

CONDENSED-MATTER SPECTROSCOPY

Coloring of Silica Glass with Silver Nanoparticles

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Abstract—The possibility of doping of surface layers of optical fused silica with silver nanogranules upon heating of a thin Ag film on the silica surface by a CO₂ laser beam ($P \approx 30$ W, $\lambda = 10.6$ μm) is established. The effect of exposure time on the doped layer structure has been investigated. The absorption band of the colloidal solution of Ag in silica has been studied. It is shown that this band is homogeneously broadened and its peak (at 420 nm) corresponds to the small volume filling factor ($q < 0.1$) at an average granule radius of about 3 nm. Based on the measurements of the radial distributions of the reflectance and refractive index over the doped region at $\lambda = 633$ nm, it is revealed that the doped layer is an area-irregular asymmetric step waveguide.

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INTRODUCTION

The technique of coloring dielectrics by introducing very small metal particles into them has been known for a very long time. However, the interest in this problem remains in view of the development of nonlinear optics, waveguide optics, and optics of nanostructures [1, 2]. The studies published approximately before 1995 and devoted to optical properties of metal clusters were reviewed in monograph [2]. In particular, it was noted in [2] that implantation of clusters into fused silica is a fairly difficult problem. In this review, the data from different studies were summarized, which indicate the possibility of implanting Ag particles in fused silica by combined vacuum deposition of metal and quartz [3] and no other doping techniques were mentioned. In [1], ion implantation was used to dope silicate glass with silver; however, according to the noted value of the refractive index ($n = 1.5$), this glass is not optical fused silica. Recently, much attention has been given to study of the clusters that are chemically implanted (with subsequent annealing) into specially prepared porous silica with pores about 10 nm in diameter [4]. In this study, we show that the surface layer of fused silica can be doped using irradiation by a vacuum-deposited thin Ag film on silica by a CO₂ laser beam.

EXPERIMENTAL

We used polished plane-parallel KU silica plates [5, 6] with a thickness of 2 mm and area of 10 cm². A thin (≈ 10 nm) Ag film was deposited in vacuum (5×10^{-5} Torr) on the surface of a cold plate. A film of such thickness was obtained upon complete evaporation of 8 mg pure Ag from a planar molybdenum evaporator located at a distance of 15 cm from the evaporator to the

substrate center. Then, the film thickness was measured by the interference method of lines of equal chromatic order [7]. Electron microscopy analysis shows that films of such thickness are not continuous but have an island structure [8].

The plate with an Ag film was then irradiated in air from the film side by a Gaussian beam of an ILGN-704 cw CO₂ laser ($\lambda = 10.6$ μm , $P \approx 30$ W, the effective beam diameter about 3–4 mm). Preliminary investigation of the thermal action of such a beam on absorbing media showed that it can heat surfaces of different samples to 900–1200°C.

The temperature of a heated surface can be estimated, first of all, from the luminescence brightness of the irradiated area and by measuring the luminous temperature with a pyrometer. The absorption coefficient α of fused silica at $\lambda = 10.6$ μm is ≈ 400 cm⁻¹ [9]; the beam penetration depth $\delta = \alpha^{-1} \approx 25$ μm is much smaller than the plate thickness and the beam is completely absorbed in it. However, the plate heating due to the beam absorption does not lead to visible luminescence of the irradiated region since the emissive power of silica is low in the visible spectral range. The temperature of the rear plate surface ($T \approx 600^\circ\text{C}$) was measured by a Chromel–Alumel thermocouple. One might predict that the front surface is heated to $T \approx 1000^\circ\text{C}$. Then, assuming that T linearly decreases along the beam axis z and the plate thickness $\Delta z = 2$ mm, we find that the temperature gradient is fairly high: $dT/dz \approx 200$ K/mm.

