

On the Conduction Mechanism of Silicate Glass Doped by Oxide Compounds of Ruthenium (Thick Film Resistors). 3. The Minimum of Temperature Dependence of Resistivity

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Abstract

This article is the final part of the investigation of conduction mechanism of silicate glass doped by oxide compounds of ruthenium (thick film resistors). In the first part [1], the formation of percolation levels due to diffusion of dopant atoms into the glass has been considered. The diffusion mechanism allowed us to explain shifting of the percolation threshold towards to lower value and the effect of firing conditions as well as the components composition on the electrical conduction of the doped glass. The coexistence of thermal activation and localization of free charge carriers as the result of nanocrystalline structure of the glass was the subject of the second part [2]. Because of it, the resistivity of the doped silicate glass is proportional to $\exp(-aT^{-\zeta})$ at low temperatures ($T < 50$ K), $0.4 < \zeta < 0.8$. Structural transitions of nanocrystals take place at high temperatures ($T > 800$ K) and the conductivity of the doped silicate glass decreases sharply. We consider the origin of the minimum in the temperature dependence of resistivity of the doped silicate glass here. It is shown that the minimum arises from merge of impurity band into the valence band of glass at temperature high enough, so thermal activation of charge carriers as well as its hopping are failed, and scattering of free charge carriers become predominant factor in the temperature dependence of the resistivity.

Keywords

Lead-Silicate Glass, Thick Film Resistors, Minimum of Resistivity, Doping, Energy Bands, Conductivity, Thermal Activation, Hopping

1. Introduction

This article is the final part of the investigation of conduction mechanism of silicate glass doped by oxide compounds of ruthenium (thick film resistors).

In the first part [1], the formation of percolation levels due to diffusion of dopant atoms into the glass has been considered. The diffusion mechanism allowed us to explain shifting of the percolation threshold towards to lower value and the effect of firing conditions as well as the components composition on the electrical conduction of the doped glass (DSG). The coexistence of thermal activation and localization of free charge carriers as the result of nanocrystalline structure of the glass was the subject of the second part [2]. Because of it, the resistivity of the doped silicate glass is proportional to $\exp(-aT^{-\zeta})$ at low temperatures ($T < 50$ K), $0.4 < \zeta < 0.8$. Structural transitions of nanocrystals take place at high temperatures ($T > 800$ K) and the conductivity of the doped silicate glass decreases sharply.

An “enigmatic” minimum near the room temperature [3]-[10] and metallic conductance beyond it [11] take place in the silicate glass doped by oxide compounds of ruthenium. Adding of other metal oxides does not change qualitatively the situation [9] [12]. The origin of the Minimum is considered here. It is shown that the minimum arises from the merge of impurity subband into the valence band of glass at temperature high enough, so thermal activation of charge carriers as well as its hopping are failed, and scattering of free charge carriers become predominant factor in the temperature dependence of the resistivity.

2. Experiment

The manufacturing process of DSG used here is standard for technology of thick film resistors and was described elsewhere (the mixture of the glass and the dopant powders on the alumina substrate have been fired at $T_f = 1073 - 1125$ K in $\tau = 10$ min). Content of RuO₂ in our samples of DSG is indicated in the figure captions. The glass compositions investigated are as follows (weight %):

Glass1 SiO₂ 27; PbO 67; BaO 4; MgO 2;

Glass2 SiO₂ 32; PbO 63; Al₂O₃ 5;

Glass3 SiO₂ 33; PbO 67.

Firing temperature T_f is 1073 K for glass1, 1123 K for glass2 and glass3.

The value of resistance was measured by digital multimeter Sch-300 having error less than 0.2%. The temperature was measured by the same multimeter and standard Pt-PtRh thermocouple. The thermocouple was calibrated in standard temperature points of water boiling (373 K), tin and silver solidification (505 and 1234 K accordingly).

The DSG samples are screen-printed and have dimensions $10 \times 10 \times 0.025$ mm³ so measured values of the resistance R (Ohm) and the resistivity ρ (Ohm·cm) are related as $\rho = Rt = 2.5 \times 10^{-3} R$, here $t = 2.5 \times 10^{-3}$ cm is the thickness of the DSG.

3. Conduction Mechanisms of DSG

The effective medium theory [3] [13] can evaluate the measurable (effective) values of permittivity ε^* and conductivity ρ^* of the DSG on the basis of known values of same parameters for the dopant and the glass (ε_d , ρ_d and ε_g , ρ_g accordingly). It is assumed in this theory that the volume content C of the dopant is known a priori. But experiments show that this assumption is not justified for the DSG due to physical or chemical interactions of components at the firing temperatures. These processes can generate new compounds or regions of unknown parameters. On the other hand, the minimum of $\rho(T)$ can arise only from coexisting of at least the two components having opposite temperature dependence of conductivity—dielectric and metallic with same values of conductivity. Unfortunately these values are strong differing in the DSG: $\rho_g > 10^{15}$ Ohm·cm and $\rho_d < 2.5 \times 10^{-4}$ Ohm·cm (for RuO₂, [14] [15]). This fact has the total effect for all the known mechanisms of the DSG conductivity and will be considered more detailed later.

