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“Silver nanoparticles in oxide glasses: technologies and properties”

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1. Introduction

Nano-size particles of noble metals (Ag, Au, Pt) are today a subject of thorough attention of scientific researchers and of technologists, because these particles reveal the wide range of physical features, absent in the case of bulk media.

Size-controlled optical properties of Ag-nanoparticles open good prospects for potential technological applications – such as diffraction elements, optical filters, nanoplasmonic devices, bi-sensors, and nonlinear media.

Silver nanoparticles can be produced in various media – in water solutions, in polymers, in glasses, and in crystalline media. For instance, the long period in photographic imaging technique was based on the photoinduced production of Ag nanoclusters in the crystals of AgHal (the latent image). At the same time one can say that the inorganic glasses are the unique matrix for silver nanoparticles formation. The wide temperature range of glass viscosity growth provides the possibility to control over the Ag nanoparticles size within the wide range by means of modifying the temperature and duration of thermal processing. In the fact, only such kind of matrix makes it possible to control and investigate all the stages of Ag nanoparticles formation, including the starting stage.

Glass coloring by introduction of the metallic Ag nanoclusters is one of the ancient methods, known by humanity [1]. The mechanisms, leading to nucleation and growth of such nanoclusters, are the scientific and technology problem, important both for colored glass production and for all other potential applications of glass with silver nanoparticles [2-5].

The researches on silver nanoclusters formation comprise numerous technical approaches. Especially interesting are the methods, based on the use of ionizing radiation, are especially interesting due to their ability provide either local irradiation or to irradiate the whole volume of the glass. In this case it is comparatively simple to provide the control over concentration and average size of metallic nanoclusters. For instance, the controlled photon irradiation is used for production of photosensitive [6], polychrome [7] and photo-thermo-refractive [8] glasses. Very often all these types of glasses are called the photosensitive one (PS). Further within this chapter we shall use this word.

2. Formation of silver nanoclusters in PS glasses by UV irradiation method

PS glasses contain Ag in the dispersed oversaturated solution. The raw PS glasses (non-irradiated and non-thermally processed), similarly to the silver-less silicate glasses, which are used for PS glass production, reveal the fundamental absorption edge nearby 3.75 eV. Their absorption spectra do not reveal significant difference, which could have been attributed to the silver presence.

The energies of the resonant doublet of free Ag atoms ($5s_{1/2} - 5p_{1/2}$ and $5s_{1/2} - 5p_{3/2}$) are equal correspondingly to 3.665 and 3.780 eV, while ions of Ag^+ do not absorb in this range. Hence one can conclude that in the non-irradiated and non-thermally processed PS glasses Ag is dissolved in the form of Ag^+ -ions. Thermal processing under 500°C for up to 10^4 minutes does not result in change of absorption of these non-irradiated specimens.

The following components can be additionally inserted into PS glasses: (1) the ions of Ce^{3+} , which modify the spectral range of glass photosensitivity (the effective radiation energy is 3.88 eV, i.e. approximately in 1 eV less than in glasses without ions of Ce^{3+}); (2) the ions of Sb^{5+} and Sn^{4+} , which are electrons acceptors, playing the important role in production of silver nanoparticles under thermal processing and providing the necessary oxidation – reduction conditions during glass production; and (3) the ions of F⁻, Br⁻ and Cl⁻, which participate in formation of various crystalline phases under the thermal processing.

Let us consider the process of photo-thermo-induced nucleation in PS glasses. The action of the UV radiation, filling into the band of Ce^{3+} absorption, the electron-hole pair is produced in the glass. The hole is trapped by the three-valence cerium and the free electron is produced within the following reaction:



In the absence of Ce^{3+} ions the action of the shorter wavelength UV radiation, X-rays or γ -quanta results in trapping the holes by the non-bridged oxygen (NBO) with production of the non-bridged oxygen hole center (NBOHC). The energy of radiation, which is efficiently producing such centers in PS-glasses, exceeds 4.5 eV. There is also some possibility of such centers production in glasses with Ce^{3+} , especially in the case of high temperature.

The fluorine ions provide significant influence onto the absorption band of Ce^{3+} ions (Fig.1).

Increase of fluorine concentration in glass results in this band maximum shifting towards shorter wavelength range, while the band intensity is slightly reduced. One can explain the spectral shift of absorption band to the shorter wavelength range with fluorine concentration by arrival of fluorine ions in the coordination environment of Ce^{3+} ions. The rate of this shift is some 10-15 nm. Hence one can say that the cerium ions reveal with the fluorine ions the so-called halide effect [9].

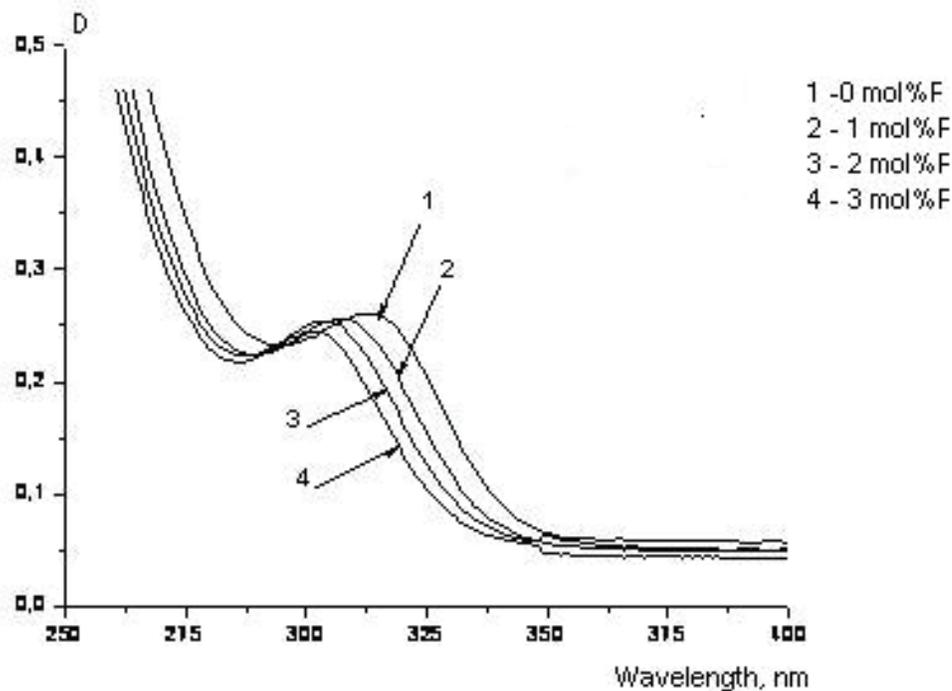


Fig. 1. Absorption spectra of PS glasses for various fluorine concentration.

It is interesting to note that in the case of bromine ions introduction into PS glass composition no halide effect with cerium ions is observed. Within the experiment accuracy variation of bromine ions concentration from 0 to 2.5 molar % does not change the position of the Ce^{3+} ions absorption band.

The freed electrons are trapped. In our case the traps can be comprised by Ag^+ , Sb^{5+} , Ce^{4+} , by anion vacancies and by other glass defects and admixtures. The following processes are most interesting in our case:



The electron, trapped by the silver ion comprises the meta-stable center even at the room temperature [10], while the center $(\text{Sb}^{5+})^-$ is preserved up to the high temperatures [11]. One can see from the absorption spectra, shown in the Fig.2, that UV irradiation of the PS glass results in reducing of the absorption, related to the Ce^{3+} ions (wavelength 312 nm), while absorption in UV and visible band (350-500 nm) grows up. One can see it in more details in the Fig.3.

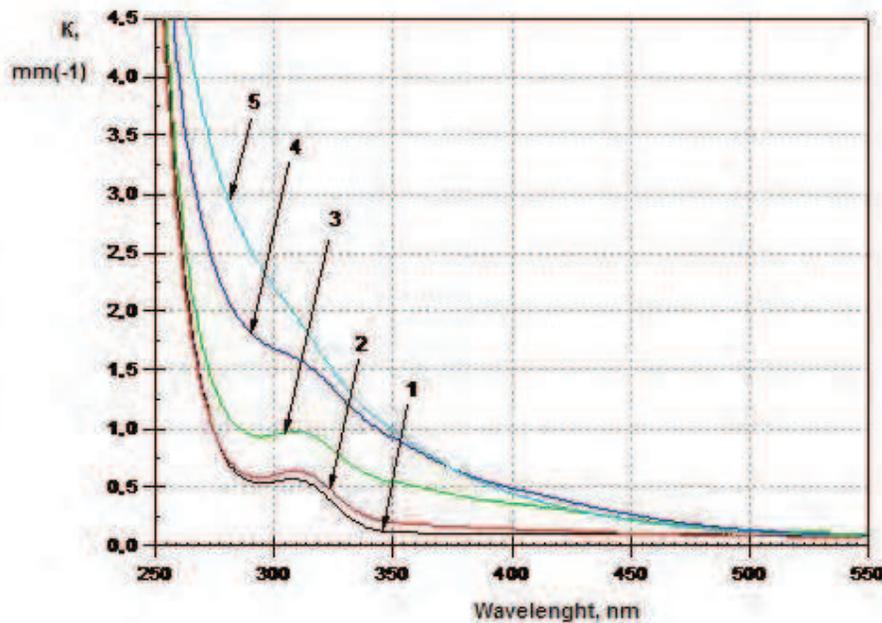


Fig. 2. Absorption spectra of irradiated PS glass (curve 1 - non-irradiated specimen, 2 - irradiation exposure dose - 10 J, 3 - 100 J, 4 - 1000, and 5 - 10000 J).