In the first stage of irradiation of the plate with an Ag film, significant changes in the film are observed. It can be seen in transmitted white light that, in the ring zone surrounding the beam, the film is rapidly colored yellow; coloring propagates in the radial direction far from

the beam center. This coloring is related to the transformations in the film structure caused by thermal diffusion processes. Upon heating, the film on the surface acquires a structure of a two-dimensional colloid and absorbs light through the known mechanism of plasma resonance [10].

After about a minute, luminescence arises in the irradiated region, which rapidly acquires an almost white color. Pyrometer measurements showed that the color temperature is about 960°C in this case. Since the true temperature is somewhat higher than the color temperature, the film is heated above the melting temperature of bulk silver ($T_m \approx 960.8^\circ\text{C}$). It has been known for a long time from measurements in the visible spectral range that island Ag films with a thickness of about 10 nm have large absorptance (30–35%, [10]). Apparently, this is the reason for the bright thermal luminescence of a film heated to high temperatures. Further exposure leads to gradual disappearance of luminescence in the central irradiation zone, and the luminous zone turns into a slowly expanding ring. At a long exposure, the luminescence in the central zone completely disappears, and the surrounding luminous ring reaches the maximum (dependent on the exposure) diameter.

For further investigations, we used the samples irradiated to the stage of appearance of luminescence in the central zone. After irradiation, a sample was immersed in a sulfuric acid solution to remove Ag from the silica surface. The silver that penetrated into the quartz is protected from the action of the acid and its state remains invariable for an arbitrarily long time (under normal conditions). The doped region is about 3–4 mm in diameter and has a yellow color upon observation in transmitted white light. In reflected light, interference coloring, similar to that of thin films, can be seen. Different colors indicate nonuniform distribution of Ag over the area and depth of the doped region. Figure 1 shows a reflected light photograph of the (a) doped region in the central irradiation zone and (b) the doped ring zone, which is obtained at a long exposure. A series of experiments showed that, despite the Gaussian intensity distribution in the CO₂ laser beam, the coloring of the doped region is not concentric. The centers of rings of the same color do not coincide and rings decompose into arcs. In black and white photographs, nonuniform coloring manifests itself as nonuniform blackening. A possible reason for nonuniform coloring is fluctuations in the azimuthal dependence of the transverse gradient $\nabla T(x, y)$.

All further investigations were performed with the sample shown in Fig. 1a. The doped surface was first studied by transmission electron microscopy. To this end, we prepared a replica of the surface after its shadowing with an ultrathin gold film deposited in vacuum at an angle of 10° to the surface. The image obtained (Fig. 2) shows that there is a very fine chaotic relief on the doped surface. Spherical protrusions have an aver-

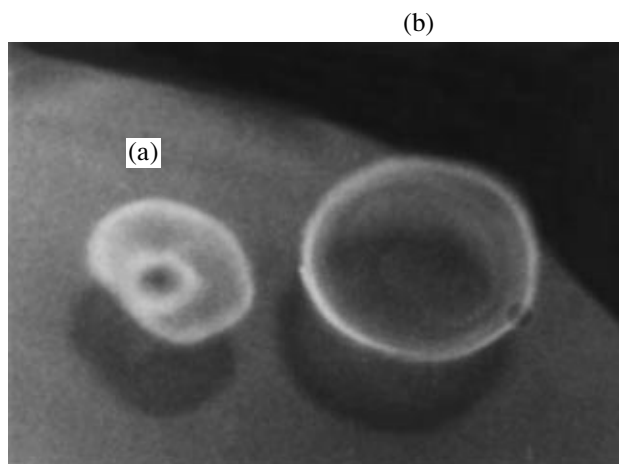


Fig. 1. Photographs of the doped regions in reflected white light: (a) irradiation by a CO₂ laser beam was interrupted in the white luminescence stage (nonuniform black and white contrast is related to the difference in the interference coloring of this doped region) and (b) long laser beam exposure with the formation of a ring. Shadow from the doped regions can be seen on the rear side of the silica plate.

age height of about 5 nm. The average distance between the relief elements is ≈ 100 nm.

