

On the Conduction Mechanism of Silicate Glass Doped by Oxide Compounds of Ruthenium (Thick Film Resistors). 2. Nanocrystals in the Glass and Charge Carrier's Localization

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Abstract Conduction mechanism of doped silicate glasses based on existence of nanocrystals is proposed. These nanocrystals are effective centers of localization of free charge carriers, and variable range hopping of last ones takes place. It is shown that dopant atoms generate narrow impurity subband of about 0.03 eV in width, which is slightly (less than 0.01 eV) separated from the top of the valence band of the glass or abutted on them, so thermal activation coexists with hopping conduction. 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. Beyond the conductivity minimum (above 1000 K) the impurity subband and the top of the valence band of glass are separated by energy gap of 0.05 – 1.5 eV in width, so doped silicate glass behaves like a typical semiconductor.

Keywords Lead-silicate Glass, Thick Film Resistors, Doping and Percolation Levels, Nanocrystals, Localization and Hopping of Charge Carriers, Impurity Subband and Thermal Activation, Conductivity, Firing Conditions

1. Introduction

We have reported earlier[1] on the transport properties of the doped silicate glass (DSG, better known as the thick film resistors), determined by diffusion of the dopant atoms into the glass and formation of diffusion zones. These processes leads to the formation of the percolation levels for free charge carriers in the glass, and can explain the effects of the dopant content, firing conditions and dispersivity of dopant powder on conductivity σ of the DSG.

There are number of investigations on the conduction mechanism of the DSG[2-6] where the interaction of the glass and the conductive phase has been declared. A detailed study of the influence of various experimental parameters (temperature, RuO₂ content, stirring, etc.) on the electrical conductivity and, in particular, on the percolation threshold in borosilicate glass–RuO₂ composites is presented in[2]. This percolation threshold is shown to

increase by a factor of two (from 0.6 to 1.2 vol%) when stirring is applied during synthesis and by more than a factor of three (>2.1 vol%) when a sol–gel route is used. Besides, the study of various synthesis temperatures reveals that the electronic part of the electrical conductivity is highly correlated to Ru solubility in the glass matrix. It was concluded from these experiments that both the presence of dissolved ruthenium in the glass matrix and the possibility of RuO₂ particles to rearrange in the melt in order to form kind of a network are necessary for a low percolation threshold. The last conclusion is erroneous because of the considerable deviations of resistivity values of samples estimated for such network of RuO₂ particles and measured experimentally for same volume content of RuO₂.

Jagtap et al[3] have added some compounds into the thick film composite (glass+conductive phase) to reduce the temperature coefficient of resistivity, but the mechanism of this effect did not explained.

Low frequency noise spectroscopy is employed in[4] to examine fluctuating phenomena that take place in the material of resistive films and in the film/termination interface of a thick-film resistor. It has been found that the excess low frequency noise apart from the 1/f component contains con-

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tributions from thermally activated noise sources with energies in the range 0.015–0.6 eV. These sources are considered to be distributed nonuniformly over the whole resistor volume, most probably in the glassy matrix or conductive grain boundaries.

It was confirmed[5] that the diffusion of ruthenium into glass affects the binding state of RuO_2 at the interface of the glass. Furthermore, an intermediate resistive layer is detected around the RuO_2 particle. These results suggest that the piezoresistive effect is related to a change in the electrical conductivity of the interfacial reaction layer caused by the diffusion of ruthenium into glass.

Noise properties of thick-film resistors of various compositions have been investigated in[6] and conclusions concerning compatibility of resistive and conductive pastes have been formulated.

Unfortunately, in all these works as well as in earlier investigations[7, 8] suggested interactions of the glass and the conductive phase (mainly RuO_2) were not summarized into the detailed conduction model of the DSG and the effect of nanoscale glass structure on the conductivity of DSG was not considered.

The conduction mechanism of DSG as the result of its nanoscale structure is investigated in the present paper.

