dependence of the softening temperature of BPhS glass on the concentration of boron and phosphor. The values of the softening temperature of BPhS glass having different compositions are given in [15]. Using the results of these measurements and the data of other authors cited in this work, we obtained the following relation:

$$T_f^0\,[^\circ\mathrm{C}] = 1160\exp\left\{-\left[0.145 + (0.04 - 0.0088C_B)\,\frac{C_B}{0.35C_B^{3/2} + 0.45C_P}\right]C_B - \right.$$

$$\left. - (0.0646 - 0.0142C_B\left(\frac{C_P}{C_B^{3/2} + C_P}\right)^{1/2} C_P\right\}, \tag{14}$$

where C_B and C_P are the concentrations of boron and phosphor expressed in wt.% (1 wt.% of phosphor corresponds to 1.1 mole % of the phosphoric anhydride P_2O_5 and 1 wt.% of boron corresponds to 2.86 mole % of the boric anhydride B_2O_3).

In deriving expression (14), account was taken of a distinctive feature (noted in [15]) of the variation in the softening temperature of BPhS glass: with a concentration of B_2O_3 lower than 13 mole %, the magnitude of T_f^0 decreases with growth in the concentration of phosphoric anhydride. When $C_{B_2O_3}$ = 13 mole %, the softening temperature is virtually independent of P_2O_5, while with a concentration of boric anhydride higher than 13 mole %, the softening temperature rises with increase in the concentration of P_2O_5.

It is obvious from Fig. 3 that the values of the softening temperature calculated from formula (14) are in satisfactory agreement with the experimental ones [15]. It should be noted here that expression (14) gives values of T_f^0 close to the experimental data, with the concentration of the phosphoric anhydride $P_2O_5 < 10$ mole % and of the boric anhydride $B_2O_3 < 45$ mole %.

In conformity with the valence-configuration theory of the viscous flow of glass [9, 16, 17], as the temperature grows, the viscosity decreases not only due to the heating of the glass but also due to the de-

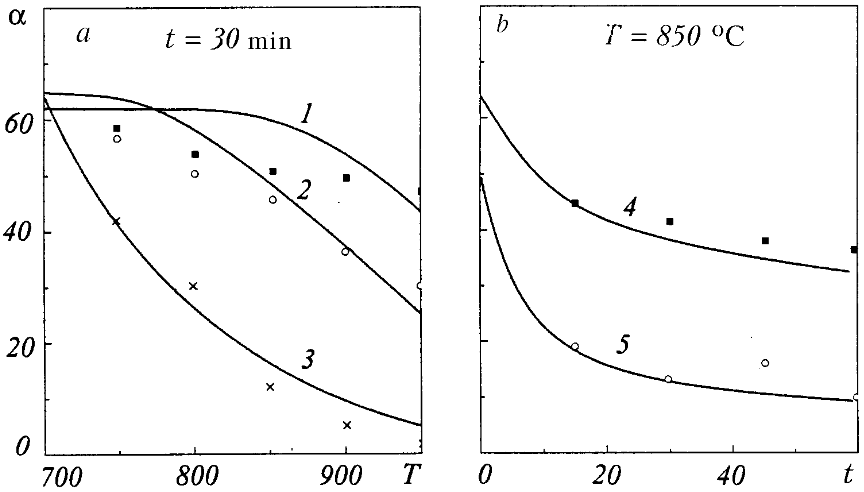

Fig. 4. Dependence of the fusion angle of steps of BPhS glass in isothermal heat treatment on the temperature (a) and time (b) of treatment. The concentrations of boron and phosphor (in wt.%) are: 1) 1.9 and 2.2; 2) 1.25 and 4.8; 3) 3.8 and 4.8; 4) 3.4 and 2.6; 5) 3.4 and 5.2. T, °C; t, min.

crease in the activation energy of the viscous flow $E(T)$, which for the melting temperature T_{mel} reaches its minimum value of $E_{\min} = E(T_{\text{mel}})$ and thereafter remains constant. As the temperature rises, the entropy of viscous-flow activation $S = -\partial E/\partial T$ also decreases from its maximum value of $S_{\max} = S(T_g)$ virtually to zero for $T = T_{\text{mel}}$ [16]. In this case, we can write approximately

$$S(T) = \frac{T_{\text{mel}}}{T_{\text{mel}} - T_g}\left(1 - \frac{T}{T_{\text{mel}}}\right) S_{\max} . \tag{15}$$