Then, we investigated the optical properties of the doped region: the radial distributions of the reflectance and the refractive index and the absorption spectrum.

The reflectance R under normal incidence was measured according to the scheme shown in Fig. 3 with the use of a focused Gaussian He–Ne laser beam ($\lambda = 633$ nm) with a waist in the focus of about 30 μm . The sample on a movable holder was displaced along the x axis passing through the center of the doped region. Values of $R(x)$ were measured with a step $\Delta x = 0.2$ mm. Due to the slight tapering of silica plate, the narrow laser beam was split into two beams after reflection from two boundaries. This circumstance made it possible to measure $R(x)$ only for the doped surface layer. The values of $R(x)$ were calculated by the formula

$$R(x) = 0.035 i(x)/i_0, \quad (1)$$

where $i(x)$ is a signal of a photoelectron multiplier from the doped region, i_0 is the signal from a pure surface, and 0.035 is the reflectance of a pure surface at $\lambda = 633$ nm. The dependence $R(x)$ is shown by a dashed line in Fig. 4. The beam from the doped region is brighter but it does not have any spatial distortions, except for a very weak scattering halo. This pattern indicates that there are no significant violations of the polished surface within the doped region.

The refractive index n was measured according to the technique described in [11] (Fig. 3). A sample was prepared as follows: a thin (≈ 30 nm) AgCl film and an Ag film with a thickness of ≈ 7 nm were subsequently

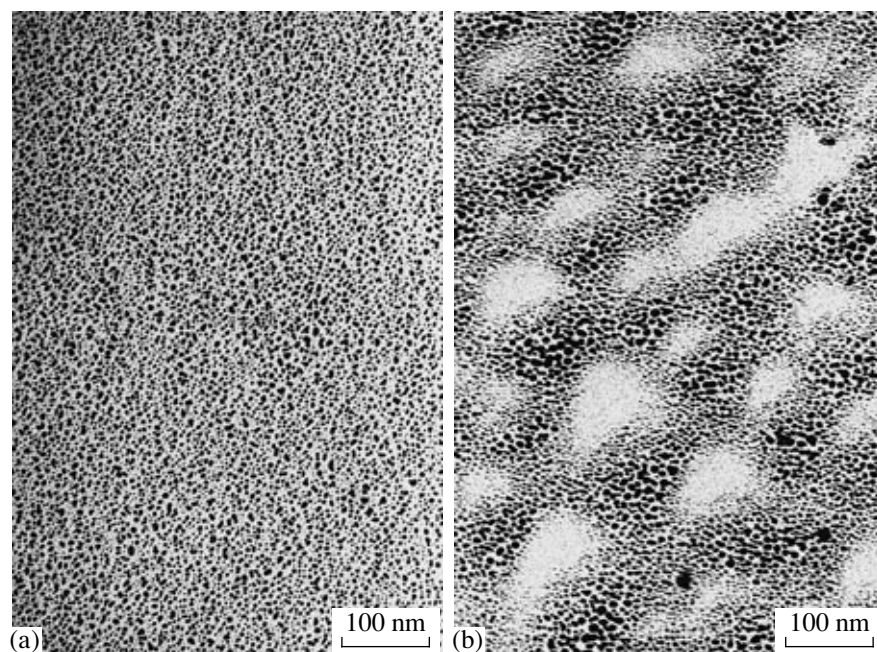


Fig. 2. Electron microscopy images of the silica surface: (a) undoped and (b) doped regions.

deposited on the sample surface in vacuum; then the sample was installed on a goniometer and irradiated with a focused s -polarized beam. As a result of scattering, the beam excites a waveguide TE_0 mode in the photosensitive AgCl–Ag film and, as will be shown below, in the doped layer. This mode induces a diffraction grating of poor quality in the photolayer. Diffraction from the grating into the order $m = -1$ results in a narrow

fringe on a screen installed parallel to the polarization vector \mathbf{E} of the beam. At the thickness of the AgCl–Ag film smaller than the cutoff thickness of the TE_0 mode (45 nm), measurement of the grating period yields the refractive index of the substrate [11]. In measurements, the angle of incidence φ of the beam is varied until the autocollimation condition is satisfied. In this case,

$$n = 3 \sin \varphi. \quad (2)$$

At the error $\Delta\varphi = \pm 0.1^\circ$, the error in n is ± 0.005 . Measurements of $n(x)$ were performed in almost the same direction x as the measurements of $R(x)$; the results are shown in Fig. 4 (curve 1).