The percolation theory leads to the percolation threshold on the conductivity

$$\sigma(C) = \sigma_0 (C - C_c)^t, \quad (1)$$

here C_c is the critical volume content of the dopant (about 16 vol% in the three dimensions), t is the critical exponent having most probable value about 1.7 in the three dimensions (must have the universality for various

percolation problems in the space of same dimensions). σ_0 is some constant.

The value of the critical exponent t for DSG is essentially differ [16]-[20] from the universal value $t_0 = 2$ in percolation theory. This distinction has been explained as the result of tunneling and percolation [16].

Conductivity of DSG has been simulated by the Monte-Carlo method [18] and above mentioned distinction in t values explained as the effect of mishmash of the dopant and the glass particles size.

The tunneling-percolation mechanism [6] [21] [22] Tunneling of charge carriers through the potential barriers compliant to thin glass layer between particles of dopant is the main factor of the conductivity in this model. Since these barriers are connected series with the dopant particles having metallic conductivity, one can write

$$\rho(T) \approx 0.5\rho_b (\sin(aT)/aT)(1 + \exp(E/kT)) + \rho_{d0}(1 + \alpha T), \quad (2)$$

here first factor in brackets is the temperature dependence of the tunneling through the barrier, the second one contains very small (about 0.4 - 5 meV) energy E , which is required to add into or remove the single charge carrier from the dopant particle. ρ_b is the barrier height, ρ_{d0} is the resistivity of the dopant particle at $T = 0$ K, and k is the Boltzmann's constant. Parameter a is the characteristic of the barrier height related to the Fermi level E_F , and researchers [6] assume that $aT/3 < 1$. The second term in (2) is the resistivity of the dopant particle, α is the temperature coefficient of resistivity of the dopant. It is considered that these barriers and dopant particles form the infinite cluster, which connects the terminations of the sample.

Expression (2) has a minimum, caused by metallic conductivity of the dopant particles (second term), but is applicable in the narrow range of temperature. On the other hand, the main distance between the dopant particles in the DSG

$$L = D\sqrt[3]{\frac{\pi}{6C}} = D\sqrt[3]{\frac{\pi}{6} \left[1 + \frac{\gamma_d}{\gamma_g} \left(\frac{1}{C_m} - 1 \right) \right]} \quad (3)$$

is about 0.1 - 1.5 μm . Appropriate thickness of the glass layer between the particles is $L - D \approx 0.6 \mu\text{m}$. It is clear that the tunneling of charge carriers is not effective on the same distances, so the description of DSG properties via tunneling runs against the problems. Here D is the diameter of the dopant particles, γ_d and γ_g are the specific weight of the dopant and the glass accordingly, C_m is the weight content of the dopant. $L \approx 0.87 \mu\text{m}$ for the powder of RuO_2 with $D \approx 0.5 \mu\text{m}$ and $C_m = 16$ wt % ($C \approx 9.9\%$). The resonance tunneling has been used [23] to have a sufficient tunneling probability through the barriers as wide as 0.1 μm or larger. This effect assumes the uniform barriers which is hardly probable in the glass having strong structural and chemical inhomogeneities in atomic as well as micrometric scale.

It should be noted also that $\sin aT/aT$ in (2) has the first minimum at $aT \approx 4.4$ and the condition $aT/3 < 1$ is violated. This minimum slightly shifts towards to lower values of aT due to the second term in (2) while experimental variation of T_m is 77 to 700 K in accordance with the glass composition, the doping level C and firing temperature T_f .

Fluctuation-induced tunneling conduction gives the temperature dependence [24]

$$\sigma(T) = \sigma_0 \exp[-T_1/(T + T_2)], \quad (4)$$

here σ_0 , T_1 and T_2 are some parameters. There is no maximum in (4) for $T_2 > 0$ without including the metallic conductivity of dopant relicts and the percolation threshold should be introduced into the model via percolation theory.

Hopping-percolation model [22] [25] is based on the Mott's theory [26] (variable range hopping) and leads to the temperature dependence of conductivity

$$\sigma(T) = AT^n \exp[-(T_h/T)^{1/4}] \quad (5)$$

with $T_h = 16a^3/(kN_{wF})$, a is the inverse decay distance of electron's spherical wave function (inverse localization distance), N_{wF} is the density of states of electrons near the Fermi level and n is the constant having most probable value about 1, A is some constant value. There is no maximum in (5) as well and hopping of carriers has not the threshold. Because of it hopping of carriers is combined with the percolation theory [27]-[29] as well as the metallic conduction of the dopant particles.

Low-temperature ($T = 0.05 - 4.2$ K) measurements show the hopping conduction of the DSG and the decreas-

ing of the hopping energy due to generation of the narrow impurity band in the forbidden gap of the glass by diffusion of the ruthenium atoms. Concentration of the diffused atoms increases as T_f increases.

There are two problems. The first one caused by the possibility of experimental corroboration of the Mott's law (5). It has been showed [30] that the expression (5) in the generalized form

$$\sigma(T) = AT^n \exp\left[-(T_h/T)^m\right] \quad (6)$$

can give good agreement with the experimental data in the wide range of $m = 0.2 - 0.55$ if choose the value of n in the interval -7.5 to 2.75 . Despite it the expression (5) with various values of n is used often as the proof of the hopping conductivity in the DSG.

