

SYNTHESIS OF SILVER NANOPARTICLES BY THE ION IMPLANTATION METHOD AND INVESTIGATION OF THEIR OPTICAL PROPERTIES

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We have investigated the process of metal nanoparticle (NP) synthesis in SiO₂ by implanting Ag⁺ ions with an energy of 30 keV depending on the dose ((2–8)·10¹⁶ cm⁻²) and the ionic current density (4–15 μA/cm²). Analysis of the composite materials formed was performed with the use of optical spectroscopy and atomic-force microscopy (AFM). The NPs synthesized in the glass demonstrate a characteristic absorption line associated with the surface plasma resonance effect. A correlation of the spectral shift of the lines caused by a change in the NP size with the diameter of the hemispherical asperities on the SiO₂ surface registered by the AFM method has been revealed. It has been found that for the case of a fixed current density in the ion beam the silver NP sizes remain practically unaltered with increasing ion dose up to a certain value (6·10¹⁶ cm⁻²), and only an increase in the concentration of NPs is observed thereby. However, a further increase in the dose causes a decrease in both the NP density and size. On the other hand, at a fixed high dose an increase in the ionic current density leads to a gradual enlargement of the NPs. We have considered the mechanisms explaining the change in the NP sizes with increasing dose and ionic current density and evaluated the possibilities of carrying out controlled synthesis by varying the implantation conditions.

Keywords: *ion implantation, nanoparticles, surface plasma resonance, optical spectroscopy, atomic-force microscopy.*

Introduction. The last few years have seen an ever-growing interest in ion implantation (II) as a method for synthesizing metal NPs in the bulk of dielectric materials due to the use of metal/dielectric composites for constructing elements with unique optical properties [1–3]. The interest in the optical characteristics of nanostructured composites is explained by the prospects of creating, on their basis, plasmon-polariton waveguides [1] and switches with ultrashort response times [4], as well as laser radiation intensity limiters [5, 6]. Most of the investigations are devoted to the gold, silver, and copper NPs implanted in various dielectric matrices and exhibiting an intensive response in the visible spectral range at wavelengths characteristic of the resonance collective excitation of conduction electrons in metal NPs, as in the case of surface plasma resonance (SPR) [2]. The interest in the NPs of metals is also due to the active studies of the ways of increasing the sensitivity of molecular spectroscopy with the use of NPs of noble metals [7].

The chief advantages of II in synthesizing NPs compared to such methods as sol-gel, ion exchange, and glass-metal fusion are the possibility of filling the implanted layer practically with any metal beyond the limit of its solubility in a dielectric and the realization of exact control of the concentration of the introduced admixture and the positioning of the ion beam on the sample surface. At the same time, the II has a number of limitations, for example, the nonuniform distribution of implanted metal ions in the depth of the material being implanted (especially in the case of high energies) leading to different concentrations of the introduced admixture throughout the depth of the implanted layer, which complicates the synthesis of NPs with a narrow size-distribution function [8, 9]. In the present

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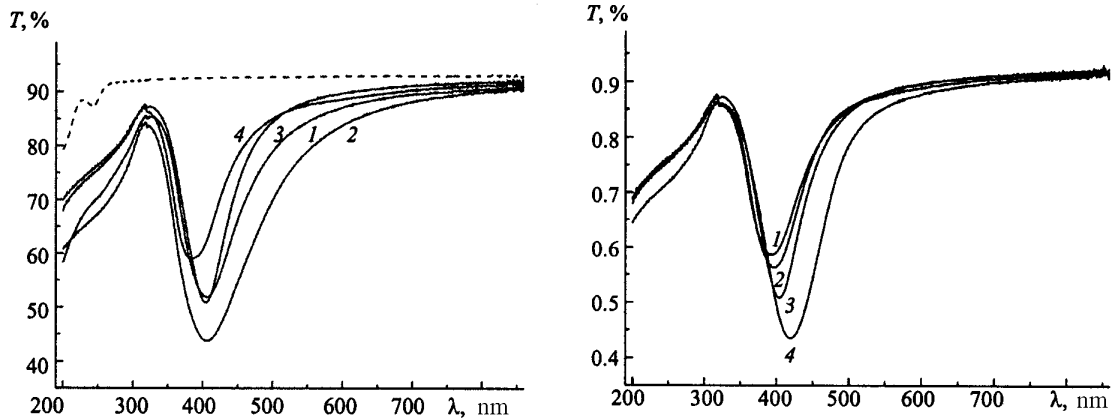


Fig. 1. Transmission spectra of SiO₂ before implantation (dashed line) and after implantation by Ag⁺ ions with doses (in units of 10¹⁶ cm⁻²): 2 (1), 4 (2), 6 (3), and 8 (4) at an ionic current density of 10 μA/cm².