Direct and doubtless evidences of the existence of nanocrystals (or microcrystallites, as they have been called earlier) in the glass are not found yet. That is why the problem of the glass structure (continuous random network, Zachariasen, 1932; microcrystallites, separated by interlayer of disordered atoms, Lebedev, 1921) is still a subject of discussion. But temperature dependence of some glass properties such as viscosity, thermal expansion coefficient, dielectric constant and dielectric loss, have anomalies which have a better agreement with microcrystalline theory. This is especially the case for many-component glasses. One should take into account that these nanocrystals are not detected by X-ray diffraction method because of their small size (about 1 – 2 nm). At the same time structure and properties of these nanocrystals can differ essentially from that of the bulk. The last fact can be clearly traced during the milling process of various materials up to submicron size.

The doping process used here is standard for technology of thick film resistors and was described elsewhere (the mixture of the glass and the dopant powders have been fired at $T_f = 1125$ K in $\tau = 10$ min). Content of RuO_2 in our samples of doped glass was 16, 20 and 30 weight %. The lead-silicate glasses investigated have the following composition (weight %):

Glass1 $\text{SiO}_2 - 33$; $\text{PbO} - 67$;

Glass2 $\text{SiO}_2 - 27$; $\text{PbO} - 67$; $\text{BaO} - 4$; $\text{MgO} - 2$.

2. Nanocrystals in the Glass and Localization of Charge Carriers

Metastability of glassy state is widely accepted[9] and all kinds of glasses will become crystalline with time. The time required for this transition may be many years or even millennium depending on its composition and thermal prehistory, i. e. depending on the height of potential barrier, separating these two states.

Crystals are formed spontaneously in the glass so the Helmholtz energy of the crystalline state is lower than that of the glassy state of same composition. It means that these crystals act as pockets of potential energy. The silicate glass is dielectric with energy gap as high as 3.3 - 7 eV (the glass $2\text{SiO}_2\cdot\text{PbO}$ and fused silica accordingly). On the other hand natural crystallization of the silicate glass is very slow (usually tens of years), and relevant energy of this process is insignificant. Because of this one can assume that the pockets are not deep (of about 0.01 – 0.03 eV) and dynamical balance of transitions from glassy state into crystalline state and back is slightly disturbed in the line of first.

Free charge carriers in DSG are holes as it is indicated by the sign of the thermopower[10]. Concentration of them is about 10^{20} cm^{-3} and the effective mass m^* is about $330 m_0$ (m_0 is mass of the free electron) as it was estimated from the resistivity ρ and the upper limit of mobility μ of DSG[11]. The increase of effective mass of electrons (holes) in the small size pockets have been demonstrated in[12] for GaN.

The bottom of the conduction band of the lead-silicate glass is formed by the shifted 3s-orbitals of the oxygen and 6d-orbitals of the lead, while the top of the valence band is formed by shifted 2p-orbitals of O_2 and 6p-orbitals of Pb[13]. As a result, lead-silicate glass is the dielectric with the band gap about 3.3 eV[14], and the silica glass has $E_g \approx 7.76$ eV[15], since the conduction and valence bands are formed by shifted 3s- and 2p-orbitals of O accordingly. Doping of the lead-silicate glass forms the impurity subband from shifted 5s-states of Ru atoms. 6p-states of Pb and 5s-states of Ru are shifted to 7.415 eV and 7.36 eV below the vacuum level (first ionization potential,[16]) accordingly. It is known that conductivity of DSG varies very slowly in the wide temperature range and the photoconductivity do not appears up to the ultraviolet, where transition of electrons from the valence band into the conduction band takes place. So one can say that ruthenium subband abutted to top of the valence band of glass or slightly (less than 0.01 eV) separated from the last (Figure 1a). Then the Fermi level E_F appears as close to the top of the valence band as 0.01 eV or less and the gas of free carriers is degenerated at room temperature.

This is confirmed by infrared (IR) and optical spectra of DSG (Figure 2 and 3). μ is absorbance (arbitrary units), λ and $\tilde{\nu}$ are wavelength and wave number accordingly in these spectra. We assume that the arms at $50 \mu\text{m}$ ($h\nu \approx 0.026$ eV) and at $12 \mu\text{m}$ ($h\nu \approx 0.1$ eV) on the IR-spectrum of DSG (Figure 2, curve 4) correspond to the electron transitions from the glass valence band into the impurity subband because they are not characteristic neither of glass (Figure 2, curve 1) nor of RuO_2 (Figure 2, curve 2), and shoulder at $12 \mu\text{m}$ can be caused by transitions from the pockets generated

by nanocrystals into the subband (Figure 4). So one can estimate the depth of the pockets as $0.1 - 0.025 = 0.075$ eV.

