Optical properties modification induced by laser radiation in noble-metal-doped glasses

N Nedyalkov¹,5, N E Stankova¹, M E Koleva¹, R Nikov¹, P Atanasov¹, M Grozeva², E Iordanova², G Yankov², L Aleksandrov³, R Iordanova³ and D Karashanova⁴

¹E. Djakov Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
²G. Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
³Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria
⁴Acad. J. Malinowski Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 109, 1113 Sofia, Bulgaria

E-mail: nned@ie.bas.bg

Abstract. We present results on laser-induced color changes in gold- and silver-doped glass. The doped borosilicate glass was prepared by conventional melt quenching. The study was focused on the change of the optical properties after irradiation of the glass by femtosecond laser pulses. Under certain conditions, the laser radiation induces defects associated with formation of color centers in the material. We studied this process in a broad range of laser radiation wavelengths – from UV to IR, and observed changes in the color of the irradiated areas after annealing of the processed glass samples, the color being red for the gold-doped glass red and yellow for the silver-doped glass. The structural and morphological analyses performed indicated that this effect is related to formation of metal nanoparticles inside the material. The results obtained show that femtosecond laser processing of noble-metal-doped glasses can be used for fabrication of 3D-nanoparticles systems in transparent materials with application as novel optical components.

1. Introduction

The research interest in nanocomposites has been continuously growing in recent years. These complex materials composed of nanostructures embedded into a host matrix express novel optical, mechanical and electric properties that open new possibilities for development of advanced devices in the field of sensors, biophotonics and MEMS, and contribute to enhancing the efficiency of light harvesting, battery performance, catalytic reactions [1-3]. The composite materials consisting of noble-metal nanoparticles are of great interest due to the specific optical properties that they express. The interaction of the electromagnetic field with the nanoparticles under the condition of resonance of the incident field frequency with that of the plasmon is characterized by a huge increase of the far-field extinction coefficient, which can reach orders of magnitude [4]. Thus, structures composed by

⁵To whom any correspondence should be addressed.
nanoparticles incorporated in a host material can present novel, more complex properties. The experimental and theoretical studies conducted in this field have shown that the plasmon frequency can be continuously tuned in a wide range by changing the particle’s parameters and the conditions of interaction with the incident radiation. In addition to the optical characteristics of the metal nanoparticles that can be observed in the far-field zone, the properties of the electromagnetic field in the nanoparticle’s near field zone also attract significant interest. This interest is based on some basic properties that are not expressed at distances larger than approximately the wavelength of the incident radiation. In this zone, the intensity of the electromagnetic field is enhanced and, under optimal conditions for plasmon excitation, it can be several orders of magnitude higher than the incident one [5]. The specific properties of the electromagnetic field in the near-field zone are the basis of effects observed in composite materials consisting of noble-metal nanoparticles, such as a large increase of the third-order nonlinear optical susceptibility in oxide/Au nanoparticles composites, an enhancement of the photoluminescence signal in ZnO/Ag, ability of modifying the conductivity in some semiconductors by embedding particles and varying their concentration [6-8]. The complex study and development of reliable applications based on such materials are still hampered by the lack of efficient fabrication techniques. The chemical and physical bottom-up methods developed so far are still expensive and slow and do not offer efficient manipulation of the composite material morphology in three dimensions.

In this paper, we discuss a method for real 3D fabrication of noble-metal nanoparticles in glass. It is based on femtosecond-laser reduction of noble metal ions to atoms that form nanoparticles upon subsequent annealing. The method has been demonstrated for different glass types containing silver and gold ions when 800-nm ultrashort laser pulses were used [9-11]. Processing by irradiation at other wavelengths has not been considered so far for this application. Furthermore, the method has rarely been applied to fabricating gold particles in borosilicate glass. In this study, we used irradiation at four wavelengths, namely 266 nm, 355 nm, 500 nm and 800 nm, in order to follow the influence of this parameter to the glass response and to the formation of nanoparticles.