Fig. 2. Transmission spectra of SiO₂ after implantation by Ag⁺ ions with a dose of 5·10¹⁶ cm⁻² at ionic current densities: 4 (1), 8 (2), 12 (3), and 15 μA/cm² (4).

work, with the aim of narrowing the profile of the distribution of ions in the sample depth and, consequently, decreasing the spread of NP sizes, low-energy II is used.

On the whole, controlled synthesis of NPs requires detailed knowledge of the physical processes proceeding in the dielectric matrix upon the high-dose implantation of accelerated ions needed for attaining a concentration of metal atoms sufficient for the subsequent nucleation and growth of particles. For example, the factors complicating the NP synthesis at a high dose are the radiation damage of the material [8] and the sputtering of the target surface. The sputtering reaches in depth a few dozen nanometers at doses of the order of 5·10¹⁶ cm⁻² [9] typical of the NP synthesis. An important parameter is also the implantation energy determining the mechanisms of deceleration of ions being implanted. Moreover, it has been shown recently that a change in the target temperature at II by only a few dozen degrees leads to an appreciable change in the optical properties of synthesized metal/dielectric composites, which points to an increased sensitivity of the process of metal NP synthesis to the effects of heat transfer and thermo-stimulated diffusion [10, 11].

In the present paper, the influence of the current dose and density in the ion beam on the formation of Ag and SiO₂ NPs at low-energy II is investigated with the aim of working out and optimizing the regimes of controlled synthesis. The choice of quartz glass as a dielectric being investigated is explained by the ease of integrating composite materials based on it into the existing electronic and optoelectronic elemental base on the basis of silicon.

Experimental. As a substrate for obtaining a composite material, we used quartz glass SiO₂ (Heraeus, Italy) with an optical transparency of ~90–92% in the 260–950-nm spectral range (dashed line in Fig. 1). Implantation was carried out by Ag⁺ ions of energy 30 keV in the interval of doses (2–8)·10¹⁶ cm⁻² at a fixed ionic current density of 10 μA/cm² or at a fixed dose of 5·10¹⁶ cm⁻² and various current densities in the ion beam from 4 to 15 μA/cm². Implantation was carried out on an ILU-3 implanter in a vacuum of 10⁻⁵ Torr at room temperature of the substrate at the initial stage of irradiation. The optical properties of the AgSiO₂ composite layers were investigated by optical spectroscopy on a Perkin Elmer Lambda 19 two-beam spectrophotometer (USA). The morphology of the surfaces of irradiated glasses was obtained with the aid of a National Instruments Dimension 3000 scanning probe microscope (USA) operating in the regime of AFM in the tapping mode.

Results and Discussion. The modeling of the profiles of the depth-distribution of implanted silver by means of the DYNA computer algorithm [12], taking into account the dynamic change in the phase composition of the target and the surface sputtering, has shown that in the near-surface implanted glass layer Ag atoms are accumulated and the maximum of the profile of the depth-distribution of the metal concentration is shifted to the sample surface with increasing dose. Already at doses of ~10¹⁶ cm⁻² the silver concentration maximum is at a depth of only ~5–10 nm and the concentration decreases monotonically into the sample depth. Thus, the effective accumulation of silver atoms and

the excess of their concentration over the solubility limit in SiO₂ promote the nucleation and growth of metal NPs in the immediate vicinity of the surface.

The formation of NPs is confirmed by measurements by the method of optical spectroscopy demonstrating a spectral absorption band, characteristic of Ag particles, in the visible region of the spectrum at the boundary with UV, which is due to the SPR effect (Figs. 1 and 2). The spectra obtained are typical of silver NPs in SiO₂, and the shift of the resonance-band minimum on the scale of wavelengths can be interpreted as a change in the NP sizes [13].