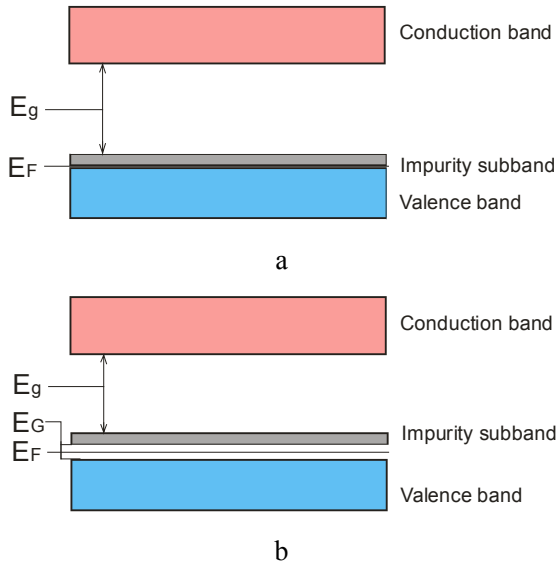


Figure 1. Energy bands in DSG at $T < 700$ K (a) and at $T > 700$ K (b).

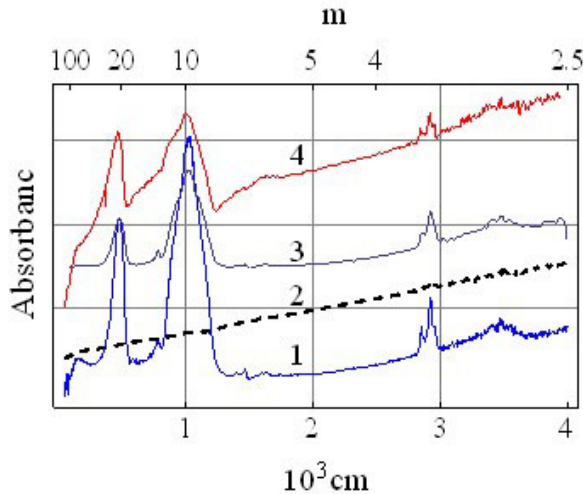


Figure 2. IR-spectra of the glass (1), RuO_2 (2), unfired mixture of them (3) and DSG (4).

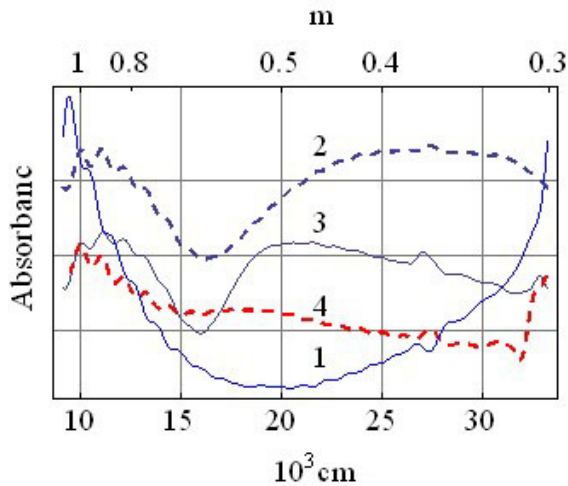


Figure 3. Optical spectra of the glass (1), RuO_2 (2), unfired mixture of them (3) and DSG (4).