The reduce of absorption in the range 250 nm during irradiation (Fig.3) makes the basis for assumption that the ions of Ag^+ are responsible for the PS glass absorption band in the range of 250 nm. This assumption exactly coincides with the similar conclusions in the papers [12]. In any case we observe the definite tendency of absorption intensity decrease during irradiation - from $\sim 7.0 \text{ mm}^{-1}$ for the starting non-irradiated glass to 4.5 mm^{-1} for 100 J exposure and 3.5 mm^{-1} for 1000 J exposure.

The simplest supposition is that during the irradiation Ag^0 is produced in accordance with reaction (1). However, we have already noted that already at the temperature of 100°C these centers are transformed into the centers of Ag_2^+ and Ag_3^+ [10] due to interaction with the silver ions. The authors of [10] have determined that Ag^0 is oxidized easier than Ag_2^+ , while Ag_3^+ and Ag_3^{2+} are yet more stable.

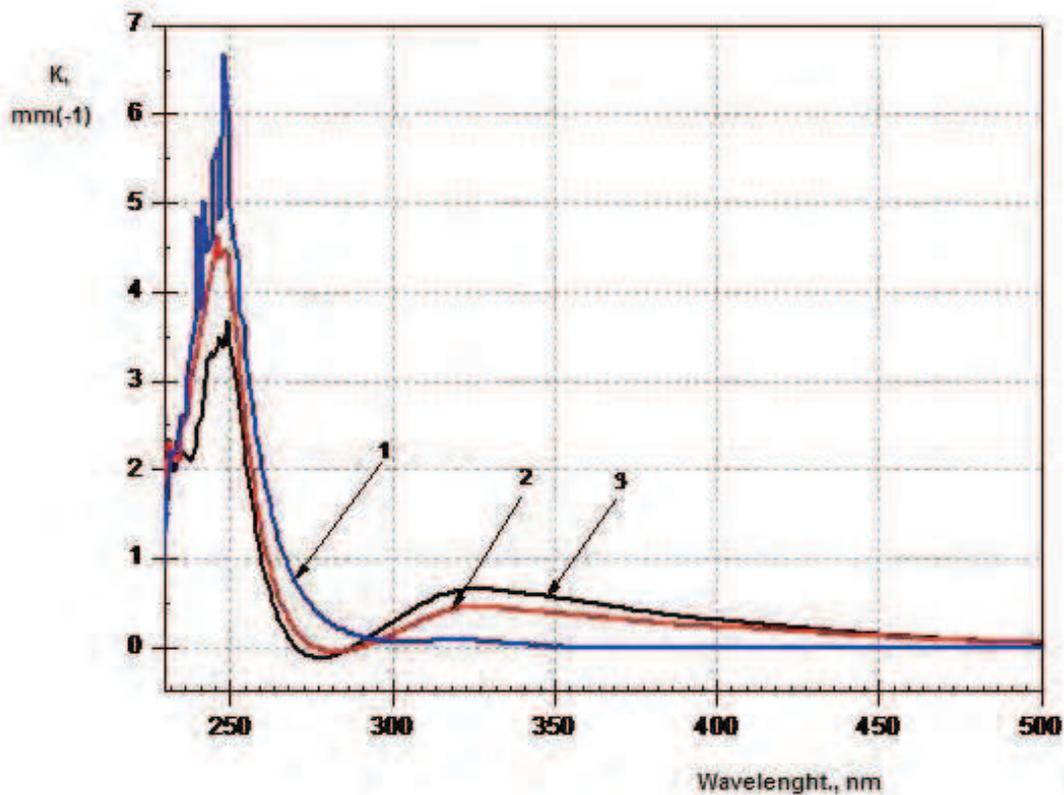


Fig. 3. Absorption spectra of irradiated PS glass (curve 1 - non-irradiated specimen, 2 - difference between spectra of PS after irradiation exposure dose 100 J and starting condition, and 3 - difference between spectra of PS after irradiation exposure dose 1000 J and starting condition).

The conclusion that the redox potential grows up with the increase of size of the molecule nucleus in water solutions provided the authors of [10] the possibility to outline the following stability series:



Hence one can connect the absorption in the range 300-500 nm, increasing with the irradiation dose (Fig.3) with the production of quasi-molecules of $(\text{Ag}_2)^+$, $(\text{Ag}_3)^+$ etc. According to the estimations of [13], the molecule Ag_2^+ absorbs radiation with the wavelengths less than 430 nm, Ag_3^+ - 435-525 nm, and Ag_4^+ - 525-705 nm.

Additional evidences for such a statement are based upon the following facts. In the silicate glasses the silver ions are substituting the sodium ones, and the sodium ions, breaking the tie Si-O-Si, are not uniformly distributed across the volume, but are producing the dimers. Hence there exists some possibility that the silver ions can substitute both sodium ions in the dimer, leading thus to production in the glass of the silver dimer like:



Such a structural unit can trap the photoelectron with production of the quasi-molecule of Ag_2^+ without movement of silver ions across the glass. The energy of thermal ionization of the Ag_2^+ quasi-molecule is about ~ 0.8 eV [13]. On the other hand, the wide absorption band from 300 to 500 nm can be related to the significant dispersion of the coupling length of Ag-Ag.

The silver particles are growing up by trapping the electrons on the nuclei, produced on the nucleation stage. These electrons are neutralized by the diffusing Ag^+ ions. Such a mechanism is well known and is used in halide-silver photographic media [14]. At the room temperature the ions of Ag^+ are frozen within the matrix; only for temperatures over, say, 400°C , their diffusion constant is sufficiently high for the measured growth rate. During the consequent thermal processing the charged centers are losing electrons within the wide range of temperatures. Electron supply can be provided by centers $(\text{Sb}^{5+})^-$, which are stable for the temperatures up to $250\text{-}300^\circ\text{C}$, or silver quasi-molecules. The following reactions can occur under such temperatures:



The relatively low matrix viscosity assists to production of the colloid silver particles Ag_n .

In the Fig.4 are shown the spectra of PS glasses absorption after multiple irradiation by UV light (dose 1000 J) and thermal processing at 450°C during 10 hours. The results, shown in the Fig.4, indicate that for the temperature slightly lower than T_g for these glasses ($\sim 500^\circ\text{C}$), irradiation and thermal processing result in the sufficiently intense absorption in the range 415-426 nm. This peak is typical for the colloid silver particles [15] and is related to the surface plasmon resonance (SPR). The curve (3) in the Fig.4 corresponds to the effect saturation state, i.e. any further repeats of irradiation and thermal processing cycles did not result in modification of either absorption maximum position nor in its intensity.

Peak amplitude of SPR is close to the measurements of the work [16]. Thus one can draw out the conclusion that in the considered specimens, only some 1% of the overall Ag^+ amount is transformed by irradiation and thermal processing into Ag^0 , forming the silver nanoparticles. Most probably, the change in maximum position is caused by the size effects. Much larger variation of SPR maximum position is observed in the case of increasing the processing temperature (Fig.5).