Finally, the absorption spectrum was measured in the wavelength range $\lambda = 270\text{--}620$ nm (Fig. 5). The measuring beam of the spectrophotometer was limited by a diaphragm so as to make the beam diameter smaller than the doped region diameter. Measurements were performed with respect to a pure silica plate.

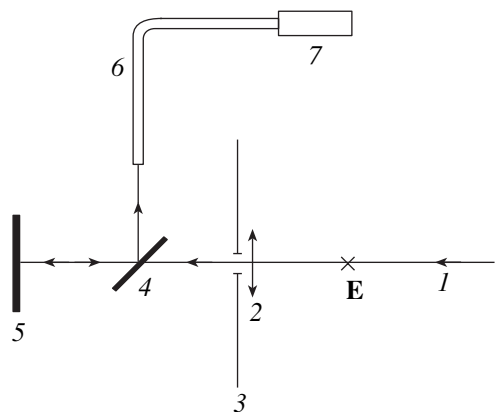


Fig. 3. Schematic diagram of the setup for measuring the optical characteristics of doped samples: (1) He–Ne laser beam ($\lambda = 633$ nm); (E) direction of linear beam polarization, perpendicular to the plane of the figure, (2) focusing lens ($F = 9.4$ cm), (3) screen with a diaphragm for beam limiting, (4) beam-splitting glass plate (installed to measure $R(x)$), (5) sample on a movable holder and goniometer; (6, 7) optical fiber and photoelectron multiplier (used to measure $R(x)$).

RESULTS AND DISCUSSION

Let us consider the doping mechanism. Apparently, when the surface temperature reaches the value of T_m , emission of electrons into silica and their trapping occur. Molten particles are positively charged, and an electrostatic field is induced between them and traps, providing detachment of Ag^+ ions and their transport to traps. This process repeats many times and, as a result, leads to precipitation of Ag granules in the surface layer of silica. Note that the granule precipitation is facili-

tated by the porosity of fused silica: the ratio of its density to the density of crystalline SiO_2 is 0.83.

The expected doping process occurs in the initial stage, when the temperature in the central zone reaches the melting point. Furthermore, luminescence at the center of the irradiated region disappears, the dark region gradually expands, and the luminescing region acquires the shape of a ring whose diameter increases with a simultaneous decrease in its width. Apparently, such transformations are related to the disappearance of Ag from the silica surface in the central zone and gradual increase in T on the surface in the directions transverse to beam direction. This large-scale doping inhomogeneity, dependent on the exposure time, corresponds to a Gaussian beam; however, thermal processes lead also to additional smaller inhomogeneities (Figs. 1a, 4).

The surface microrelief (Fig. 2) revealed by electron microscopy is due to doping. Formation of Ag particles should increase the volume and induce internal stress in the silica. If a particle is located directly under the surface, a convexity should arise on the surface, whose size and shape are related to the size and shape of the particle. Since some microrelief elements have a spherical shape, we can suggest that they are formed by spherical granules with a radius approximately equal to the height of the relief element (≈ 5 nm).