Figure 1 shows the transmission spectra of the glass as a function of the dose of implanted silver at a fixed ionic current density. It is seen that the glasses implanted with doses $(2-6) \cdot 10^{16} \text{ cm}^{-2}$ are characterized by SPR bands with transmission minima located in the vicinity of the $\sim 405\text{-nm}$ wavelength (spectra 1–3), which points to the formation in these samples of metal NPs close in size. The increase in this absorption-band intensity at the stage of increasing the ion dose to $4 \cdot 10^{16} \text{ cm}^{-2}$ (compare spectra 1 and 2 in Fig. 1) is attributed to the increase in the concentration of NPs. However, a further increase in the ion dose to $6 \cdot 10^{16} \text{ cm}^{-2}$ leads to a decrease in the absorption-band intensity in the same spectral range, which can be due to the decrease in the number of NPs in the implanted layer without an appreciable change in their mean sizes. Moreover, at II with a dose of $8 \cdot 10^{16} \text{ cm}^{-2}$ both a decrease in the SPR absorption-band intensity and a short-wave ($\approx 390 \text{ nm}$) shift of the minimum are observed in the samples. This change in the spectrum corresponds to a decrease in the mean size of the NPs. In this case, a decrease in their concentration compared to the previous samples is not excluded either. The results obtained look somewhat surprising, since earlier in experiments on II of metals into dielectrics with increasing ion dose only enlargement of the NPs was observed [14, 15]. It should be noted, however, that the II was performed by higher energies (160 keV and more) as opposed to the case under consideration.

Figure 2 presents the dependence of the optical transmission of the samples on the current density in the ion beam at a fixed implantation dose. It is seen that the transmission-band minimum gradually shifts to the long-wavelength region (from 395 to 415 nm), and the absorption-band intensity increases with increasing ionic current density, which corresponds to an enlargement of the silver NPs and, possibly, an increase in their number.

As mentioned above, at a high-dose implantation one of the determining factors is the surface sputtering. If we assume that the sputtering rate of the dielectric exceeds the sputtering rate of the metal NPs, then one would expect "uncovering" of NPs on the glass surface. Indeed, earlier in a number of AFM-measurements it was shown that at a low energy ($<60 \text{ keV}$), high-dose implantation of Fe⁺ ions into SiO₂ [16], Ag⁺ ions into Ta₂O₅, SiO₂, and Si₃N₄ [17, 18] and into sodium-calcium glass [19], as well as Cu⁺ ions into Al₂O₃ [20] hemispherical asperities appeared on the dielectric surface. These asperities were identified as synthesized metal NPs (e.g., by the X-ray diffraction method [17]).

Thus, AFM measurements can be used to estimate the sizes of metal NPs synthesized by low-energy II, but only in the case where the particles appear on the surface. However, it is necessary to take into account that for objects comparable in size to the radius of curvature of the scanning part of the probe (needle), $\sim 10 \text{ nm}$ in our case, the relative error of determining the cross sections can reach 30% in the direction of increasing values because of the image convolution associated with the shape and dimensions of the probe tip. Additional errors in estimating the real sizes of NPs are due to the fact that the accuracy of measuring the portion of the spherical particle extending above the dielectric surface is limited. Nevertheless, as will be shown below, AFM-measurements are an effective method for comparative (qualitative) estimation of the morphology of implanted surfaces and the synthesized NP sizes.

Figure 3 shows the AFM-images of the surface of samples implanted by different doses at a fixed ionic current density. The optical spectra for these samples are given in Fig. 1. It should be noted that the surface roughness of the implanted glass did not exceed 0.5 nm. On the surface of the implanted SiO₂ samples hemispherical formations are observed (Fig. 3). They are associated, as mentioned above, with the spherical NPs of silver that extend above the surface or, in other words, are partially uncovered. Comparison of the AFM images with the spectra in Fig. 1 points to a qualitative agreement between the notions on the dynamics of change in the silver NP sizes with increasing implantation dose if the glass sputtering factor is taken into consideration. For example, the NP size in Fig. 3a is smaller than in Fig. 3b and c, while the spectral minima of transmission for these samples coincide (Fig. 1, spectra 1–3). It may be suggested that the difference between the hemisphere diameters for the AFM images in this case is due to the difference between the thicknesses of the sputtered glass layer, which are smaller for the dose of $2 \cdot 10^{16} \text{ cm}^{-2}$ as compared to higher doses. At a low II dose, the uncovering of NPs is less effective and, consequently, in Fig. 3a only the