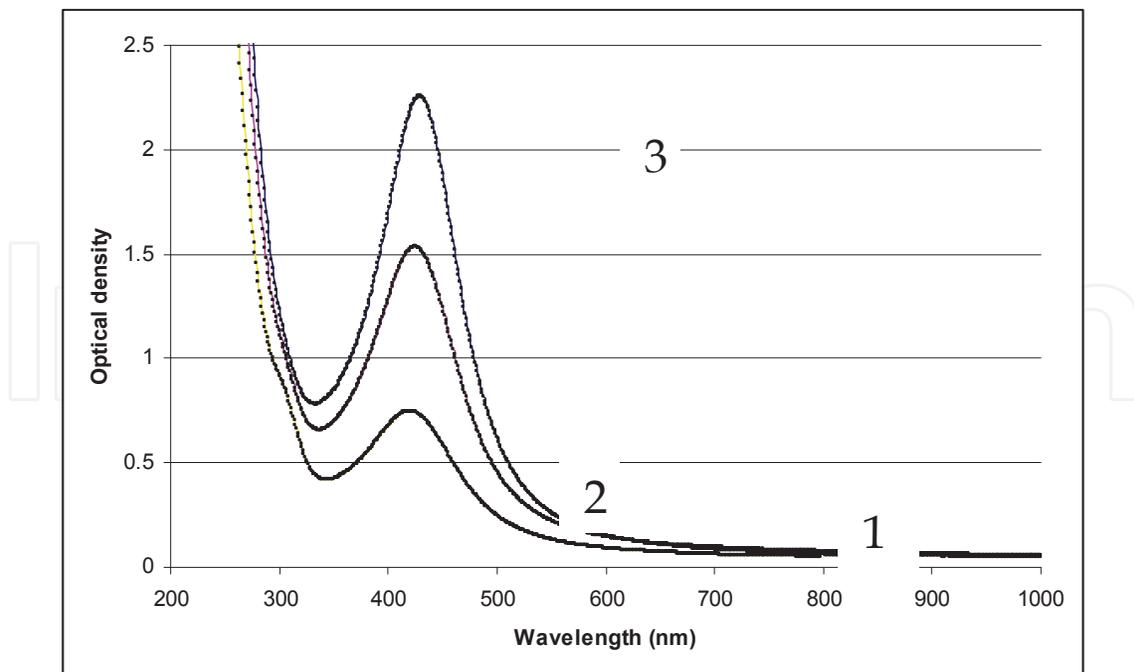


Fig. 4. Absorption spectrum of PS glass specimens after multiple irradiation with exposure 1000 J and processed under the temperature 450°C for 10 hours: 1 - after single time irradiation and thermal processing; 2 - after 3-times processing; and 3 - after 5-times processing.

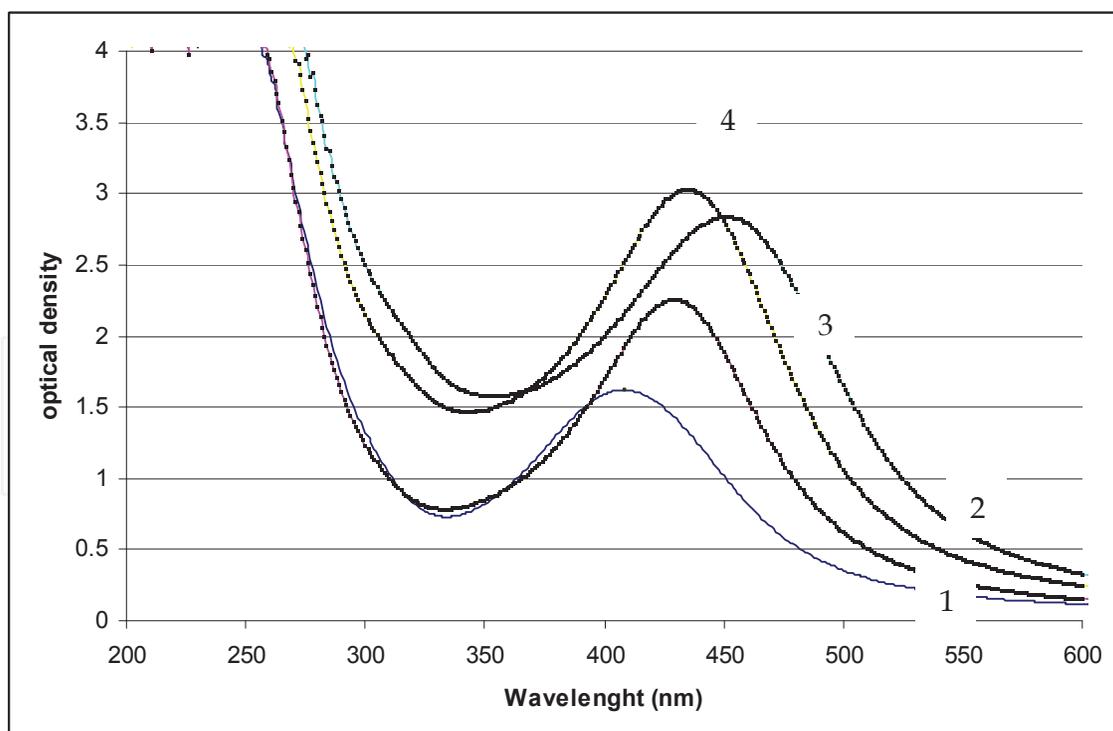


Fig. 5. The absorption spectra of PS glass specimens, multiple irradiated by the dose of 1000 J and processed during 10 hours under the temperature of: 1 - 400°C, 2-450°C, 3-500°C, 4-520°C.

One can see from the Fig.5 that the variation of the processing temperature from 400 to 520°C results not only in shift of the SPR band maximum (from 405 to 460 nm), but also in changing the band halfwidth. Observation of the absorption bands, caused by the silver colloid particles (> 1 nm), under the temperatures, which are much lower than T_g, i.e. under 400-450°C, is the evidence, indicating that, most probably, the silver nanoparticles are produced in the glass cavities, whose size grows up with the temperature increase. For the temperatures higher than T_g the colloid silver deposition can be additionally accompanied by the increase of the internal cavities due to the viscous current.

3. The factors, which influence onto the spectral position of plasmon resonance of silver nanoparticles in glass

Let us consider some possible reasons of the spectral shift of the plasmon resonance band in glass, containing the silver nanoparticles [16]. The following factors can lead to the SPR band shift:

1. modification of the chemical content and crystalline structure of silver nanoparticle, influencing onto its dielectric permeability;
2. modification of the chemical content of the edge nanoparticle - glass, which influences onto the process of scattering the free electrons of the metal on the nanoparticle surface;
3. variation (increase) of the silver nanoparticle size during thermal processing of the glass without modification of its shape;
4. modification of the geometric shape of nanoparticle during irradiation and thermal processing of the glass;
5. modification of the refraction index of matrix, surrounding the silver nanoparticle.

All these factor can influence significantly onto the dielectric permeability of silver nanoparticles even in the case of very small variation of chemical content of nanoparticle.

Let us consider in more details the influence of the last three factors onto the spectral position of absorption band of silver nanoparticles in glass matrix. Let us make the following assumptions: the size of nanoparticles is much less than the radiation wavelength; the concentration of nanoparticles in glass is low; particles do not reveal mutual electromagnetic interaction.

The model, which is based on the Drude-Lorentz theory and is taking into account the scattering of free electrons on the nanoparticle surface, leads to the following relationship for the dielectric permeability [17]:

$$\varepsilon(\omega, r) = \varepsilon_0(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega\gamma} - \frac{\omega_p^2}{\omega^2 + i\omega(\gamma + Av_F/r)}$$

Here ω is the circular frequency of radiation; r is the nanoparticle radius; ε_0 is the dielectric permeability of the bulk silver; ω_p is the plasmonic frequency of silver; γ and A are the constants, accounting for the processes of scattering of free electrons in metal on electrons, phonons and the nanoparticle surface ($A < 1$); v_F is the Fermi speed of free electrons.

According to the estimations the change of diameter of spherical silver nanoparticle from 3 to 4 nm without shape changes leads to the shift of plasmonic resonance frequency to the longer wavelength side in $\Delta\lambda \approx 10$ nm. This result well correlates with the conclusions of [18],

drawn out from the absorption spectra of phosphate glass with silver nanoparticles. One can explain the long wavelength shift after light and thermal processing (Fig.4) and, to smaller extent, after increase of the processing temperature (Fig.5) by the increase of the silver nanoparticles size. However, according to estimations, one cannot explain the observed shift only by changes of silver nanoparticles size.

The geometry shape of silver nanoparticles in glass can differ from the ideal sphere. For example, in the boron-silicate glass the silver nanoparticles can reveal the shape of extended ellipsoid [19, 20]. One can see from the electron microscopy images of silver nanoparticles in phosphate glass, presented in [18, 21], that their shape is also non-spherical. The authors of paper [22], devoted to the polychrome glasses, who have varied the irradiation dose and temperature of processing at the nucleation stage and the stage of nanocrystal growth, have managed to realize the whole gamma of glass colors from yellow to green.