Optical measurements can yield information on the doped layer structure. The absorption spectrum (Fig. 5) is shown in the energy range from 2 to 4.6 eV, which contains not only the resonant band of Ag particles but also the intrinsic absorption edge of silver. It can be seen that the absorption band peaks at $\hbar\omega_m = 2.95$ eV ($\lambda_m = 420$ nm) and has the half-width $\gamma = 0.47$ eV. The band is almost symmetric and the profile is close to Lorentzian:

$$D = D_m \frac{\gamma^2}{4[\hbar^2(\omega - \omega_m)^2 + \gamma^2/4]}, \quad (3)$$

where $D = \alpha h$ is the optical density, α is the absorption coefficient, h is the thickness of the doped layer, and $D_m = 1.49$ is the maximum optical density.

The Lorentzian profile indicates homogeneous broadening of the absorption band. Obviously, inhomogeneous broadening also contributes to the bandwidth. However, this contribution can be estimated from the filling number q . Calculation by the Maxwell–Garnet formula shows that, at a change in the filling number in the range $0 \leq q \leq 0.15$, the band peak shift is only 0.05 eV; i.e., the inhomogeneous broadening is an order of magnitude smaller than the homogeneous broadening (0.47 eV). A homogeneously broadened band can be due to very small isolated granules of almost identical size. In this case, the frequency ω_m should obey the Fröhlich formula [12]; i.e., $\omega_m = \omega_F$, where

$$\omega_F = \omega_p / (\epsilon_M + 2\epsilon_0)^{1/2}. \quad (4)$$

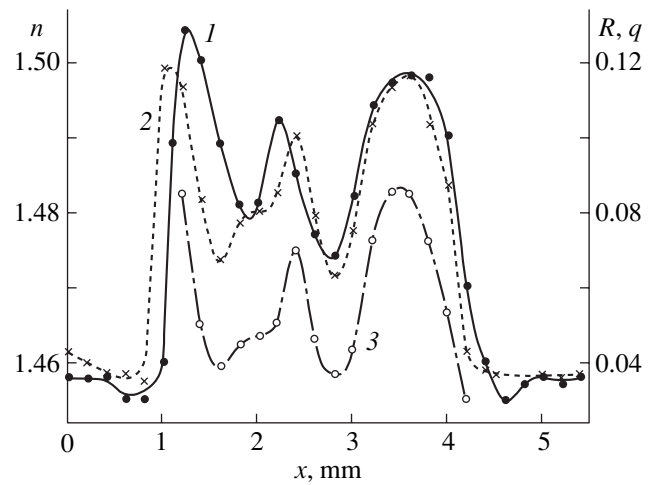


Fig. 4. Dependences (1) $n(x)$, (2) $R(x)$, and (3) $q(x)$.

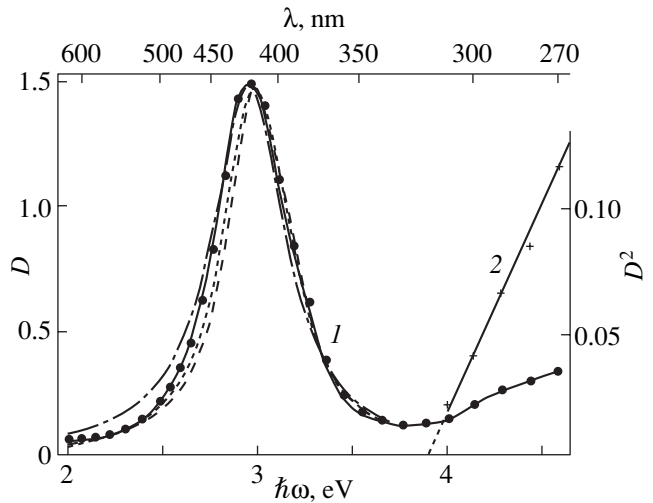


Fig. 5. (1) Absorption spectrum and (2) the dependence $D^2(\hbar\omega)$. Circles and solid lines show the experimental data. The dot-and-dash curve is the Lorentzian profile. The long- and short dashed curves show the profiles calculated by the Maxwell–Garnet formula at $q = 0.05$ and 0.1 , respectively.