The second problem is the result of the fact that carriers hopping (which is actually the quantum-mechanical tunneling) is not effective in distance about $0.1 - 1.5 \mu\text{m}$ that corresponded to mean distance between the dopant particles in the DSG. It forces the researchers to consider the diffusion of dopant atoms into the glass or the particles to be far smaller than they are actually.

Authors [31] as well as Shoepe [4] have derive experimentally at low temperatures ($0.05 - 2 \text{ K}$) the expression

$$\sigma(T) \sim \exp\left[-(\Theta/T)^x\right] \quad (7)$$

with $x = 0.5$ for DSG conductivity and explained it as result of tunneling though graded barriers. For $x = 0.5$ one finds $p = 2$ in three dimensions ($d = 3$), and this value corresponds to the density of states variations expected to result from Coulomb interaction between localized carriers [28]. Here d is the dimensionality and p is the power by which the density of states $g(E)$ rises about the Fermi level: $g(E) = |E - E_f|^p$. Subsequently the authors [5]

have calculated for mentioned experimental results the localization radius $a_0 = e^2 / (\varepsilon \varepsilon_0 k T_h)$, here e is the electron charge, ε_0 is the permittivity of free space, $\varepsilon = 10$ is the static dielectric constant of DSG. It was found that $a_0 \approx 2 \mu\text{m}$ and the estimated activation energy less than kT . Such value of a_0 is meaningless because of the mean size of the dopant particles where carriers to be localized is about $0.1 - 1 \mu\text{m}$. So authors [5] conclude that the percolation theory is not applicable to the DSG.

It was concluded in [32] that hopping mechanism is important at low temperatures and tunneling takes place at high T .

Conduction through the narrow impurity band generated in the forbidden band of the glass by diffused dopant atoms due to firing have been considered in [33] [34]. Robertson [34] has proved this model by effect of firing duration τ and size D of dopant particles on the DSG conductivity. Increasing of τ results higher concentration of the dopant atoms diffused into the glass and reduces the hopping distance so conductivity increases. But there is no detailed development of this model.

Mismatch of the thermal expansion coefficients of the DSG and the substrate [35] leads to

$$\rho(T) = \rho_\Theta \left\{ \exp\left(\frac{\beta}{T} - \frac{\beta}{\Theta}\right) + \psi(T - \Theta) k_\Theta [1 + \chi(T - \Theta)] \right\}, \quad (8)$$

which takes into account the tension ψ of the DSG layer through the mismatch of thermal expansion coefficients of the glass and the ceramic substrate. Here ρ_Θ is the value of $\rho(T)$ at temperature Θ , k_Θ is the gauge factor of DSG at Θ , χ is the temperature coefficient of the gauge factor. $k\beta$ is the activation energy of DSG.

This mismatch was taken for in [36] as well. It is found that this factor can correct the measured value of temperature coefficient of resistivity on $\pm 100 \times 10^{-6} \text{ K}^{-1}$.

Samples of the DSG glass + RuO_2 without the ceramic substrate have been examined in [37]. It is considered that the predominant conductivity is metallic at $C > 20\%$ and ionic at $C < 3\%$. At the intermediate region tunneling and hopping of carriers are coexisted.

Combination of the metallic and thermal activated (semiconducting) conductivity [7] [38] gives

$$\rho(T) = \rho_{g_0} \exp(E_a/2kT) + \rho_{a_0} (1 + \alpha T), \quad (9)$$

which is in the good agreement with experiment at $T > T_m$, but out of keeping at $T < T_m$. First term in (9) is the contribution of the glass layers between the dopant particles having metallic conductivity (the second one).

Prudenziati has pointed out [39] that possible conduction mechanisms of the DSG are hopping, tunneling and transport through the narrow impurity band, formed in the glass interlayers by chemical interactions of the glass

and dopant.

Effects of firing temperature on the parameters of the DSG have been investigated in [40] and it is concluded that any theoretical models of the DSG conductivity is not adequate to the wide variation range of the DSG parameters. Such conclusion is contained in the number of other articles [31].

Unsoundness of the two-phase system model [6] has been noticed in [12].

Electron microprobe analyses and atomic force microscope investigations [7] [41]-[43] of the interface of glass—RuO₂ show that there are the zone of higher concentration of Ru atoms in the glass round the RuO₂ particles. These zones are formed by diffusion of Ru atoms into the glass. It is showed as well [44] that diffusion length of Ru atoms higher than 1 μm and content of them is less than 7 atomic%. The authors conclude that the conductivity of RuO₂ based DSG is realized by hopping of carriers among the Ru clusters of 2 to 4 nm in size.

Unfortunately, relations of the diffusion zones and the minimum of the temperature dependence of DSG resistivity have not investigated in these works.