In the Fig.6 is shown the variation of absorption spectra of the PS glass specimens, irradiated by various doses on the nucleation stage. One can note that the increase of the exposure dose on the nucleation stage reduces the deviation of particle shape from spherical, which reveals itself in reduce of the gap between the main bands. Irradiation of PS glass specimens by the dose over 500 J results in observation of only one absorption band, which is an evidence of the spherical shape of colloid nanoparticles.

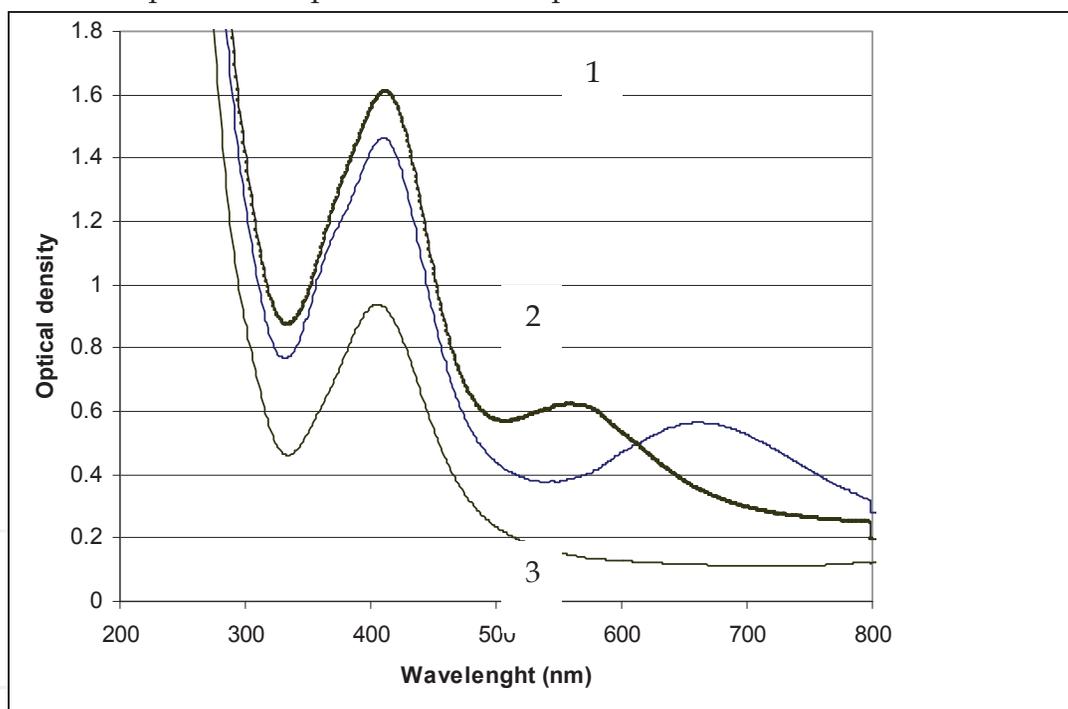


Fig. 6. Absorption spectra of the specimens, whose nucleation took place under UV irradiation by various exposure doses: 1 - 200 J, 2 - 100 J, and 3 - 10 J.

The most interesting results was observed in the case of PS glass irradiation at the stage of nucleation by the dose of 10 J. One can see from the Fig.6 that in this case one can see in the visible range only one band with the maximum around 395 nm. One can see from the Fig.7 that these specimens reveal one more absorption band in the near IR spectral range; the repetition of the irradiation and thermal processing stages results in additional shift of the

second band to the longer wavelength spectral range, i.e. this process is also accompanied by the gap increase.

Since recently photoactivation of PS glasses is very often produced by femtosecond pulsed lasers, emitting in near IR spectral range [23]. In this case it is not necessary to dope the glass by ions of Ce^{3+} , Cu^+ etc., which work as electron donors during UV irradiation.

Especially interesting is application of short pulse laser radiation for modification of spherical shape of silver nanoparticles in glass [24-28].

Optical microscopy studies [24] have shown that irradiation by circularly polarized femtosecond laser radiation can change the spherical shape of silver nanoparticles in glass. There was outlined the hypothesis that the shape transformation occurs via the stage nanoparticles photoionization by laser irradiation. The rate of dichroism, which can be achieved by laser use, depends upon the initial properties of nanoparticles. For instance, provision of maximum dichroism for the particles with SPR at 413 nm requires irradiation by light with much larger wavelength, and the wavelength has to be increased during irradiation. Such sequence of irradiation at 535 and 670 nm can cause modification of shape from spherical nanoparticle to ellipsoid with the axis ratio >3 [28].

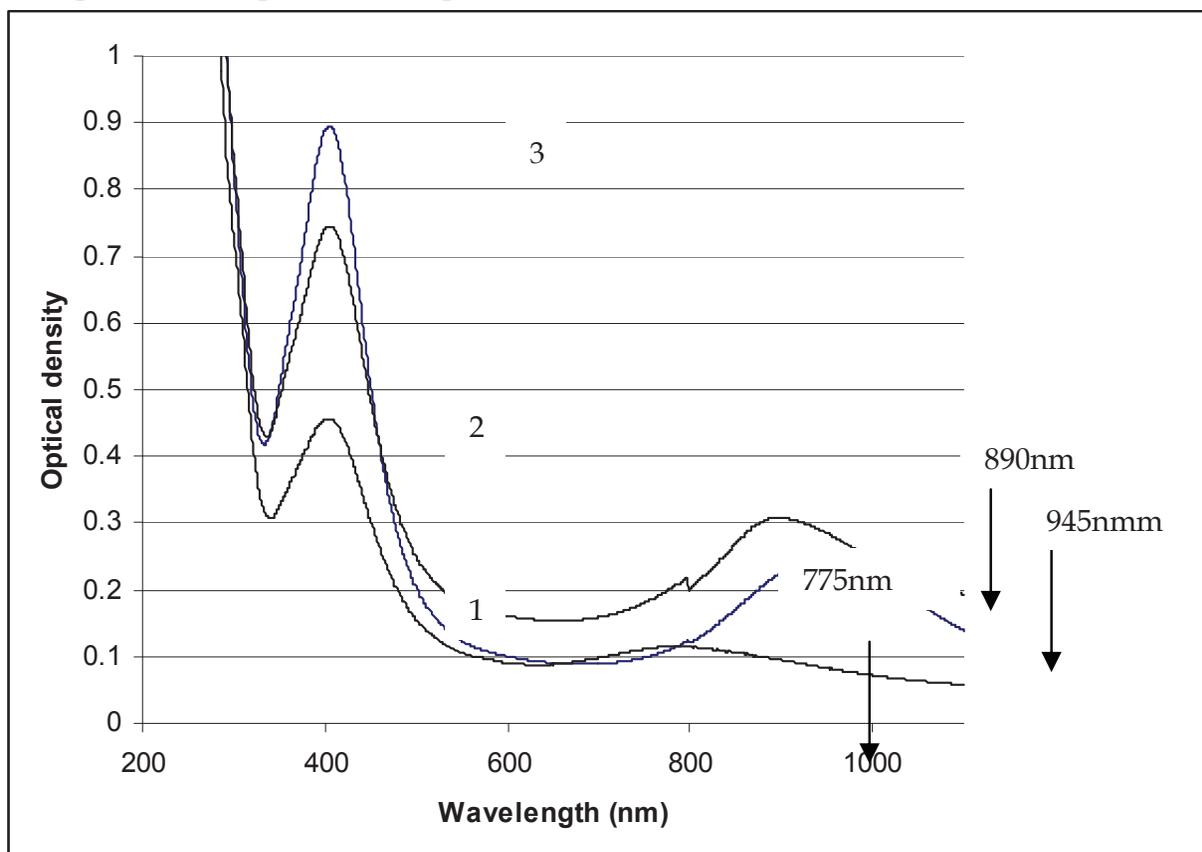


Fig. 7. Absorption spectra of PS specimens, whose nucleation was carried out by UV irradiation at 10 J, while processing occurred in several stages (1, 2 and 3).

We have already noted the SPR maximum position can be strongly influenced by the refraction index of the matrix, surrounding the glass nanoparticle. Naturally, the strongest influence of dielectric environment reveals itself in the spectral position of plasmonic resonance of the silver nanoparticle.