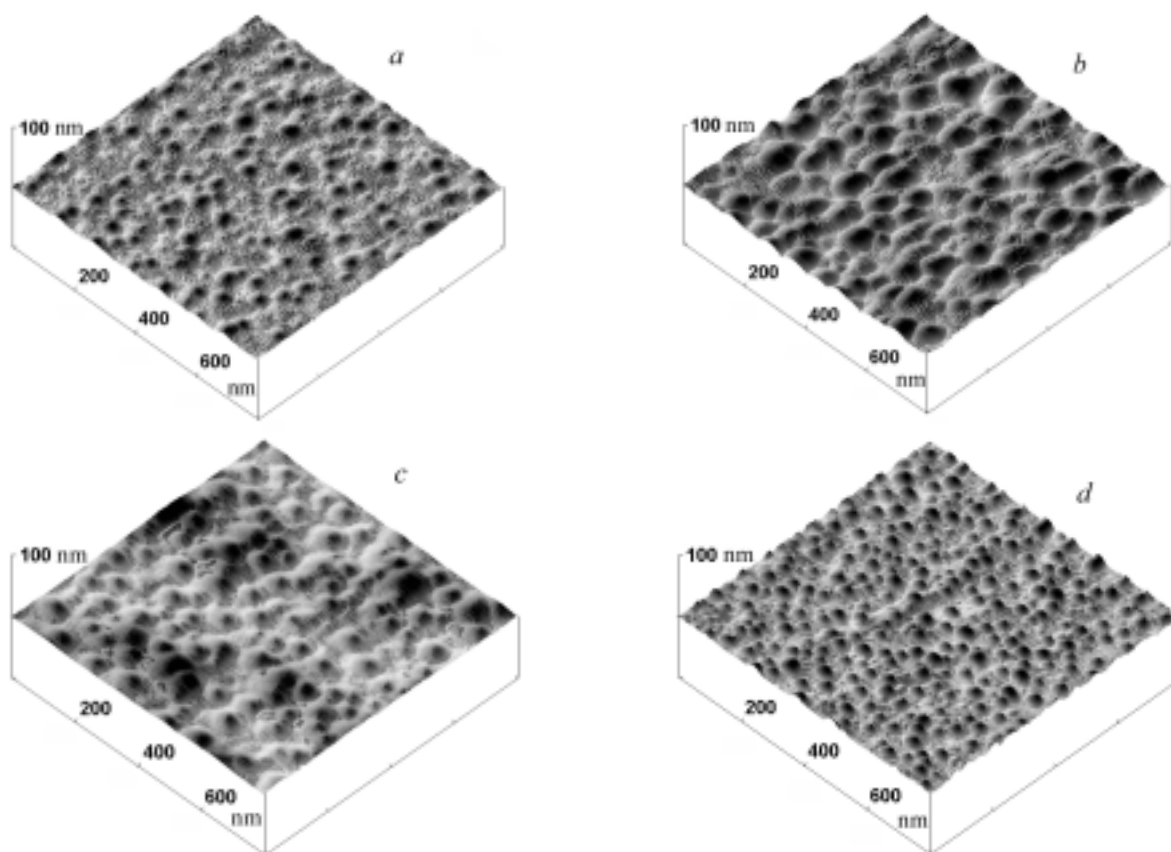


Fig. 3. AFM images of the SiO₂ surface after implantation by Ag⁺ ions with doses (10^{16} cm^{-2}): 2 (a), 4 (b), 6 (c), and 8 (d) at an ionic current density of $10 \mu\text{A}/\text{cm}^2$.

tops of the NPs are observed, whereas in Fig. 3b and c the NPs extend above the surface with their larger part. The diameter of the hemispheres observed in Fig. 3d for the sample implanted by the maximum dose is the smallest, which agrees with the short-wave position of the SPR band (Fig. 1, spectrum 4).