2. Experimental

The samples studied were made of borosilicate glass fabricated by melt quenching with composition 50% SiO₂, 20% Al₂O₃, 20%B₂O₃, 5% CaO, 2% Li₂O, 3% MgO (in wt %). Gold and silver ions were included as HAuCl₄·3H₂O or AgNO₃ added to the initial mixture. The mixed material was melted in a Pt crucible and kept at a temperature of 1450 °C for three hours. Using different amounts of the noble-metal donor compounds, glasses with gold concentration of 0.015 and 1 % and silver of 1% were prepared and used in the experiments. The irradiation of the samples was performed by a Ti:Sapphire femtosecond laser system (Spectra Physics) that includes an optical parametric amplifier and emits at a central wavelength of 800 nm with a pulse duration of 35 fs and 1-kHz repetition rate. The optical parametric amplifier covers the wavelength range from 240 nm to 2600 nm. In the present experiments we selected the wavelengths of 266 nm, 355 nm, 500 nm and 800 nm and focused the laser beam by a 20 cm-lens. The transmission spectra of the samples in the range 200 – 1000 nm were taken by an HR 4000 Ocean Optics spectrometer. The thermal annealing of the glass samples was performed in a standard oven with controllable heating parameters. The structural characteristics of the samples were visualized by a JEM 2100 JOEL TEM, while the optical images of the processed areas were obtained by an Optica B-150 optical microscope.

3. Results and discussion

The glass samples fabricated were cut in pieces with a thickness of 2 mm and polished. The material was transparent and colorless. Figure 1 shows the transmission spectra of the samples considered in this study. It is seen that the glasses are opaque at wavelengths shorter than approximately 300 nm; i.e., the difference in their composition concerning the content of gold and silver affected negligibly their optical properties. The laser wavelengths used were chosen to represent different cases of laser radiation interaction with the investigated material. Thus, the wavelength of 266 nm is in the range of
high absorption of the material; 355 nm is the wavelength where the glass transmits about 50% of the incident radiation; at the wavelengths of 500 nm and 800 nm the glass samples are transparent. Further, the wavelength of 500 nm falls in the absorption band corresponding to the typical defects (color centers) induced in silicate glasses by irradiation [12], while the wavelength of 800 nm, being typical for ultrashort laser systems, was used for comparison with other works.

The irradiation by femtosecond laser pulses induced clear brown coloring of the samples. Figure 2 shows the optical transmission spectra of glass with gold concentration of 0.015% after irradiation by 40 000 femtosecond laser pulses at the wavelengths of 266, 355, 500 and 800 nm. The laser fluences used were 1.5 J/cm², 1.8 J/cm², 1.8 J/cm², and 1.9 J/cm², respectively.

The transmission curves are plotted with respect to the transmission of a non-irradiated sample. One can distinguish two pronounced zones: the first one is at wavelengths lower than approximately 450 nm and a dip centered at about 500 nm. These regions can be attributed to the absorption of color centers formed in the sample and related to intrinsic oxygen-deficiency defects in a glass matrix [11, 12]. The lower-wavelength absorption can be associated with two types of defects – an unpaired electron in sp3 of a single silicon atom with an oxygen vacancy, and a hole trapped in an oxygen vacancy. The defects that absorb in the visible spectral range are related to non-bridging oxygen hole centers. A bond modification in B₂O₃, whose concentration in the samples is 20%, could also have a small contribution to the spectra. Defects induced in borate oxide have strong absorption in the visible range at about 590 nm [13]. The spectra presented in figure 2 indicate that the application of laser radiation at different wavelengths produces similar types of changes in the transmission spectra, i.e. formation of similar types of defects. In the case of 266 nm, the laser energy is absorbed in the surface layer due to the strong absorption. The color changes are also localized in the surface layer. At the other wavelengths, defects are formed when clear evidence of nonlinear interaction is seen. The color modification observed when the wavelength of 500 nm or 800 nm were used was accompanied by a spectral broadening of the laser pulses. Figure 3 presents the spectrum of the radiation (wavelength of 800 nm, fluence of 1.9 J/cm²) transmitted through the glass sample with a gold concentration of 0.015%. The spectral broadening is a complex phenomenon and could be the result of different mechanisms, as self-modulation, THz generation, or wave mixing [14]. The spectral broadening in the case of irradiation at 355 nm is barely seen due to the glass absorption in the shorter-wavelengths range. It should be mentioned that, under the conditions described, the brown-colored areas expanded throughout the entire sample thickness for the wavelengths of 355 nm, 500 nm and 800 nm.