The exact value of the plasmon frequency ω_p for Ag is unknown. According to the data of different researchers, the plasmon energy lies in the range $\hbar\omega_p = 8.6$ – 9.1 eV [13]. To calculate $\hbar\omega_F$, we will take the average value $\hbar\omega_p = 8.85$ eV. The dielectric constant ϵ_M of the metal is related to interband transitions in Ag. According to the data of [13] $\epsilon_M = 4.5$ for the energy $\hbar\omega_m$. The permittivity of silica for the same energy is $\epsilon_0 = n_0^2 = 2.15$. Calculation according to (4) for these data yields $\hbar\omega_F = 2.98$ eV, which is in good agreement with the value of 2.95 eV for the experimentally determined band peak position.

The threshold energy is known for silver beginning with which absorption of light is due to direct interband transitions. The measurements we performed cover the interband absorption edge. Direct transitions suggest a linear dependence $D^2(\hbar\omega)$, which is actually observed (Fig. 5). Intersection of the straight line with the energy axis gives the known value $\hbar\omega_{th} \approx 3.9$ eV [2]. The coincidence of the experimental value of $\hbar\omega_{th}$ with the threshold energy for bulk silver indicates the absence of quantum size effects despite the small size of silver particles.

The granules precipitated in the silica should form a three-dimensional colloid. Therefore, to describe the band shape, it is also expedient to apply the well-known Maxwell–Garnet formula. This formula relates the effective permittivity ϵ_{ef} of the bulk colloid with the complex permittivity ϵ of the metal in granules [2, 10]:

$$(\epsilon_{ef} - \epsilon_0)/(\epsilon_{ef} + 2\epsilon_0) = q(\epsilon - \epsilon_0)/(\epsilon + 2\epsilon_0), \quad (5)$$

where $q = NV$ is the average volume filling factor of the dielectric with granules and N and V are, respectively, the concentration and average volume of granules. The absorption band is almost entirely beyond the interband absorption region (Fig. 5). Therefore, the frequency dependence $\epsilon = \epsilon_1 - i\epsilon_2$ can be described by the Drude–Lorentz formula:

$$\begin{aligned} \epsilon_1 &= \epsilon_M(\omega) - \omega_p^2/(\omega^2 + \nu^2), \\ \epsilon_2 &= \omega_p^2\nu/(\omega(\omega^2 + \nu^2)). \end{aligned} \quad (6)$$

To calculate ϵ_1 and ϵ_2 , we used the above-mentioned value of $\hbar\omega_p$ and took into account the dispersion of $\epsilon_M(\omega)$ since, in the measured region, the value of $\epsilon_M(\omega)$ ranges from 4.0 at $\hbar\omega = 2.00$ eV to 5.3 at $\hbar\omega = 3.70$ eV [13]. Expression (6) contains the electron scattering frequency ν , which significantly differs from the corresponding bulk value in very small granules [12]. Taking into account that electron scattering occurs mainly at the boundaries of a granule of radius a , ν can be written as

$$\nu = \nu_0 + \kappa v_F/a, \quad (7)$$

where κ is a coefficient that depends on the granule shape and is close to unity, v_F is the velocity of electrons on the Fermi surface, and ν_0 is the scattering frequency in silver bulk (according to the data of [14], $\nu_F = 2.3 \times 10^8$ cm s⁻¹ and $\nu_0 \sim 10^{13}$ s⁻¹). Since ν determines the broadening of the colloid absorption band, we can assume that $\nu = \gamma/\hbar = 7.14 \times 10^{14}$ s⁻¹. At these values and $\kappa = 1$, we derive from (7) the average granule radius $a \approx 3$ nm. Note that good agreement between formula (5) and the reflection and absorption spectra of spherical granules with $a \leq 10$ nm was found in [15]; i.e., in the case under consideration, application of (5) is quite justified.