For the observed anomalous decrease in the sizes of NPs synthesized at a dose of $8 \cdot 10^{16} \text{ cm}^{-2}$, it is suggested to consider the following mechanisms. Under the II conditions the formation and growth of NPs occur under non-equilibrium thermodynamic conditions. In so doing, the appearance of competing processes, on the one hand, promoting the NP synthesis (e.g., radiation-stimulated diffusion of implanted silver atoms, increasing their mobility and the efficiency of merging to form NPs [9]), and, on the other hand, leading to a dissociation of NPs (e.g., NP fusion in the case of an effective heating of the substrate [19] or destruction of NPs when accelerated ions get into them) is possible. At ion-induced shock collisions the implanted ions or the secondary scattered atoms of the target knock atoms or groups of atoms out of the already formed NPs, which was visually demonstrated at a high-energy (MeV) irradiation of dielectrics containing metal NPs [21]. However, under the conditions of low-energy II such an effect of NP destruction has not been observed before. It may be suggested that in our case of low-energy II the determining factor is the very high doses, whose action has not been studied well, and, therefore, the mechanism of ion-shock collisions can take place. The proposed mechanism of NP comminution requires further more detailed experimental and theoretical studies.

Another and possibly determining factor capable of influencing the NP sizes is the ion-induced sputtering of the sample surface, i.e., of both the glass matrix atoms and the silver NPs formed. In so doing, the sputtering may lead to a decrease in the concentration of the Ag atoms already implanted and dispersed in the thin near-surface layer, thus impeding the NP growth and causing the total decrease in their concentration that appears in the optical spectrum (Fig. 1, spectra 3 and 4). Moreover, as mentioned above, the largest NPs are located in the immediate vicinity of the