Figure 4 shows the transmission spectra of glass samples with different compositions after irradiation by 40 000 laser pulses at the wavelength of 800 nm and fluence of 1.9 J/cm². The spectrum of the glass without inclusion of a noble metal is also shown (BS0). The appearance is seen of a dip at about 700 nm with the increase of the gold concentration from 0.015 to 1 %. The spectrum of the silver-containing glass differs from that of the gold-containing one, namely, a sharp decrease of the transmission is observed at wavelengths below approximately 520 nm. Extracting the transmission
spectrum of the glass without noble metal inclusion, one can find that this transmission reduction is due to a dip centered at about 400 nm. Its nature is not clear, but one may speculate that in this case the laser radiation induces the formation of Ag nanoparticles that have a plasmon absorption band at a wavelength of about 400 nm [4]. Further analyses are needed to clarify the validity of this proposition.

Figure 3. Spectrum of an 800-nm fs laser pulse transmitted through a glass sample with gold concentration of 0.015%. The laser fluence is 1.9 J/cm².

Figure 4. Transmission spectra of glass samples with different noble-metal concentration irradiated by 40 000 laser pulses at wavelength of 800 nm and laser fluence of 1.9 J/cm².

After irradiation, the samples were annealed. The optimal conditions were established by experiments performed at different temperatures in the range from 500 °C to 800 °C. After annealing for 30 min above 650 °C, the gold containing samples acquired a red coloration. Annealing of the same duration at temperatures below 550 °C did not induce any change in the sample color. Annealing the irradiated samples at a temperature of 600 °C resulted in the appearance of red color in the irradiated areas only, while the rest of the material remained colorless. Thus, a red coloring was observed only when the laser radiation induced the formation of defects, i.e., in the brown areas only. Figure 5 shows an optical microscope image of colored areas obtained by scanning the sample. The wavelength used was 500 nm, the sample contained gold at a concentration of 0.015%. The scanning conditions ensured the overlap of about 50 000 laser shots.

Figure 6 is a TEM image of the material in the colored area. It shows a part of a gold nanoparticle with a size of about 20 nm: i.e., the red color of the treated areas has to do with the formation of gold nanoparticles in the sample. Their optical properties, as defined by the plasmon resonance, give rise to the specific color of the area. Figure 7 shows the transmission spectra of areas irradiated at different wavelengths and annealed at 600 °C for 30 min. The laser fluences used were 1.5 J/cm², 1.8 J/cm², 1.8 J/cm², and 1.9 J/cm², for the wavelengths of 266 nm, 355 nm, 500 nm, and 800 nm, respectively.

Figure 5. Optical microscope image of area irradiated by laser radiation at λ = 500 nm and annealed at 600 °C for 30 min. The laser fluence is 1.5 J/cm².

Figure 6. TEM image of a gold nanoparticle in the area irradiated by laser radiation at λ = 500 nm and annealed at 600 °C for 30 min.
The spectrum of that glass sample containing Ag is also shown. In this case the irradiation was at 800 nm with a fluence of 1.9 J/cm².