4. Applicability of the Known Models to the $\rho(T)$ of the DSG

Let us to consider the DSG containing $C_m = 16$ wt% of RuO₂ and 84 wt% of lead-silicate glass 2. $C = 9.9\%$ and the mean distance between centers of spherical particles of the dopant $L = 0.87$ μm for its diameter $D = 0.5$ μm here. DSG is the foil of $l \cdot w \cdot t = 10 \times 10 \times 0.025$ mm³. Here w , l , t are width, length and thickness of the sample accordingly. $t = 0.0025$ cm is the standard thickness of the thick film resistors.

Specific weights are $\gamma_d = 6.85$ g/cm³ for the dopant (RuO₂) and $\gamma_g = 4$ g/cm³ for the glass. Resistivity is $\rho_d = 4 \times 10^{-5}$ Ohm·cm (RuO₂) and $\rho_g > 10^{16}$ Ohm·cm (the glass). Volume of the sample is $v = 2.5 \times 10^{-3}$ cm³, volume of the dopant is $v_d = Cv = 0.099 \times 2.5 \times 10^{-3} \approx 2.5 \times 10^{-4}$ cm³.

We will estimate now the upper and lower limits of the resistivity for the DSG sample. There are two extreme distributions of the dopant particles in the sample (Figure 1). Resistivity of the sample will be intermediate for all other cases.

In the first case the dopant forms the solid film of length l and thickness t along the electric field, *i.e.* the film closes the metallic terminations (Figure 1(a)). Wideness of the same film is $w_d = Cw = 0.099$ cm and its resistance is $R_{d1} = \rho_d l / (w_d \cdot t) = 4 \times 10^{-5} / (0.099 \times 2.5 \times 10^{-3}) = 0.162$ Ohm. The resistance of the glass film connected in parallel is $R_{g1} = \rho_g l / ((1 - w_d) \cdot t) = 10^{16} / (2.5 \times 10^{-3} \times 0.901) = 4.4 \times 10^{18}$ Ohm. One can see that the full resistance of the sample $R_1 = (R_{d1}^{-1} + R_{g1}^{-1})^{-1} = 0.162$ Ohm is determined by resistance of the dopant film.

In the second case the dopant film is across the electric field (Figure 1(b)) and its resistance is $R_{d2} = \rho_d w_d / (w \cdot t) = 4 \times 10^{-5} \times 0.099 / 2.5 \times 10^{-3} = 1.58 \times 10^{-3}$ Ohm. The resistance of the glass layer in series is $R_{g2} = \rho_g (1 - w_d) / (w \cdot t) = 10^{16} \times 0.901 / 2.5 \times 10^{-3} = 3.6 \times 10^{18}$ Ohm and the total resistance of the sample $R_2 = R_{d2} + R_{g2} = 1.58 \times 10^{-3} + 3.6 \times 10^{18} = 3.6 \times 10^{18}$ Ohm is determined by the glass film resistance. Accordingly, the temperature dependence of the sample resistance is determined by the dopant layer in the first case and by the glass layer in the second case:

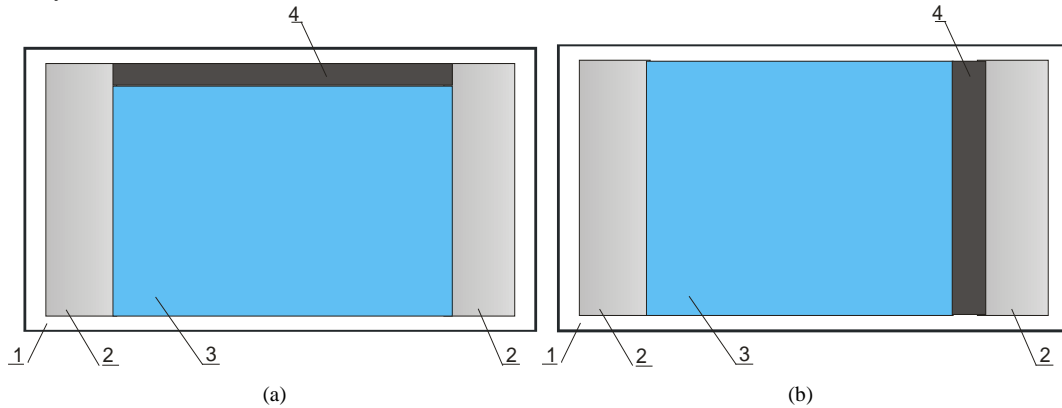


Figure 1. Configuration of the DSG sample in the cases: dopant layer is along the electric field (a) and across (b). 1 is the substrate, 2 is the metallic terminations, 3 is the glass layer and 4 is the RuO₂ layer.

$$TCR_1 = dR_1/(R_0 dT) = d(1 + \alpha \Delta T)/dT = \alpha \quad (10.1)$$

and

$$TCR_2 = dR_2/(R_{20} dT) = -E_a \exp(E_a \Delta T / 2kT_0 T) / (2kT^2). \quad (10.2)$$

Here R_0 and R_{20} are values of resistance at some reference temperature T_0 , $\Delta T = T - T_0$ is the deviation of temperature from T_0 . The minimum of the

$$R(T) = R_{g0} \exp(E/2kT) + R_{d0} (1 + \alpha \Delta T)$$

is possible only if

$$\alpha > \left| -E_a \exp(E_a \Delta T / 2kT_0 T) / (2kT^2) \right|$$

near the minimum.