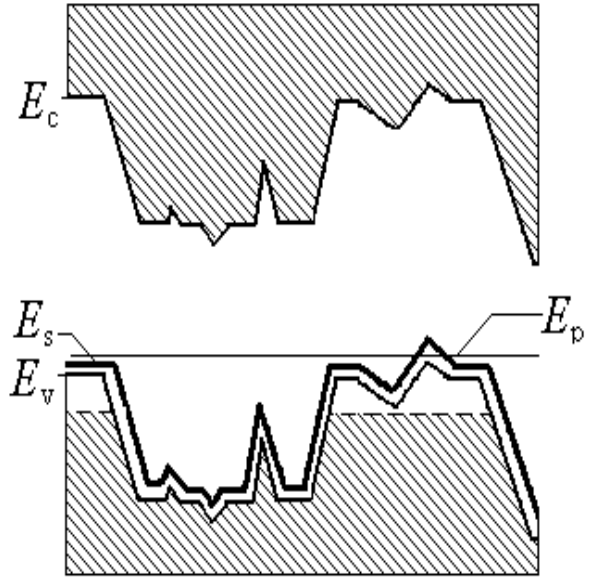


Figure 4. Energy pockets of nanocrystals in the glass, impurity subband and the regions of free carriers localization. E_c and E_v are the conductivity and the valence bands of the glass accordingly, E_s is the impurity subband, E_p is the percolation level.

3. Concentration of the Free Charge Carriers, IR- and Optical Spectra

The IR-spectrum of RuO_2 powder (Figure 2, curve 2) is the most curious one, where the absorbance decreases monotonically without appearance of any noticeable bands as the wavelength increases. Such spectrum is typical for absorption of the electromagnetic waves by free charge carriers in the plasma resonance region[17]. This means that the concentration of free carriers in RuO_2 powder is high and absorption on them suppresses the molecular absorption[18]. IR-spectrum of the DSG in the $2.5 - 7 \mu\text{m}$ range on repeats the IR-spectrum of RuO_2 , i.e. the concentration of free carriers in DSG is high enough, although the molecular absorption bands of higher intensity at 10 and $20 \mu\text{m}$ (intrinsic vibrations of the $[\text{SiO}_4]$ -tetrahedra) are still visible.

Optical spectra (Figure 3) show that all the characteristic absorption bands of the glass (curve 1) and the RuO_2 (curve 2) disappear in the DSG (curve 4) while in the spectrum of unfired mixture of these powders (curve 3) they are clearly seen.

These spectra confirm that there are no deep energy levels in the energy gap of the glass and absorption starts beyond the $0.3 \mu\text{m}$ where interband transitions of the glass take place (we have not taken into account there the impurity subband because of its small width and displacement close to top of the valence band). Impurity subband formation close to the top of the glass valence band (acceptor states) was pointed out in[19].

This implies that all the states in the impurity subband are ionized at room temperature and conductivity of DSG does not vary substantially with the temperature.

4. Temperature Dependence of Conductivity of the DSG

Coexistence of glassy and crystalline sections (and potential energy pockets as accordingly) in DSG as well as narrowness of the impurity subband and its proximity to the top of the glass valence band leads to the following:

1) All the states in the impurity subband are ionized at room temperature, gas of carriers is degenerated and the temperature dependence of the conductivity of DSG $\sigma(T)$ is very weak.

2) Particularly, at low temperatures when the impurity states are ionized, the simultaneous action of the activation and hopping mechanisms of conductivity in DSG is possible, so the total conductivity is

$$\sigma(T) = AT \exp(-E_g(T)/2kT) + BT^{0.5} \exp(-(T_0/T)^{1/4}), \quad (1)$$

where the first term corresponds to the activation mechanism with the activation energy $E_g(T)$ and the second term corresponds to the variable range hopping (Mott's law[20]). A and B are constants depending on the relative volumes of glassy and nanocrystalline sections, k is the Boltzmann's constant, T_0 is the temperature constant ($T_0 \sim 10^6$ K). The temperature dependence of the activation energy is given as[21]

$$E_g(T) = E_{g0} - \xi \langle \hbar\omega \rangle (\text{cth}(\langle \hbar\omega \rangle / 2kT) - 1), \quad (2)$$

here E_{g0} is the activation energy at $T = 0$ K, ξ is the dimensionless constant of electron-phonon coupling and $\langle \hbar\omega \rangle$ is an average phonon energy.

The equation (1) can be fairly well approximated by

$$\sigma(T) = \sigma_0 T^{0.5} \exp(-(K/T)^\zeta) \quad (3)$$

with $0.4 < \zeta < 0.8$ as it is often observed in experiments.

Figure 5 shows that it is problematic to discriminate equations (1) and (3) experimentally.