In the dipole approximation the cross-section of absorption by the spherical particle with the shell is described by the following relationship [29]:

$$\sigma_a = \frac{8\pi^2 \sqrt{\epsilon_h} r_s^3}{\lambda} \cdot \text{Im}(\delta)$$

Here δ is the nanoparticle polarisability:

$$\delta = \frac{\epsilon_s \epsilon_a - \epsilon_h \epsilon_b}{\epsilon_s \epsilon_a + 2 \epsilon_h \epsilon_b}, \quad \epsilon_a = \epsilon_c \cdot (3 - 2P) + 2 \epsilon_s P, \quad \epsilon_b = \epsilon_c + \epsilon_c \cdot (3 - P)$$

$$P = 1 - \left(\frac{r_c}{r_s} \right)^3$$

ϵ_h , ϵ_c , ϵ_s are the values of the dielectric permeability of medium, core and shell correspondingly, r_c is the core radius, r_s is the shell radius, and λ is the radiation wavelength.

The condition of plasmon resonance is equality to zero of the real part of nanoparticle polarisability denominator [29]:

$$\text{Re}(A) = \text{Re}(\epsilon_s \epsilon_a + 2 \epsilon_h \epsilon_b) = 0.$$

One can conclude from these relationships that the thickness of dielectric shell and its dielectric permeability provide the most significant influence onto spectral position of the plasmonic resonance.

The numerical simulation was carried out [30] for the following parameters: refraction index of the medium $n_h = 1.5$; core material - silver (the optical constants of the silver film were taken from [31] for the spectral range $\lambda = 0.4 - 0.6 \mu\text{m}$); the refraction index of the shell $n_s = 2.2$ (silver bromide was used as the example); core radius was $r_c = 2 \text{ nm}$; and the shell thickness $h = r_s - r_c$ varied from 0 to 3 nm.

In the Fig.8 are shown the spectral dependencies of absorption cross-section of spherical nanoparticles with silver core and silver bromide shells of different thickness. One can see from the Figure that the increase of shell thickness from 0 to 3 nm results in shift of plasmonic resonance of nanoparticle to the longer wavelength side in $\sim 100 \text{ nm}$.

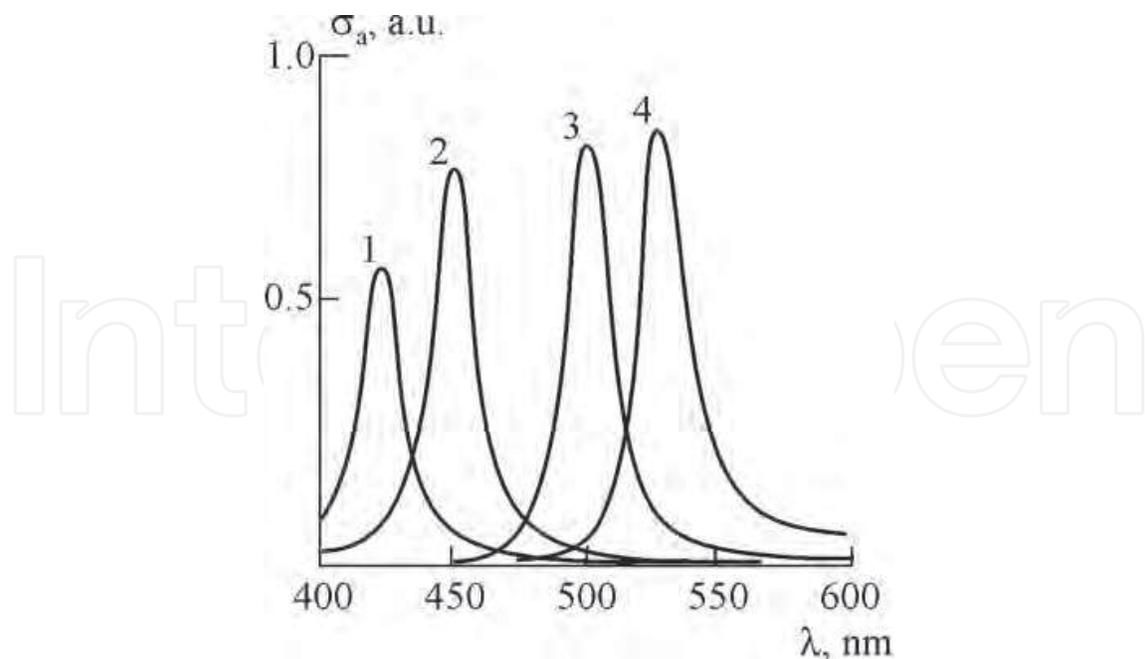


Fig. 8. Spectral dependencies of absorption cross-section for silver nanoparticles with silver bromide shell. 1 - $h = 0$ nm, 2 - 0.5, 3 - 1.5, 4 - 3 [30].

Let us return to specific media. One can assume that during thermal processing can occur not only variation of thickness of the shell, surrounding the silver nanoparticle, but also variation of this shell refractive index. In the Fig.9 are shown the dependencies of spectral position of nanoparticle plasmonic resonance upon the shell refractive index [30]. One can see from the Figure the increase of the shell refractive index results in shift of plasmonic resonance to the longer wavelength spectral range. The dependence is practically linear. Increase of shell thickness leads to slight increase of slope of dependence of $\lambda_{\max}(n_s)$.

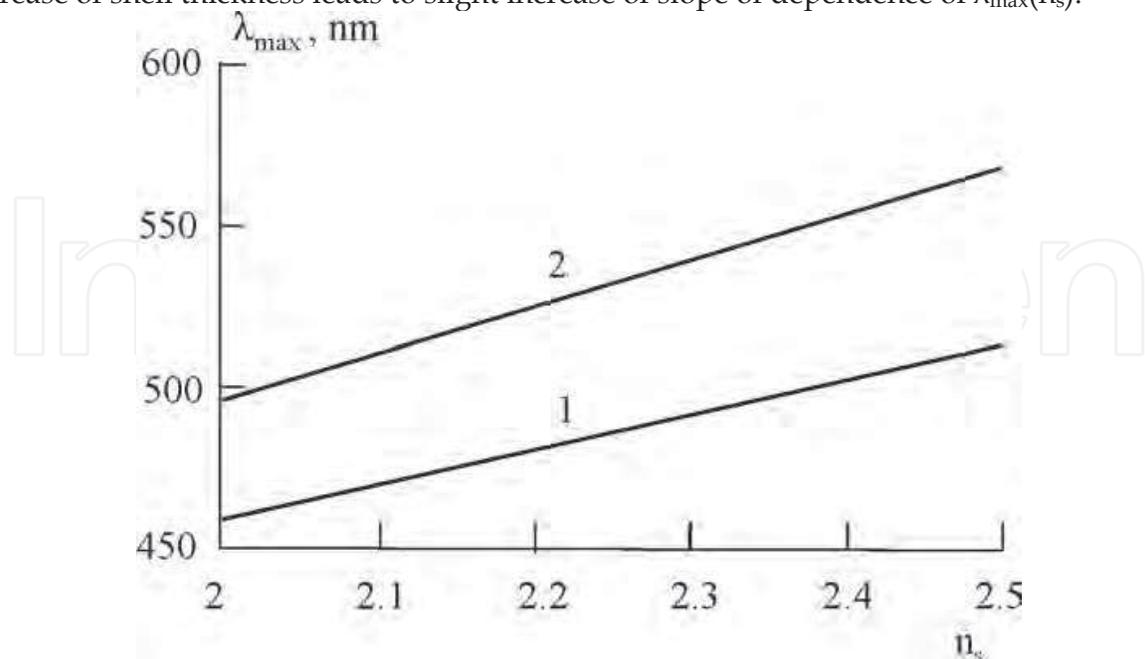


Fig. 9. Dependence of spectral position of nanoparticle plasmonic resonance maximum upon shell refractive index. 1 - $h = 1$ nm, 2 - 3 [30].

Hence, formation of the dielectric shell on the silver nanoparticle and variation of this shell's thickness during the thermal processing of the glass can provide the rather strong influence onto the spectral position of the plasmon resonance. For instance, in [32] it was noticed that the 3-nm silver particles, produced by γ -irradiation and consequent thermal processing, can be subjected to oxidizing due to interaction with defects on the non-bridged oxygen (NBOs) in the case of temperature growth up to 500°C.

The paper [10] outlines some analogies between silver behavior in glass and its behavior in water solutions from the point of view of tendency of silver particles to be oxidized and thus to reduce their size or disappear with the temperature growth. Let us consider this analogy and note the very low solvability of silver halides in water. Hence one can say that there is a very high probability, especially when the temperature is high, that on the surface of the silver nanoparticle, dissolved in a glass, will be produced the following compounds:



The Table presents the values of refraction index (n) of these compounds and their melting temperature (T_m). These compounds may impose significant effect onto spectral position of the plasmon resonance. They are very important for mechanisms of production and behavior of a wide group of light sensitive glasses like photochrome, polychrome, photo-thermo-refractive etc.