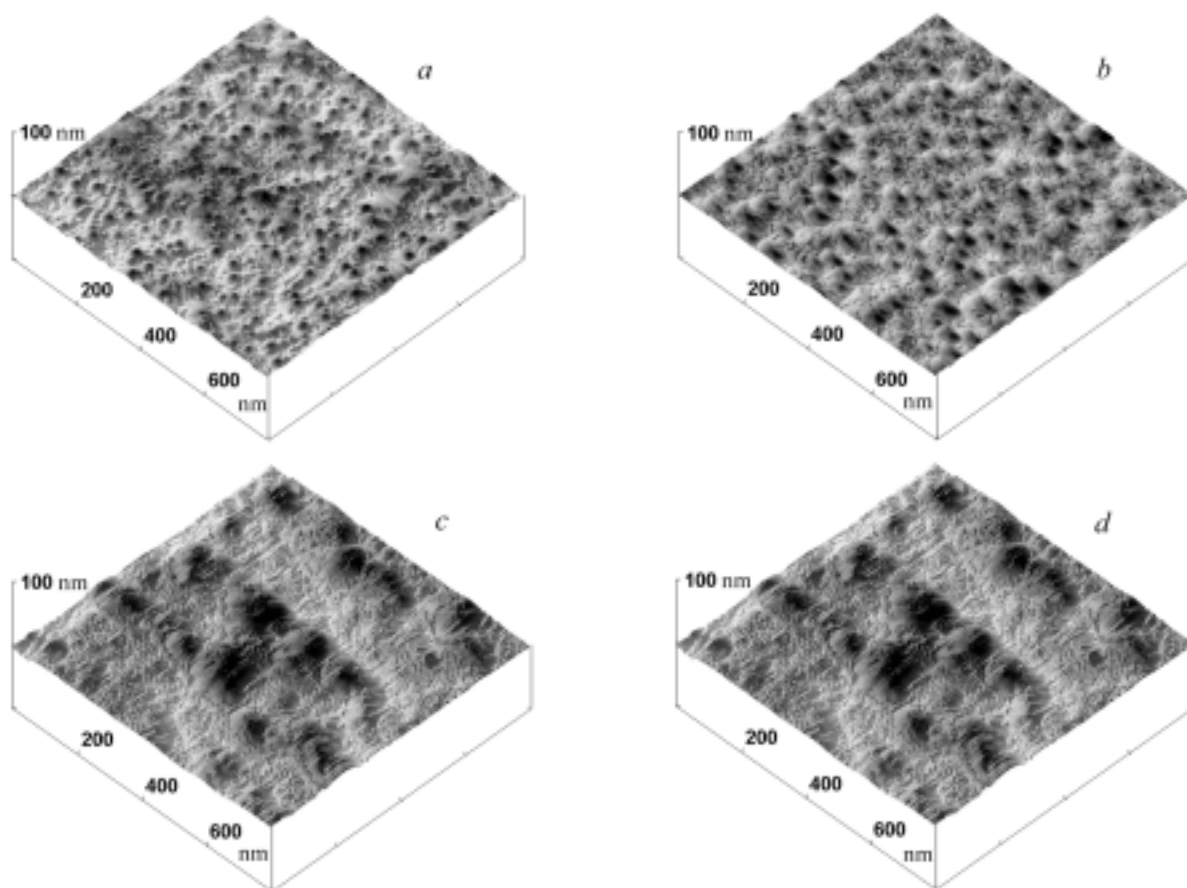


Fig. 4. AFM images of the SiO₂ surface after implantation by Ag⁺ ions with a dose of $5 \cdot 10^{16} \text{ cm}^{-2}$ at ionic current densities: 4 (a), 8 (b), 12 (c), and 15 $\mu\text{A}/\text{cm}^2$ (d).

sample surface, whereas smaller ones are located in the depth of the implanted layer. The surface sputtering first removes the larger NPs to reveal the smaller-depth NPs.

The images of the sample surfaces shown in Fig. 4 point to a monotonic increase in the diameter of the hemispherical formations with increasing ionic current density but at a fixed implantation dose ($5 \cdot 10^{16} \text{ cm}^{-2}$). An increase in the diameter completely correlates with the long-wave shift of the transmission-band minimum (Fig. 2) and corresponds to an increase in the mean size of synthesized Ag NPs in the implanted SiO₂ layer.

The most probable reason for the increase in the silver NP sizes at high ionic current densities is the change in the implanted glass temperature [10, 11]. At the initial moment of irradiation all samples were under equal conditions, i.e., at room temperature. The difference in the value of the ionic current density leads to a difference in the density gradient of the energy transferred to the target. A considerable portion of the ion energy at a low-energy implantation transforms into the generation of phonons [22], i.e., into the glass heating. Thus, the temperature gradient and the temperature of the near-surface SiO₂ layer are, of course, higher under irradiation at a higher ionic current density. According to the estimates made, in our case an increase in the current density in the ion beam from 4 to 15 $\mu\text{A}/\text{cm}^2$ may cause an increase in the sample temperature in the near-surface layer up to $\sim 80\text{--}100^\circ\text{C}$. According to [23], modeling of the silver diffusion in the glass yields an increase in the diffusion coefficient by three orders of magnitude as the temperature is increased from 20 to 100°C . Comparing our data with the results of the theoretical calculations, we can speak of a radiation-stimulated temperature-accelerated diffusion of a metal in the glass under the conditions of implantation at a higher ionic current density. A high diffusion mobility of silver atoms leads to their more effective flow onto the nuclei formed, as a result of which an enlargement of NPs (diffusion growth) occurs. Moreover, the conditions for the growth of NPs due to the mechanism of Ostwald ripening arise. With this mechanism

the small nuclei, having a lower melting point, dissociate, and the freed material is expended in enlarging the other NPs. Obviously, under the implantation conditions used in the given experiments, the matrix temperature increases but does not reach the critical value at which diffusion outflow of embedded silver atoms from the implanted layer into the depth of the substrate or thermostimulated dissociation of NPs would occur.

Conclusions. As a result of the investigation of the optical properties and morphology of the surface of SiO₂ glasses with silver NPs synthesized by ion implantation, a correlation between the data of optical spectroscopy and AFM that permits following the change in the NP sizes has been revealed. It has been shown that by varying the implantation dose and the ionic current density, it is possible to control effectively the NP size, which creates prerequisites for working out practical recommendations for optimizing the regimes of ion synthesis. It has been established that an increase in the dose at a fixed current density in the ion beam leads to an unusual dependence of the Ag NP growth, namely, at a high dose (in our case $8 \cdot 10^{16} \text{ cm}^{-2}$) there is a decrease in the NP sizes, whereas an increase in the ionic current density at a fixed dose causes a gradual enlargement of the NPs. The possible mechanisms explaining the change in the NP sizes with increasing dose and ionic current density have been considered.

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