The results indicate that in all cases of different wavelengths used for irradiation, a selective formation of nanoparticles can be achieved. The well-pronounced transmission dip is an evidence of the formation of nanoparticles possessing specific optical properties due to the plasmon resonance. The irradiation at 266 nm results in the appearance of areas containing nanoparticles on the surface of the sample, while for the other wavelengths such areas spread over the whole sample. However, using tight focusing, one can obtain a localized nanoparticles-containing area, whose position can be tuned in 3D. The clear correlation between the position of the color centers induced after laser irradiation and the areas containing nanoparticles after annealing suggest that laser processing is a necessary condition for nanoparticle formation. It has been proposed [10, 11] that the electrons released after laser irradiation may induce reduction of the noble-metal ions. The annealing process then provokes the coalescence of atoms into nanoparticles. We showed that the formation of defects and, subsequently, of nanoparticles does not depend significantly on the irradiation wavelength. In addition, we showed that the wavelength of the transmission dip could be tuned by varying the irradiation time and laser fluence, since the effect of irradiation at the different wavelengths used was similar. The ability of implementing the method at different wavelength opens a possibility of fabricating wavelength-dependent structures in glasses, such as ripples, that can be used as selective optical components.

4. Conclusions
A technique is presented for space-selective fabrication of noble metal nanoparticles inside glass samples. The method includes laser irradiation of ion-doped glass samples and subsequent annealing. The laser irradiation is performed by femtosecond laser pulses at different wavelengths – in the UV, VIS, and IR spectral range. Under certain conditions, the laser irradiation induces defect (color) centers in the glass samples. After annealing at 600 °C for 30 min, the color centers change their color from brown to red in the case of Au-doped glass, and to yellow for Ag-doped glass. The analysis performed indicates that this change is related to formation of nanoparticles, as their optical properties define the color observed. The process of nanoparticle formation can be realized at the different wavelengths used. Thus, the mechanism of laser absorption and the photon energy seem to play a minor role in the process when ultrashort pulses are used. It is found that the formation of color centers is the mark which indicates the possibility of formation of nanoparticles at the annealing stage. The method presented can be used for fabrication of 3D structures in glasses that may find applications in data storage, as optical components and sensors.

Acknowledgment
This work was supported by the Bulgarian National Science Fund under project DN 08/16.

References
[1] Petronella F, Truppi A, Ingrosso C, Placido T, Striccoli M, Curri M L, Agostiano A and Comparelli R 2017 Catalysis Today 281 85
[2] Zhan C, Yu G, Lu Y, Wang L, Wujick E and Wei S 2017 J. Mater. Chem. C 5 1569
[3] Beecroft L L and Ober C K 1997 Chem. Mater. 9 1302
[4] Noguez C 2007 J. Phys. Chem. C 111 3806
[5] Plech A, Leiderer P and Boneberg J 2008 Laser Photon. Rev. 2 1
[6] Hanemann Th and Szabó D V 2010 Materials 3 3468
[7] Koleva M E, Nedyalkov N N, Dikovska A Og, Atanasov P A, Avdeev G V, Shimizu H, Terakawa M, Obara M, Pallotti D, Orabona E, Maddalena P and Lettieri S 2014 JOAM 16 144
[8] Sasai J and Hirao K J 2001 Appl. Phys. B 89 4548
[9] Dai Y, Yu G, He M, Ma H, Yan X and Ma G 2011 Appl. Phys. B 103 663
[10] Almeida J M P, Tribuzi V, Fonseca R D, Otuka A J G, Ferreira P H D, Mastelaro V R, Brajato P, Hernandes A C, Dev A, Voss T, Correa D S and Mendonca C R 2013 Opt. Mater. 35 2643
[11] Hu X, Zhao Q, Jiang X, Zhu C and Qiu J 2006 Sol. State Commun. 138 43
[12] Salh R 2011 Defect related luminescence in silicon dioxide network: A Review in Crystalline Silicon - Properties and Uses Basu S ed (Rijeka Shanghai InTech) ISBN: 978-953-307-587-7
[13] Saka S 1970 Bull. Inst. Chem. Res. Kyoto Univ. 48 53
[14] Tan D, Sharafuddeen K N, Yue Y and Qiu J 2016 Progress in Mater. Sci. 76 154