Compound	Refraction index (n)	Melting temperature (T_m)
Ag_2O	2.7	decompose 300°C
AgF	~2.03	435°C
AgCl	2.07	455°C
AgBr	2.25	434°C

The above given analysis has shown that the thickness and refraction index of the shell, surrounding the nanoparticle, provides significant influence onto position of the plasmon resonance maximum.

Let us note the relatively low melting temperatures of the compounds, presented in the Table. They are, in any case, lower than that of T_g PS glasses and than the temperatures, usually used for thermal processing with the purpose of Ag nanoparticles formation (450-600°C). Taking also in account the dependence of melting temperature upon the particle size (Thomson equation), one can say, that all these compounds (with the exception of Ag_2O) are liquid during the thermal processing of the PS glasses. This can be the explanation for the following effects:

1. Unusual - for glasses - influence of very small admixtures (like Cu, Cd, Pb etc.) onto the glass properties - the photochrome glasses [33].
2. Dissolution of compounds like NaF and LiF in the liquid phase (photo-thermo-refractive and photosensitive glasses).

True, less than 0.1% Cu_2O is introduced into the halide-silver glasses, providing the drastic changes in glass properties and in properties of the extracted crystalline phase of AgHal

[33]. It would not be so unusual in the case of growing up the monocrystal or synthesis of polycrystalline compound. The glass structure – even with the account for the micro-inhomogeneous content – provides a great number of positions for copper ions, which they can substitute with a high probability. However, in this case, substituting, say, the ions of Na^+ , they do not have an opportunity to form their own environment in a solid glass. The situation is, however, different in the case when they (copper ions, for instance) transfer to a liquid phase.

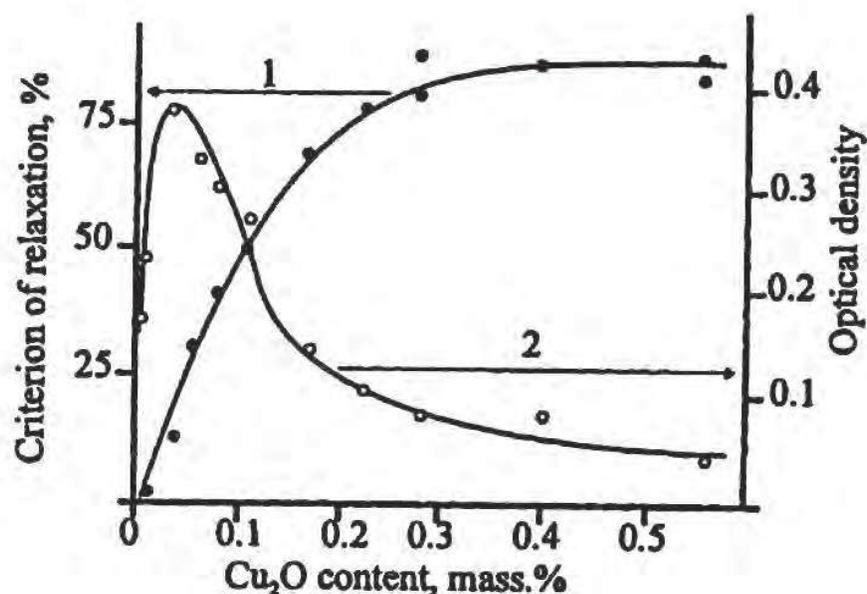


Fig. 10. The influence of copper ions content in the glass onto its photochromic properties (changes in optical density during irradiation and the rate of thermal bleaching (relaxation criterion))

In the Fig.10 is shown the influence of copper ions content in the glass onto the photosensitive properties of the photochromic glasses. One can note the very strong and variable influence. To our opinion, this is an evidence, supporting the hypothesis that during thermal processing the copper ions are entering the liquid silver-halide phase. Similar ideas can be outlined concerning the mechanism of deposition the crystals of NaF on the photoinduced nanoparticles of Ag in photo-thermo-refractive glasses. It is well known that the sodium fluoride is hardly solvable in silicate glass; it is evaporating from the glass surface even at the comparatively low temperatures. In [34, 35] was shown that in the photo-thermo-refractive glasses no photoinduced deposition of NaF takes place in the absence of KBr in the glass composition. In [35] in such glass was observed the absorption band of colloid silver, covered by the layer of AgBr. Hence, in fact, the sodium fluoride is dissolved in liquid AgBr. Under such temperatures ($\sim 500^\circ\text{C}$) is produced the liquid phase, consisting of AgBr and NaF. The crystalline sodium fluoride is deposited during this phase cooling.

4. Special features of silver nanoparticles formation in PS-glasses under electron beam and thermal action

The classic method of Ag nanoparticles formation in PS glasses, based on UV and thermal action, provides the possibility to obtain the nanoparticles within the overall glass volume. In this case, however, the volume concentration of nanoparticles is low. The reason is that it is impossible to introduce the big number of Ag ions into the starting glass composition. In addition, the starting glass has to contain the sensitizing ions of Ce, Sb and Sn. The method of ion implantation [36, 37], which makes it possible to provide high concentration of metal ions in a thin surface layer of glass, is free of the said limitation. In this case under definite conditions the metal nanoparticles are formed already on the implantation stage – without additional thermal processing.

The last years has brought the growing interest to the possibility of modification of the glass surface layers by electron beam. In particular, it was found out that electron irradiation leads to formation of the negatively charged region nearby the glass surface. The latter initiates the field diffusion of the movable positive metal ions – for instance, of K^+ [38]. Redistribution of potassium ions within the glass modifies its chemical composition and provides mechanical stress and refraction index gradient formation. The electrons reveal the emphasized reducing properties, and thus electron irradiation can lead not only to spatial redistribution of glass composition elements, but also to reducing of the positive ions down to the neutral atoms [39, 40] and stimulate growth of nanocrystals in glass [41].

Hence one can post the question – is it possible to form the silver nanoparticles in PS glass under the electron irradiation action, and what are this process peculiarities? We have studied the process of formation of Ag nanoparticles in PS glasses, based on the preliminary irradiation of glass surface by electrons with the energy of 5-30 kV and consequent thermal processing [42, 43]. Our studies have shown that this method makes it possible provide the high concentration of Ag nanoparticles in the surface glass layers even in the case when the starting glass contains the low concentration of silver ions. We have studied in experiment the PS glasses of composition $Na_2O-SiO_2-ZnO-Al_2O_3-Ag_2O-CeO_2-Sb_2O_3-Br-F$; the content of Ag_2O in the starting glass was 0.5% (mass). The irradiation was carried out under the room temperature by electron beam with electron energy 7-30 keV and electron current density $50 \mu A/cm^2$. Irradiation duration was varied from 100 to 1000 s. The layer of Al with the thickness 100-200 nm was deposited onto the glass surface for charge removal; after irradiation this layer was removed by means of chemical etching. In the Fig.11 are shown the spectra of PS glass optical density before electron irradiation, after it and after several cycles of thermal processing. The irradiation was carried out by electrons with energy 20 keV, and the irradiation dose Q was equal to $100 mC/cm^2$. In the Fig.11 is also shown the routine of one thermal processing cycle. One can see from this Figure that irradiation by the electron beam with the said parameters leads to increase of glass absorption in short wavelength spectral range. However, no plasmonic absorption band is observed in this case, indicating thus the lack of metallic silver nanoparticles. Already the first cycle of thermal processing realizes in glass the intense absorption band in the spectral range 390-420 nm, corresponding to the plasmonic resonance of silver nanoparticles. Further thermal processing results in broadening of plasmonic band and modification of its amplitude. Modification of amplitude with the increase of thermal processing cycles' number can be of non-monotonous nature.