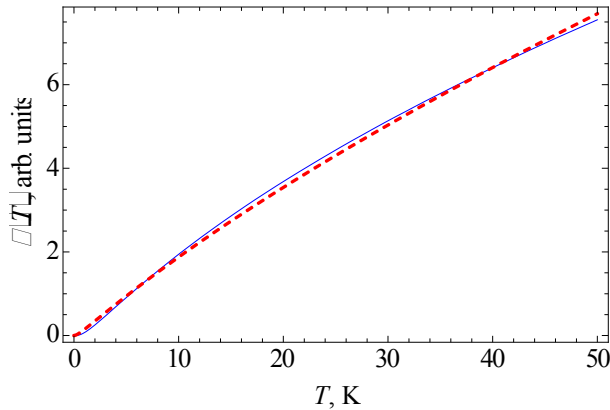


Figure 5. Temperature dependence of the DSG conductivity – comparison of expressions (1) (dotted line) and (3) (solid line) at: $A = 10^{40}$; $B = 3.5$; $T_0 = 100$ K; $E_{g0} = 10^{-2}$ eV; $\xi = 1.1$; $\langle \hbar\omega \rangle = 22.5$ K; $\sigma_0 = 1.67$; $K = 10$ K; $\zeta = 0.5$.

The value of activation energy $E_g = 10^{-2}$ eV derived from the fitting process of the eq. (1) to the eq. (2) also confirms that impurity subband is displaced close to the top of the glass valence band.

3) Silica SiO_2 has some crystalline modifications which can undergo the structural transitions[9, 22]. In addition structural transitions are possible in the nanocrystals of sili-

cates at high temperatures when interatomic distances vary suddenly and it must result in the reduction of the conductivity of DSG analogous to ferroelectrics[23].

The sharp decrease of the conductivity of DSG we have observed (Figure 6) at sufficiently high temperatures[24] and the starting point of this process depend on the glass composition. But further increase of temperature leads to the rise of σ and this rise has activating nature at the energies about 0.095 – 1.52 eV depending on the glass composition (Figure 7). This means that the impurity subband splits off the glass valence band at $T > 800$ K because of structural transitions of nanocrystals (Figure 1b) and narrow energy gap forms between them. The thermal generation of free carriers takes place through this gap and DSG turns into a typical semiconductor.

It should be noted that the structural transitions in nanocrystals consisting of silicates do not occur suddenly but occupy some temperature interval. At the beginning of this interval nuclei of the new phases are generated and they accumulate gradually until whole sample transits into a new phase at the transition point (at the end of the temperature interval)[25].

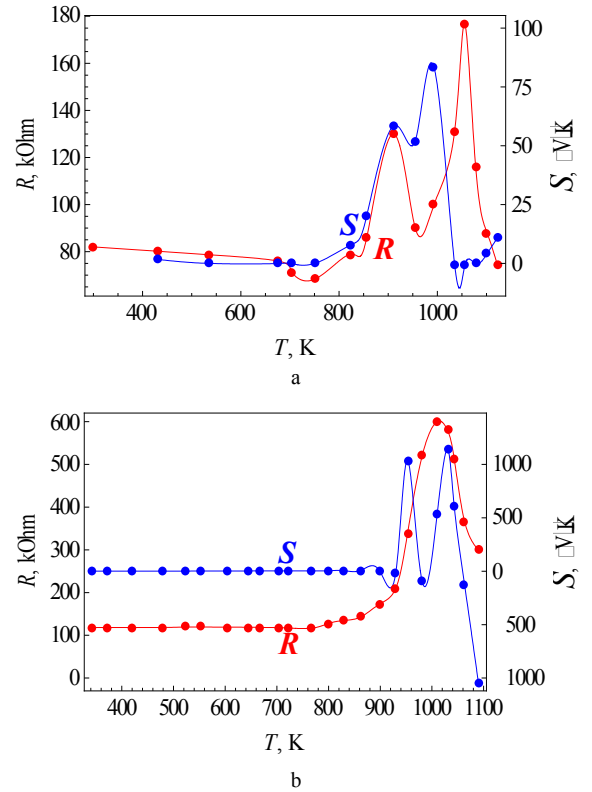


Figure 6. Temperature dependence of the resistance R and the thermopower S of DSG based on the glass1 (a) and glass2 (b).