Simulation of the temperature dependence of the DSG resistance in these cases is shown in **Figure 2**. In the case of the dopant layer along the electric field, $R(T)$ is linear at low temperatures and has the maximum instead of the experimental minimum so this case is not applicable for DSG.

For this reason we will consider now the metallic and semiconducting sections connected in series (**Figure 1(b)**) and attempt to find out the correlation between the resistivity values of these sections at the minimum of the total resistivity. For this purpose we rewrite (9):

$$\rho(T) = a \rho_{g0} \exp(E_a / 2kT) + (1 - a) \rho_{d0} (1 + \alpha T), \quad (11)$$

here a and $1 - a$ are the contributions of the semiconducting and metallic sections to the total resistivity. The condition of the minimum $d\rho(T)/dT = 0$ at $T = T_m$ gives a as a function of T_m :

$$a(T_m) = \left(1 + \frac{1}{\alpha} \frac{\rho_{g0}}{\rho_{d0}} \frac{E_a}{2kT_m^2} \exp \frac{E_a}{2kT_m} \right)^{-1}. \quad (12)$$

$a(T_m)$ as function of T_m is showed in **Figure 3**. It is seen from **Figure 3** that $a \approx 0.3 - 0.9$ is required to have $T_m \approx 300$ K, as it has often observed experimentally, and $\rho(T_m)$ must be in order of the $\rho_{g0}(T_m) \exp(E_a / 2kT_m)$ as well as $\rho_{d0}(1 + \alpha T_m)$. But this condition cannot be realized in the DSG, where $\rho_d(300 \text{ K}) \approx 4 \times 10^{-5}$ Ohm·cm for RuO_2 and $\rho_g(300 \text{ K}) > 10^{16}$ Ohm·cm for the glass $2\text{SiO}_2 \cdot \text{PbO}$ while $\rho(300 \text{ K}) \approx 10^{-2} - 10^4$ Ohm·cm for DSG. It means that the resistivity of RuO_2 or other dopant particles cannot be used for interpret $\rho(T_m)$ in terms of the (12) and the physical or chemical mechanism for reducing of the glass resistivity down to $\rho(300 \text{ K})$ should be considered here.

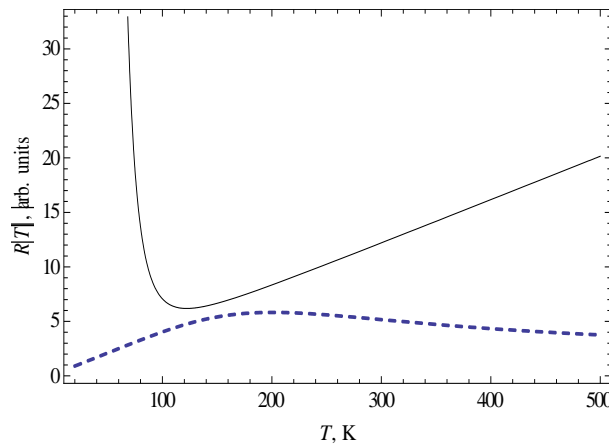


Figure 2. Simulation of the $R(T)$ of the DSG for the dopant layer orientations: along the electric field (dashed line) and across the electric field (solid line). Simulation was carried out for $R(T) = ((0.1(1 + 0.4T))^{-1} + (1.7 \exp(0.45/kT))^{-1})^{-1}$ and $R(T) = 0.1(1 + 0.4T) + 0.02 \exp(0.45/kT)$ accordingly.

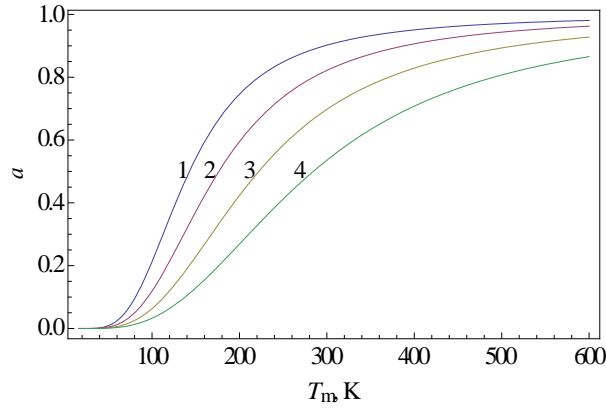


Figure 3. Contribution of the semiconducting section a vs. the temperature of minimum T_m for $E_\sigma = 50$ meV, $\alpha = 0.004$ K $^{-1}$ and ρ_g/ρ_{d0} : 6.7×10^8 (1); 1.35×10^9 (2); 2.7×10^9 (3); 5.4×10^9 (4).

5. Our Model, Experimental Results and Discussion

The model and simulations It was pointed out above that the resistivity of the RuO₂ used in DSG is lower of the resistivity of the DSG by factor of $10^{-3} - 10^{-4}$. As a result the mechanism for lowering the ρ_g from 10^{16} Ohm-cm down to the ρ of DSG (at least in order of value) should be considered.