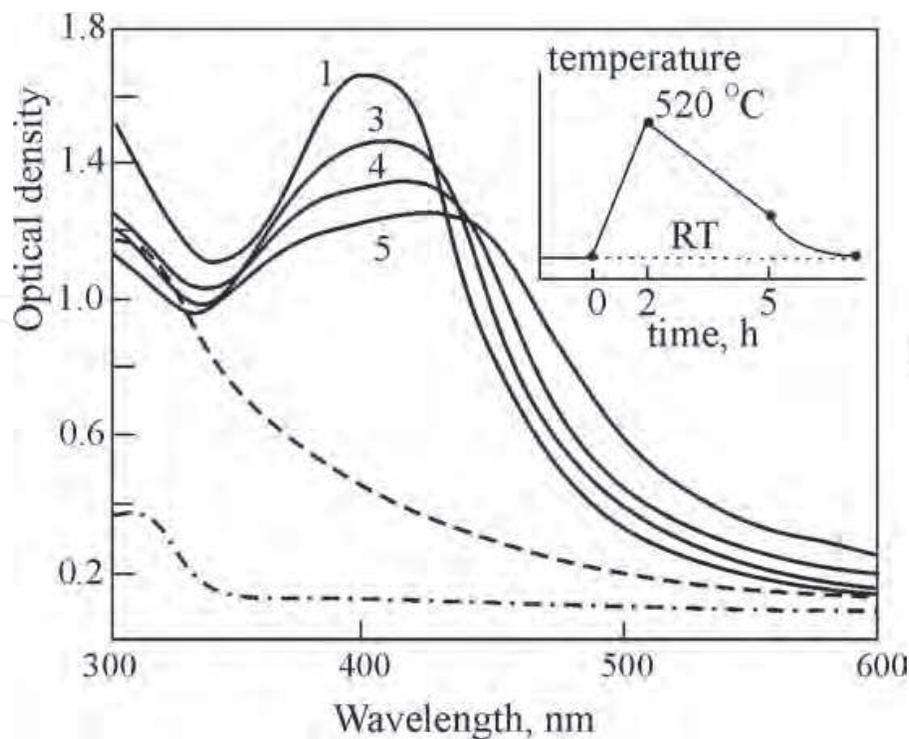


Fig. 11. Transformation of optical spectra of PS glass after electron-beam irradiation and thermal treatment. $E_0 = 20$ keV, $Q = 100$ mC/cm², irradiation time - 2000 s, (- · - · -) - initial glass; (- - -) - electron-beam irradiated glass; 1...5 - number of thermal treatment. Insert - the mode of thermal treatment.

In the Fig.12 is shown the TEM-image of the PS glass surface layer after electron irradiation and thermal processing ($E_0 = 20$ keV, $Q = 100$ mC/cm²). One can see from the Figure that the average size of silver nanoparticles is 10-12 nm. Their concentration is rather high, and the distance between nanoparticles is sometimes smaller than their diameter. This is an explanation for the absorption spectrum transformation during irradiated glass thermal production. In the case of high concentration of particles and the distance between them less than the radiation wavelength the particles become the electromagnetically coupled. This results in significant increase of plasmonic absorption band [44].

Unlike the classical method of silver nanoparticles formation (UV irradiation and thermal processing), in the case of electron beam irradiation the silver nanoparticles are not uniformly distributed across the volume, but are concentrated in the thin layers nearby the glass surface and parallel to it. The thickness of such layers does not exceed 2 μ m, while in some cases it is just approximately 20 nm. In the Fig.13 is shown the image of silver nanoparticles' layer, whose thickness does not exceed two diameters of nanoparticle, while the distance between the particles is 2-5 nm.

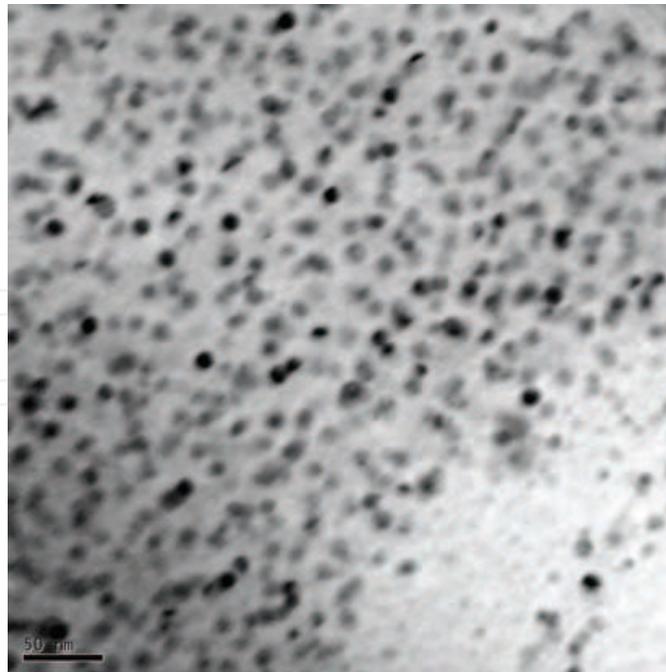


Fig. 12. TEM-image of the PS glass surface layer after electron irradiation and thermal processing. Size of silver nanoparticles 10-12 nm. Scale - 50 nm.

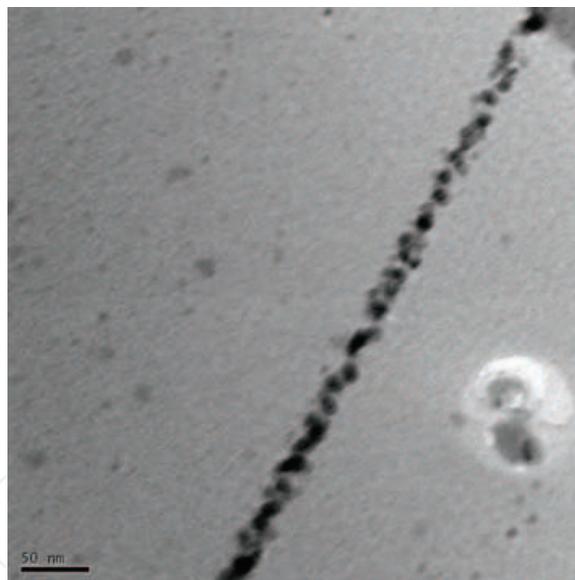


Fig. 13. TEM-image of silver nanoparticles' layer in PS glass. Scale - 50 nm.

One has to note that in the case of the electron energy less than 10 keV and irradiation zone 50-100 mC/cm² one can see - just by the naked eye - on the glass surface the silver layer. However, in this case the absorption spectra lack the plasmonic band. It means that in this case the silver layer is continuous or is comprised by the silver nanoparticles, contacting each other. During the thermal processing this layer is gradually disappearing due to silver dissolution in the glass, while the plasmonic band arises in the absorption band.

Let us consider special features of silver nanoparticles formation under electron beam irradiation conditions and the differences of this method from the classical one. In the Fig.14 is shown the geometry of the model, which was used during analysis.

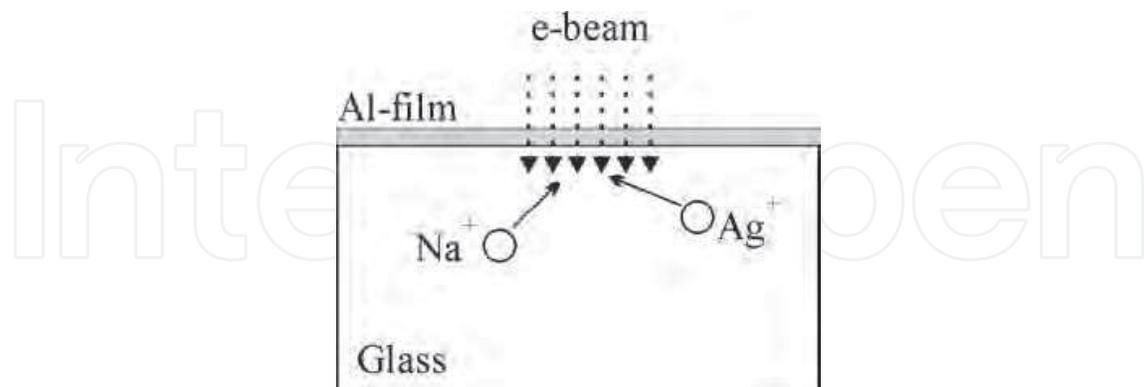


Fig. 14. Geometry of the model.

The depth of electrons' penetration. One can evaluate the depth of electrons' penetration into the glass from spatial distribution of energy losses of electrons. The losses of electron energy are determined by the atomic weight and atomic number of main glass components – of O, Si and Na, and also by glass density. In the Fig.15 are shown the calculated dependencies of electron energy losses for incident beam energies of 5, 20 and 30 keV. One can see from the Figure that for the energy of 5 keV the thickness of the layer, where electron braking takes place, is 250-300 nm, and the losses maximum fills to the depth of 100 nm from the surface. For electrons energy of 20 keV these values are 3 μm and 1 μm correspondingly, while for 30 keV – 6 μm and 25 μm . These layers determine the depth of spatial position in the glass of the volume charge region and of the region of electrons' interaction with the positive metal ions. At the same time the electrons, whose energy still exceeds that of atoms' ionization, can once again ionize the metal atoms. Hence, in these layers two competing processes can take place – reducing and ionization.