The value of the thermopower S of the DSG corresponds to that of metals (about 10 $\mu\text{V/K}$) and its temperature dependence confirms that the concentration of charge carriers does not change significantly in the 300 K $< T < 800$ K interval (Figure 6). At the temperature corresponding to the minimum of $\sigma(T)$ the modulus of S increases sharply and reaches up to 1 mV/K for the DSG of various compositions.

This indicates the decrease of the concentration of carriers. Beyond the minimum of $\sigma(T)$ value of S reduces in accordance with the increase of the carriers' concentration due to thermal generation of the split impurity subband from the valence band of the glass. The energy gap between the top of the glass valence band and the impurity subband is about 0.095 – 1.52 eV depending on the glass composition as mentioned above (Figure 7).

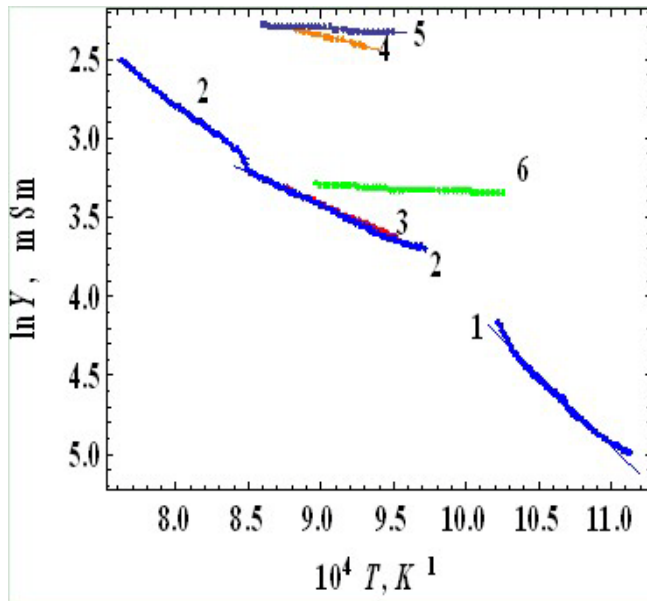


Figure 7. Temperature dependence of the conductivity $Y(T)$ after minimum for the samples of the doped glass1 (1) and glass2 (2 – 6) with RuO_2 content about 16 wt % (1, 2), 20 wt% (3, 4) and 30 wt% (5, 6). Activation energy of conductivity E_σ is about (eV): 1.77 (1); 1.54 (2, lower T) and 0.93 (2, high T); 0.9 (3); 0.52 (4); 0.05 (5) and 0.047 (6). The solid lines are the fit of the experimental data to the expression $\ln Y = a + E_\sigma / 2kT$.

Another implication of the existence of nanocrystals in the glass and the DSG is the intensive scattering of the free charge carriers on these pockets of potential energy. This scattering can be as effective as the scattering on dislocations, domain walls and other stretched defects of the crystal lattice[26] because of comparable size of them.

Collection of these factors leads to the temperature dependence of the DSG resistivity as it was shown schematically in Figure 1 in our paper[1].

5. Conclusions

1. Narrow impurity subband close to the top of the glass valence band and spontaneously formed nanocrystals in the glass create conditions for simultaneous act of the activation and the hopping conduction at low temperatures. Cooperation of these mechanisms in DSG leads to the temperature dependence of resistivity in the form $R(T) \sim \exp(-K/T^6)$ with $0.4 < \zeta < 0.8$ as it observed often in the experiments.

2. It follows from the IR- and optical spectra that main factor of absorption in the RuO_2 and DSG is the free carriers, whose concentration at room temperature is about 10^{20} cm^{-3} (gas of them is degenerate). Because of this the conductivity

of the DSG varies negligibly at intermediate temperatures ($77 \text{ K} < T < 800 \text{ K}$).

3. Increase of temperature up to 800 K leads to the structural transitions of nanocrystals in the DSG and interatomic distances race up. As a result the impurity subband splits off the top of the glass valence band and energy gap as wide as 0.095 – 1.52 eV opens up. Beyond the $\sigma(T)$ minimum, concentration of free carriers decreases, degeneracy is lifted and the DSG turns into a typical semiconductor.

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