With allowance for the empirical relation $T_g/T_{\text{mel}} = 2/3$ (the Kautsmant criterion [13]), we obtain that

$$S(T) = 3\left(1 - \frac{T}{T_{\text{mel}}}\right) S_{\max} . \tag{16}$$

If we assume further that the entropy-free component of the activation energy of the viscous flow is temperature-independent and equals $E_{\min}$, then an expression for the activation energy of the viscous flow for the temperature $T(T_g < T < T_{\text{mel}})$ can be written in the form

$$E(T) = E_{\min} = \int_T^{T_{\text{mel}}} S(T')\, dT' = E_{\min} + \frac{3}{2} T_{\text{mel}} \left(1 - \frac{T}{T_{\text{mel}}}\right)^2 S_{\max} . \tag{17}$$

In heat treatment, the fusion angle for the step of PhS or BPhS glass was calculated from Eq. (7) with account for Eqs. (8), (11)–(14), and (17) for the values of $\mu_0 = 10^{-3}$ P and $\sigma = 400$ erg/cm^2 [8]. The magnitude of the activation energy of the viscous flow was determined from the expression

$$E_{\min} = (400 - 18.5 C_B - 13.5 C_P) \ \text{kJ/mole} , \tag{18}$$

which was obtained from a preliminary analysis of the experimental data [1–3]. For the entropy $S_{\max}$ we used three values depending on the total concentration of the impurities $C = C_B + C_P$: 10 J/(mole·K) for $C < 5$ wt.%, 60 J/(mole·K) for 5 wt.% $< C < 8$ wt.%, and 180 J/(mole·K) for $C > 8$ wt.%.

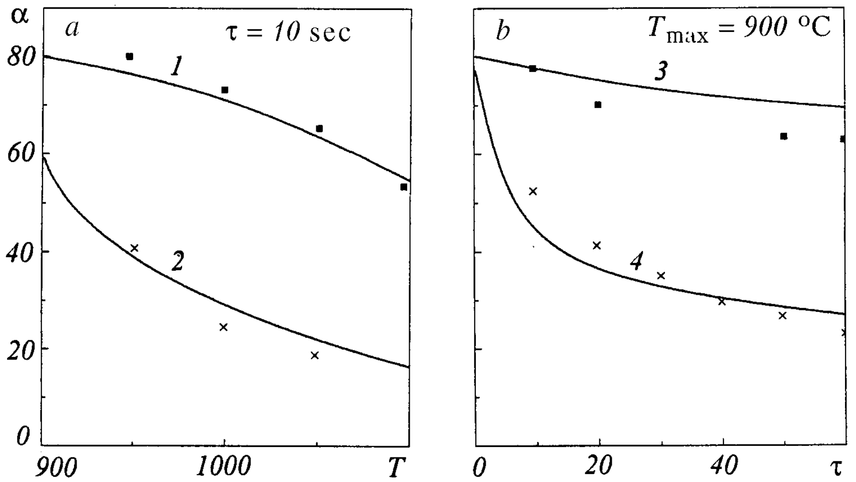

Fig. 5. Dependence of the fusion angle of steps of BPhS glass in rapid thermal annealing on the maximum temperature (a) and time (b) of heating. The concentrations of boron and phosphor (in wt.%) are: 1) 2.5 and 3.5; 2) 6.3 and 2.9; 3) 3.6 and 2.4; 4) 6.5 and 3.5. τ, sec

Figure 4 presents experimental dependences [3] of the fusion angle on the temperature and time of treatment in isothermal annealing of BPhS glass and also calculation results. The calculated values of $\alpha(T, t)$ agree rather well with the experimental data. The noticeable deviation of $\alpha(T)$ from the experimental values in the range of low temperatures ($T < 850^{o}$C, curves 1 and 2 in Fig. 4a) is associated with the relatively high softening temperature ($T_g = 797^{o}$C is denoted by curve 1 and 780^{o}C, by curve 2), which is calculated from formula (14).

The results of calculations of the pulse heat treatment of BPhS glass were compared with the experimental data [1]. As is obvious from Fig. 5, here, too, good agreement is obtained. In the calculations, for curves 2 and 4 we used the value of $\sigma = 100$ erg/cm^2, since in conformity with dependence (14) and the Kautsman criterion the melting temperature of BPhS glass with $C_{\text{B}} = 6.3$ wt.% and $C_{\text{P}} = 2.9$ wt.% is equal to 920^{o}C, while with the concentration of $C_{\text{B}} = 6.5$ wt.% and $C_{\text{P}} = 3.5$ wt.%, $T_{\text{mel}} = 915^{o}$C, i.e., the fusion process occurs for $T > T_{\text{mel}}$ and, consequently, the surface tension of the fused glass must be less than in the case of the softened glass for $T_g < T < T_{\text{mel}}$.