Any of the tunneling of free carriers though the glass interlayer or hopping of them from the one dopant particle to another cannot reduce the glass resistivity down to resistivity of the DSG as well as provide the $R(T)$ with the minimum.

Therefore observed properties of the DSG can be caused by doping of the glass interlayer between the dopant particles due to diffusion of the dopant atoms only, and the temperature dependence $\rho(T) \sim T$ or $\rho(T) \sim T^2$ should be the property of the doped glass but no that of the RuO₂ particles. This condition is satisfied for the electron-phonon or the electron-electron scattering.

So let us to consider now the combination of thermal activation, hopping and scattering of charge carriers as the main conduction mechanism of the DSG.

As reported earlier [2] the nanocrystals of silicates in the glass and narrow impurity band formed in firing process can explain the experimental [3] [4] low-temperature resistance of DSG in the form

$$R(T) \sim T^{-0.5} \exp(K/T)^\zeta, \quad (13)$$

if the temperature dependence of the energy gap between the impurity band and the valence band of the glass is taken into account.

It is should be noted that the temperature dependence (13) with $\zeta = 0.5$ takes place in the hopping model of the doped semiconductors as the result of the Coulomb gap in the energy spectrum of the electrons as well [29] but it was noted ibid, that such a consideration is qualified in the crystalline semiconductors and Coulomb gap is not effective in amorphous materials.

We have taken into account therein the temperature dependence of width $E_G(T)$ of the band-gap between the top of the glass valence band and the impurity band bottom caused by electron-phonon coupling [45]-[50]:

$$E_G(T) \approx E_G(0) - \zeta T^2, \quad (14)$$

and the temperature coefficient ζ is about 10^{-6} eV·K $^{-2}$, so this effect is not essential in the wide-band semiconductors such as Ge, Si, GaAs or C (diamond). Here $E_G(0)$ is the width of the band gap at $T = 0$ K.

Expression (14) is the experimental and is not suitable enough at low temperatures ($T < \Theta_D$, here Θ_D is the Debye temperature).

The expression [50]

$$E_G(T) = E_G(0) - \xi \langle \hbar\omega \rangle \left(\text{cth} \left(\frac{\langle \hbar\omega \rangle}{2kT} \right) - 1 \right), \quad (15)$$

is more correctly at $kT < \langle \hbar\omega \rangle$, here $E_G(0)$ is the band-gap width at $T = 0$ K (Figure 4), ξ is the electron-pho-

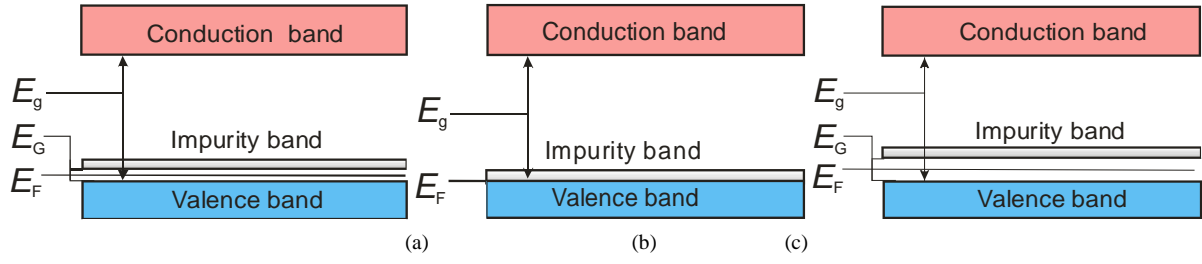


Figure 4. Energy bands and the band-gap E_G in DSG at temperatures T (schematically, K): 0 (a), about 300 (b) and >900 (c).

non coupling constant, $\langle \hbar\omega \rangle$ is the main phonon energy in the material. This effect narrows the band gap E_G and it disappears at the certain temperature T_m in the semiconductors having the narrow band gap (less than 10 - 50 meV [51]):

$$E_G(T_m) = 0. \quad (16)$$

$$T_m = \frac{\langle \hbar\omega \rangle}{k \ln(1 + 2\xi \langle \hbar\omega \rangle / E_G(0))}. \quad (17)$$

The impurity band and the valence band merge and form unite partially filled valence band as in the metals (**Figure 4**) at $T \geq T_m$, so concentration of the charge carriers become constant. The main factor of the temperature dependence of resistivity of the DSG is thereafter the charge carriers scattering on phonons, neutral and ionized impurities or on the other charge carriers, which lead to

$$\rho(T) \sim T, \quad (18)$$

$$\rho(T) \sim T^2 \quad (19)$$

or

$$\rho(T) \sim T^{-3/2}. \quad (20)$$

Geometry of the impurity band in the glass band-gap at some characteristic temperatures is shown in **Figure 4**. Temperature dependence of the impurity band-gap E_G is shown in **Figure 5**.