Formulas (5) and (6) were used to derive expressions for ϵ_{1ef} and ϵ_{2ef} and calculate the optical constants n_{ef} and κ_{ef} and the absorption coefficient $\alpha_{ef} = (2\omega/c)\kappa_{ef}$, which determines the optical density $D = \alpha_{ef}h$. The values of α_{ef} were calculated for $q = 0.05$ and 0.1 . In both cases, maxima of $\alpha_{ef}(\omega)$ were obtained at $\hbar\omega = 2.98$ eV, which coincides with the Fröhlich energy calculated above and (within the calculation and measurement errors) the experimental value 2.95 eV.

In comparison of the calculated and experimental data, it was assumed that $D_{max} = \alpha_{max,1}h_1 = \alpha_{max,2}h_2$. Here, the subscripts 1 and 2 refer to $q = 0.05$ and 0.1 , respectively, and $h_1 = 96.5$ nm and $h_2 = h_1/2$ are the thicknesses of the surface doped layers for these values of q . The assumption that D_{max} is an invariant independent of q is justified by the fact that the diffusion flux of electrons and ions at the center of the irradiated region is directed mainly along the normal to the sample surface. It can be seen in Fig. 5 that the calculated dependences $D_1(\omega)$ and $D_2(\omega)$ almost merge, which is indicative of small contribution of the inhomogeneous broadening related to the dispersion of the filling number q at $q \leq 0.1$.

The calculated values of n_{ef} at $\omega < \omega_m$ are larger than n_0 of silica. This fact indicates that, in the transparency region ($\hbar\omega \leq 2$ eV), the surface layer containing Ag granules is a planar asymmetric waveguide, irregular in thickness and mode indices. At first glance, with allowance for the diffusion of electrons and Ag⁺ ions, the waveguide should be a gradient with a change in n_{ef} from the maximum value at $z = 0$ to n_0 at large z (the z axis is directed along the normal into the silica bulk). However, the presence of interference colors on the irradiated area contradicts this suggestion. In addition, it is inconsistent with the data on the radial reflectance distribution (Fig. 4). For a gradient waveguide of this type in the transparency region, R is determined as [16]

$$R = r_1 = \left[\frac{n_{ef}(z=0) - 1}{n_{ef}(z=0) + 1} \right]^2. \quad (8)$$

Calculation of r_1 for $\lambda = 633$ nm at $q = 0.1$ gives $r_1 = 0.08$, whereas, on the experimental dependence of R (Fig. 4), $R > 0.1$ for a number of points. For this reason, we suggested that the waveguide is not a gradient but has a step form with a narrow boundary between the doped layer and pure silica. Note that this form of a waveguide is known for the case of photodiffusion doping of As₂S₃ films with silver [17].

At a step change in n_{ef} at the rear boundary ($n_{ef}(z = h) = n_{ef}(z = 0)$), the reflectance should obey the Airy formula. On the assumption of weak absorption ($n_{ef} \gg \kappa_{ef}$), this formula can be written as

$$R = \frac{r_1 + r_2\eta^2 - 2\sqrt{r_1r_2}\eta \cos 2\delta}{1 + r_1r_2\eta^2 - 2\sqrt{r_1r_2}\eta \cos 2\delta}, \quad (9)$$

where $r_2 = (n_{\text{ef}} - n_0)^2 / (n_{\text{ef}} + n_0)^2$, $\delta = (\omega/c)n_{\text{ef}}h$, and $\eta = \exp(-\alpha_{\text{ef}}h)$.

Large changes in $R(x)$ (Fig. 4) indicate significant changes in n_{ef} , q , and h within the doped region. Since the values of R were measured using a focused beam with a small waist ($\approx 30 \mu\text{m}$), we can assume that each value of x corresponds to a plane-parallel layer of very small area, which satisfies formula (9). This formula was used to solve the inverse problem: the values of $q(x)$ and $h(x)$ were found by matching the values of R calculated by formula (9) with the measured values. To this end, according to (5) and (6), we calculated n for $\lambda = 633 \text{ nm}$ and q in the range from 0.03 to 0.1. Applying the previously used relation $\kappa_{\text{ef}}h = \text{const}$ at $h = 96.5 \text{ nm}$, which was previously found at $q = 0.05$ from the value of D_{max} at $\lambda = 420 \text{ nm}$, we determined the radial distribution $q(x)$ (Fig. 4). It can be seen that, within the doped region, the factor q changes from 0.04 to 0.085 with respect to the average value $q \approx 0.06$. This range is in agreement with the previous estimate $q = 0.05\text{--}0.1$ made in the analysis of the resonant absorption band.