Thus, the investigation performed shows that the process of planarization of the relief of microelectron structures in high-temperature treatment is rather well described within the framework of the model of Newtonian viscous flow of PhS glass (BPhS glass) under the action of surface-tension forces. An empirical formula is suggested that establishes the functional interrelation between the softening temperature of the BPhS glass (PhS glass) and the concentrations of boron and phosphor impurities. Using the results of analytical solution of the problem of the viscous flow of glass in heating, it is indicated that account for the dependence of the softening temperature of glass on the concentration of doping impurities and for the dependence of the activation energy of viscous flow on temperature enables one to adequately describe the influence of the temperature-time regimes of isothermal annealing and rapid heat treatment on the finite angle of fusion of a step of PhS and BPhS glasses in planarization of the relief of microelectron structures.

NOTATION

T, temperature; t, time; x and y, coordinates; μ, viscosity; α, fusion angle of the glass step; σ, surface tension; h, glass-film thickness; v_x, flow velocity over the x axis; r, radius of curvature; U, mean velocity; E, activation energy of viscous flow; R, universal gas constant; $T_{\max}$, maximum temperature of heating; T_g, vitrification temperature; T_f, softening temperature of the glass; T_f^0, softening temperature on heating the glass at a rate of 0.05 K/sec; T_{mel}, melting temperature; S, activation entropy of viscous flow. Subscripts: 0, initial state; max, maximum value; min, minimum; mel, melting; g, vitrification; f, softening.

REFERENCES

1. F. S. Becker, D. Pawlik, H. Schafer, and G. Standigl, *J. Vac. Technol. B*, **4**, No. 3, 732–744 (1986).
2. J. S. Mercier, *Solid State Technol.*, **30**, No. 7, 85–90 (1987).
3. V. Yu. Vasil’ev and T. G. Dukhanova, *Élektron. Tekh., Ser. 3, Mikroélektronika*, No. 4, 38–41 (1991).
4. V. Yu. Vasil’ev, T. G. Dukhanova, V. I. Kosyakov, and V. A. Shestakov, *Élektron. Prom.*, Issue 5, 40–41 (1988).
5. L. K. White, N. A. Miszkowski, W. A. Kurylo, and J. M. Shaw, *J. Electrochem. Soc.*, **139**, No. 3, 822–826 (1992).
6. G. Thallikar, H. Liao, T. S. Cale, and F. R. Myers, *J. Vac. Sci. Technol. B*, **13**, No. 14, 1875–1878 (1995).
7. P. G. De Gennes, *Usp. Fiz. Nauk*, **151**, No. 4, 619–681 (1987).
8. O. V. Mazurin, M. V. Strel’tsina, and T. P. Shvaiko-Shvaikovskaya, in: *Properties of Glasses and Glass-Forming Melts: Handbook* [in Russian], Vol. 1, Leningrad (1973).
9. R. L. Müller, *Zh. Prikl. Khim.*, **28**, No. 10, 1077–1087 (1955).
10. K. Matusita, M. Koide, and T. Komatsu, *J. Non-Cryst. Solids*, **140**, 141–145 (1992).
11. V. E. Borisenko, S. N. Kornilov, V. A. Labunov, and Yu. V. Kucherenko, *Zarub. Élektron. Tekh.*, **6**, 45–65 (1985).
12. V. A. Pilipenko and Yu. P. Popov, *Élektron. Prom.*, No. 5, 3–9 (1988).
13. G. M. Bartenev, *Structure and Mechanical Properties of Inorganic Glasses* [in Russian], Moscow (1966).
14. J. E. Tong, K. Schertenleib, and R. A. Carpio, *Solid State Technol.*, **27**, No. 1, 161–170 (1984).
15. K. Nassau, R. A. Levy, and D. L. Chadwik, *J. Electrochem. Soc.*, **132**, No. 2, 409–415 (1985).
16. S. V. Nemilov, *Fiz. Khim. Stekla*, **2**, No. 3, 193–203 (1976).
17. S. V. Nemilov, *Fiz. Khim. Stekla*, **4**, No. 2, 129–148 (1978).