Thermal activation and hopping of the charge carriers act simultaneously and increase the DSG conductivity while electron-phonon or electron-electron scattering decreases it so one can write for resistivity of DSG

$$\rho(T) = [\sigma_a(T) + \sigma_h(T)]^{-1} + \rho_{\text{met}}(T), \quad (21)$$

here

$$\sigma_a(T) = AT \exp[-E_G(T)/2kT] \quad (22)$$

is the conductivity due to thermal activation of carriers,

$$\sigma_h = BT^{0.5} \exp[-(T_h/T)^{1/4}] \quad (23)$$

is the hopping conductivity, and

$$\rho_{\text{met}}(T) = \rho_{m0} (1 + \alpha T + \beta T^2 + \gamma T^{-3/2}) \quad (24)$$

is the metallic conductivity, caused by scattering of carriers on neutral defects (ρ_{m0}), phonons (αT), charged impurities ($\gamma T^{-3/2}$) or other charge carriers (βT^2) [52] [53]. The expression (24) assumes that various scattering processes act simultaneously in the DSG.

It should be emphasized that $\rho_{\text{met}}(T)$ is the intrinsic property of the doped glass here in contrary to the (2) and (10), where $\rho_{d0}(1 + \alpha T)$ is the parameter of the dopant particles. Expression (21) with (15), (22), (23) and (24) is shown in **Figure 6**.

Experimental results Comparison of the experimental results of the temperature dependence of the resis-

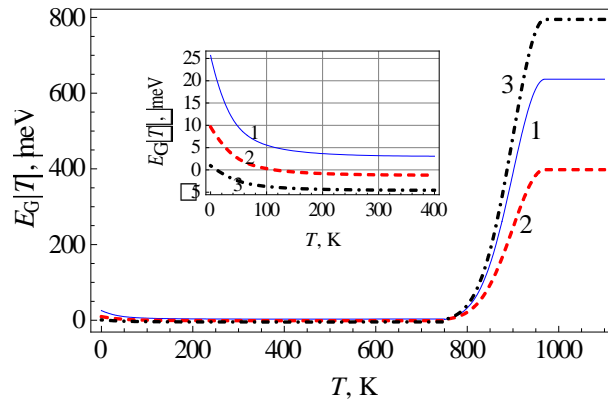


Figure 5. Band-gap width E_G versus temperature including the equation (15) ($T < 200$ K) and structure transitions of silicate nanocrystals ($T > 800$ K). Inset is the enlarged part of the main curves. Curves 1, 2 and 3 are responsible for the various width of the band gap at $T = 0$ K and beyond the 900 K (structure transitions have been completed, see [3]).

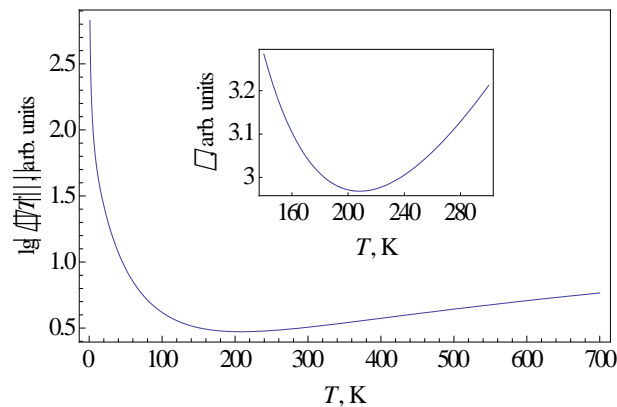


Figure 6. Simulation of the $\rho(T)$ (21) for $A = 10^{40}$; $B = 3.5$; $T_h = 100$ K; $E_G(0) = 10^{-2}$ eV; $\langle \hbar\omega \rangle = 22.5$ K; $\zeta = 0.5$. The inset is the enlarged region near the minimum.

tance $R(T)$ of the DSG samples and our model (21) in the temperature range 160 - 800 K shows the good agreement (Figures 7-9).

It is seen from these figures that

- 1) $R(T)$ of the all investigated DSG is not quadratic

$$R(T) = R_m + B(T - T_m)^2, \quad (25)$$

in contrast with the common opinion [8] [10];

- 2) The temperature T_m of the minimum is affected by DSG composition and firing conditions (T_f and τ);

3) The temperature T_m of the minimum increases with the resistivity ρ of the DSG so can be distorted (Figure 9) by structure transitions of silicate nanocrystals in the DSG [3].

6. Conclusions

1) The known conduction mechanisms of the DSG cannot explain the origin of the minimum of the temperature dependence of resistivity and the effect of the glass and dopant composition, firing conditions (T_f and τ) on its location (temperature T_m and resistivity ρ_m).