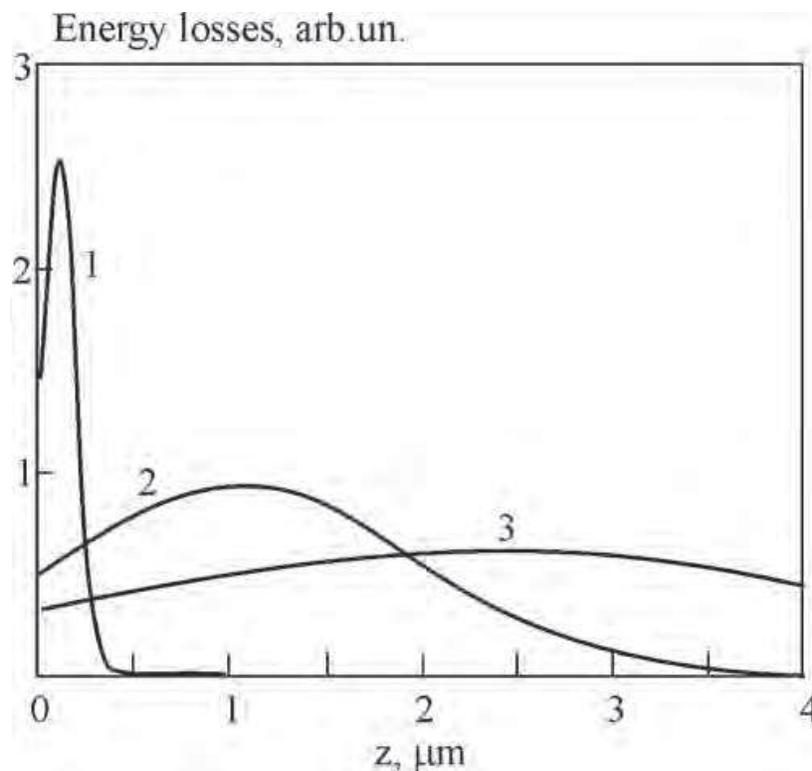


Fig. 15. Distribution of electron energy losses in PS glass. 1- $E_0 = 5$ keV; 2 - 20; 3 - 30.

Glass heating by electron beam. During glass surface irradiation by the high-energy electrons the major part of their energy is transformed, finally, into heat. The local heating can influence onto the processes of silver ions and atoms diffusion in the irradiated glass zone. Let us consider the influence of glass heating by the electron beam onto the processes of thermal diffusion. The calculation was carried out by means of solving the 3D-problem of thermal conductivity in the cylindrical coordinates for electron beam with the energy 20 keV, beam current density $50 \mu\text{A}/\text{cm}^2$ and irradiation dose $100 \text{ mC}/\text{cm}^2$. The calculation has shown that under such conditions the maximal temperature in the surface layer of the glass with the thickness $1 \mu\text{m}$ does not exceed 150°C . At the distance $20 \mu\text{m}$ from the surface the temperature is equal to 100°C . The coefficient of thermal diffusion of atoms and ions reveals the exponential dependence upon the temperature, and hence the diffusion processes start playing the significant role for the temperatures higher than 300°C . So one can draw out the conclusion that in the case of electron irradiation by the beam with the above mentioned parameters the impact of thermal diffusion of silver ions and atoms into the general picture of the process is small.

Tension of the field, produced by volume charge. Electron irradiation of glass produces formation of three electron flows in it – the flow of high-energy electrons of the primary beam, opposite-directed flow of the secondary electrons and the opposite directed flow of the thermalized electrons, which are moving from the specimen to metallic layer on the specimen surface. The solution of the problem of electric conductivity for given conditions made it possible to determine the volume charge, formed inside glass during the electron irradiation, and to evaluate the tension of the electric field, produced by this volume charge. For the electron energy 20 keV and beam current density $50 \mu\text{A}/\text{cm}^2$ the field tension is 30-

50 kV/cm. At such tension the field diffusion of positive glass ions has to influence significantly onto the process kinetics.

Field diffusion of positive ions. Among all positive ions, presented in the glass combinations, those of sodium and silver are the most movable ones [45]. Spatial distribution of these ions under electron irradiation was determined by solving the field diffusion equation with the account for the jump ion conductivity. The calculation was carried out for the specimen temperature, equal to 150 °C. The results of calculation are shown in the Fig.16. One has to note that the presented curves have the qualitative character, because the values of the coefficients of thermal and field diffusion of sodium and silver ions, presented in literature, are published as the approximate ones, and strongly depend upon the specific glass composition. In addition, the calculation did not took into account the arise in the glass of the opposite directed electric field, related to the negative volume charge, produced by the non-moving negative ions of oxygen and halides.

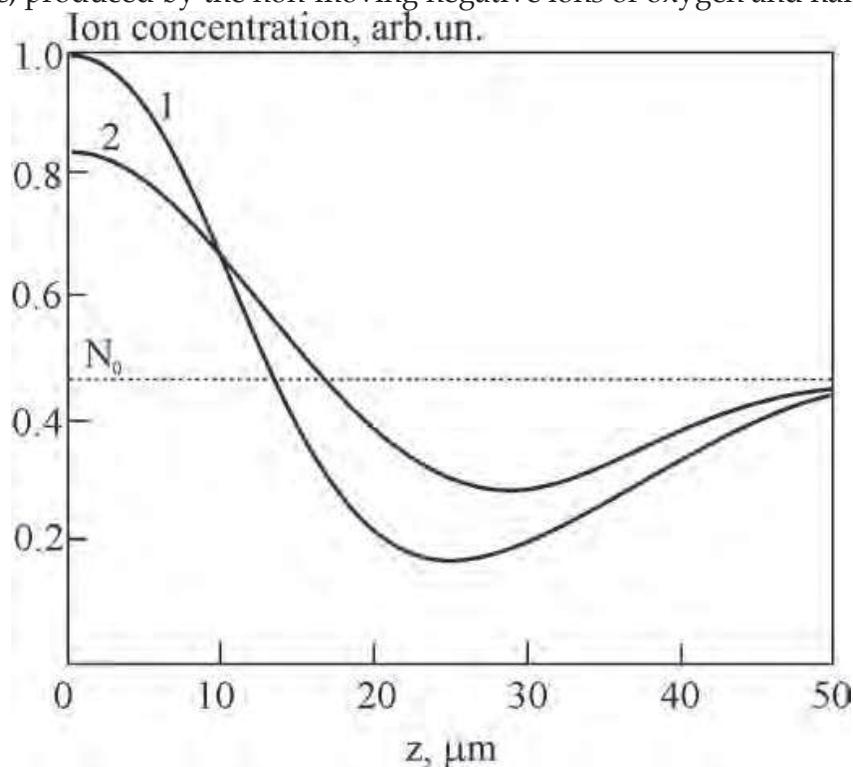


Fig. 16. Distribution of ion concentration after the field diffusion. $E_0 = 20$ keV. $t = 1000$ s. 1 - Na^+ ; 2 - Ag^+ . N_0 - initial concentration of ions

One can see from the Figure that the presence of the negative volume charge nearby the glass surface leads to spatial redistribution of sodium and silver ions - nearby the glass surface is formed the region with the high ions' concentration and in the depth - the range with the reduced concentration. Field diffusion increases significantly the concentration of silver ions and atoms in the surface layer of the glass. This is an explanation of the high concentration of silver nanoparticles nearby the surface which is observed in the experiment. Redistribution of silver and sodium ions leads to modification of glass chemical combination in the surface layer and produces the significant mechanical stresses. These two factors can be the reason of silver nanoparticles distribution in thin layers. Other possible reason of layered structures production can be the electric field arising in the glass between

the non-moving negative ions and positive ions, which have moved towards the glass surface. When the tension of this field in the glass layer becomes equal to tension of the field, produced by the volume charge of electrons, the diffusion of positive ions in this layer is stopped, but it continues in the gap between this layer and glass surface. At some moment of time the compensating field is produced already at this gap, stopping thus the diffusion etc.

So one can outline the following special features of silver nanoparticles formation in glass under the electron irradiation and the factors, influencing onto this process:

1. The processes of silver ions reduction and silver atoms ionization by electron beam;
2. Formation of volume charge and of electric field with high tension;
3. The processes of field diffusion, increasing the concentration of silver and sodium ions nearby the glass surface;
4. Modification of chemical composition of the glass in its surface layer;
5. Producing the mechanical tensions.

Summarizing one can outline the conclusion that formation of silver nanoparticles in PS glasses by electron irradiation is a prospective method of formation the nano-size metallic structures on the glass surface and nearby it for nanoplasmonics and integrated optics purposes. Easy combining of this method with the electron lithography technology makes it possible to create on the glass the metallic elements of complicated configuration, which can be used for metamaterials production. At the same time the processes, which take place during electron irradiation and consequent thermal processing are still not investigated in details and require further studies.

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