Measurements of the radial distribution of the refractive index $n(x)$ (Fig. 4) by the method proposed in [11] showed that n irregularly changes in the range 1.473–1.503 within the doped region and coincides with the value $n = 1.457$ for silica beyond this region. The values of $n(x)$ are much smaller than the calculated values of n_{ef} : with a change in q from 0.03 to 0.1, n changes from 1.56 to 1.8. Therefore, we assumed that, in the case under consideration, the method proposed in [11] gives, not the value of n_{ef} , but the effective refractive index n_{TE} for the waveguide TE_0 mode. To verify this suggestion, we used the model of a two-layer step waveguide consisting of an $\text{AgCl}\text{--Ag}$ film with $n_1 = 2.06$ ($\lambda = 633 \text{ nm}$) and $h_1 = 30 \text{ nm}$ and a doped layer silica with $n_2 \equiv n_{\text{ef}}$ and the thickness h_2 located on a silica substrate. The dispersion equation for this case [18] can be written as

$$\tan(kh_2p_2) = \frac{p_1p_2(p_0 + p_3) + p_2(p_3p_0 - p_1^2)\tan(kh_1p_1)}{p_1(p_2^2 - p_3p_0) + (p_3p_1^2 + p_2^2p_0)\tan(kh_1p_1)}, \quad (10)$$

where $k = 2\pi/\lambda$, $p_0 = (n_{\text{TE}}^2 - 1)^{1/2}$, $p_1 = (n_1^2 - n_{\text{TE}}^2)^{1/2}$, $p_2 = (n_2^2 - n_{\text{TE}}^2)^{1/2}$, $p_3 = (n_{\text{TE}}^2 - n_3^2)^{1/2}$, and $n_3 \equiv n_0 = 1.457$ ($n_0 = 1.457$ is the silica refractive index). For example, using (10), we calculated n_{TE} for the average value $q = 0.06$ using the previously calculated values $n_2 \equiv n_{\text{ef}} = 1.673$ and $h_2 = 80 \text{ nm}$, as well as the values of h_1 , n_1 , and n_3 . The calculation gave $n_{\text{TE}} = 1.472$. For the central part of the doped region, this value, in comparison with n_{ef} , is in much better agreement with the average experimental value $\bar{n} = 1.487$ at $q = 0.06$ (Fig. 4).

This example is an additional proof that the doped region is a step waveguide.

CONCLUSIONS

We found the possibility of doping thin ($\approx 50\text{--}100 \text{ nm}$) surface layers of optical silica glass with colloidal Ag (granule size 3 nm) by heating a thin Ag film on the silica surface by a CO_2 laser beam ($\lambda = 10.6 \mu\text{m}$, $P \approx 30 \text{ W}$). It is shown that the doped layer is an area-irregular step waveguide for red and near-infrared spectral ranges.

Note that the method considered here is valid specifically for fused silica since this material has a high melting temperature (1773°C) and a high absorption coefficient (at $\lambda = 10.6 \mu\text{m}$); is heat-resistant upon local heating by a laser beam; and, finally, has a porous structure allowing formation of small Ag granules in such a matrix. With all that, the following conditions are very important: the initial Ag film on the surface must be thin, have an island structure, and be heated by a beam to the melting temperature.

Doped layers can be used for stable labeling and coloring of fused silica particles, fabricating waveguide paths, imprinting into silica holographic and another structures formed previously in a thin silver film [19] on its surface, etc.

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