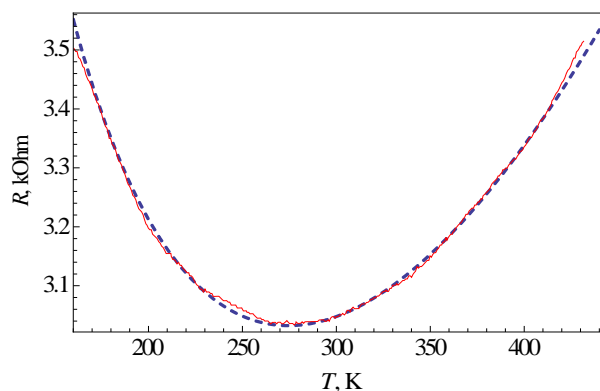


Figure 7. Temperature dependence of resistance of the DSG 1 with 20 w% RuO₂. Dotted line is the function (21) with (15), (21)-(24) for $A = 2.5 \times 10^{-7} \text{ Ohm}^{-1} \cdot \text{K}^{-1}$, $E_G(0) = 10 \text{ meV}$, $\zeta = 1.1$, $\langle \hbar\omega \rangle = 2 \text{ meV}$, $B = 1.75 \times 10^{-5} \text{ Ohm}^{-1} \cdot \text{K}^{-0.5}$, $T_h = 100 \text{ K}$, $R_{m0} = \rho_{m0}/t = 1.342 \times 10^3 \text{ Ohm}$, $\alpha = 0$, $\beta = 3.94 \times 10^{-6} \text{ Ohm} \cdot \text{K}^{-2}$.

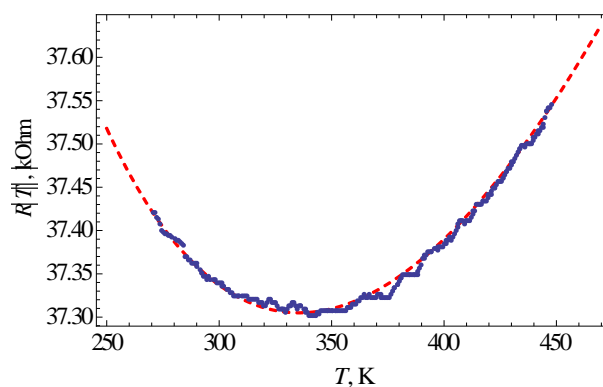


Figure 8. Temperature dependence of resistance of the DSG 3 with 16.5 w% RuO₂. The dotted line is function (21) with (15), (22)-(24) for $A = 4.42 \times 10^{-7} \text{ Ohm}^{-1} \cdot \text{K}^{-1}$, $E_G(0) = 12.3 \text{ meV}$, $\zeta = 1.1$, $\langle \hbar\omega \rangle = 4.8 \text{ meV}$, $B = 3.91 \times 10^{-5} \text{ Ohm}^{-1} \cdot \text{K}^{-0.5}$, $T_h = 250 \text{ K}$, $R_{m0} = \rho_{m0}/t = 34.85 \times 10^3 \text{ Ohm}$, $\alpha = 1.2 \times 10^{-5} \text{ K}^{-1}$.

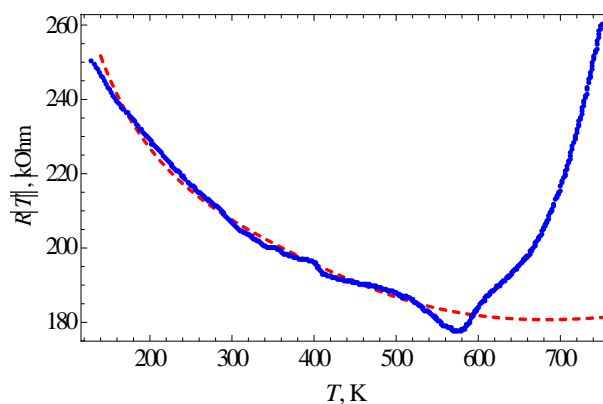


Figure 9. Temperature dependence of resistance of the DSG 2 with 16 w% RuO₂. The dotted line is the function (21) with (15), (22)-(24) for $A = 3.27 \times 10^{-8} \text{ Ohm}^{-1} \cdot \text{K}^{-1}$, $E_G(0) = 430 \text{ meV}$, $\zeta = 0.01$, $\langle \hbar\omega \rangle = 3.86 \text{ meV}$, $B = 4.75 \times 10^{-6} \text{ Ohm}^{-1} \cdot \text{K}^{-0.5}$, $T_h = 1050 \text{ K}$, $R_{m0} = \rho_{m0}/t = 1.58 \times 10^5 \text{ Ohm}$, $\alpha = 1.452 \times 10^{-4} \text{ K}^{-1}$, $\beta = 2.952 \times 10^{-5} \text{ Ohm} \cdot \text{K}^{-2}$. The minimum is distorted by the resistivity variations due to structure transitions of the silicate nanocrystals in the glass at $T = 575 \text{ K}$ and $T > 800 \text{ K}$ [3].

2) The minimum of the temperature dependence of the DSG resistivity is the result of decreasing of the energy gap between the impurity band and the valence band of the glass by temperature. It is very important here to note that the impurity band-gap is narrow (about tens of meV) as the electron-phonon coupling constant has small value. So the band-gap can vanish at temperature T_m near the room temperature (the broad band-gap will disappear at high T_m and we can't observe its vanishing due to the structural transitions of nanocrystals [2]). Thereafter the joined partially filled valence band is formed in the DSG, the concentration of the free carriers $n(T)$ becomes constant and the resistivity of the DSG will be affected by temperature due to electron-phonon or electron-electron scattering only so $R(T) \sim T$ or $R(T) \sim T^2$ as in the typical metals.

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