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Optical properties modification of gold doped glass induced by nanosecond laser radiation and annealing

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In this work the effects of laser radiation and annealing process on the change of the optical properties of gold doped borosilicate glass are presented. The glass is fabricated by conventional melt quenching method as samples with three different concentrations of gold are produced. The laser irradiation is performed by a Nd:YAG system that generates nanosecond pulses at wavelengths of 1064, 532, 355, and 266 nm. The optical properties of the glass samples are studied on the basis of their transmission spectra in the UV- near IR spectral range. The results indicate that irradiation at wavelength of 266 nm induces color changes assigned to formation of defects (color centers). Annealing of the samples results in formation of red colored zones which positions correspond to the irradiated ones. The optical properties and TEM observation indicate that this effect is related to formation of gold nanoparticles. The optical spectra of the areas irradiated by laser pulses and annealed are studied for different processing parameters – pulse number, laser fluence, annealing temperature, annealing time, and the gold concentration in the glass. Processing parameters that ensure efficient tuning of the optical spectra are defined. The presented study can be a basis for a method for surface modification of glass samples that can lead to formation of nanoparticle composed layer with tunable optical properties for applications as novel optical elements.

1. Introduction

Composite materials that consist of noble metal nanoparticles are attractive object for present fundamental research and applications. The combination of the specific properties of nanoparticles and the host material may result in appearance of novel optical, mechanical and electric properties [1,2]. The noble metal nanoparticles exhibit unique optical properties due to efficient plasmon excitation in the near UV and visible spectral range. These result in an enormous increase of the extinction cross sections, an effect that found application in enhanced efficiency of photovoltaic elements, in biophotonics for development of imaging techniques, photothermal cancer cell therapy and enhanced emission performance [3–6]. The interaction of the noble metal nanoparticles with electromagnetic field at plasmon resonance conditions also is accompanied by a drastic enhancement of the near field intensity [7]. The phenomenon is of significant importance for development of different near field analytical and processing techniques and in high sensitive analysis as Surface Enhanced Raman Spectroscopy [8]. When nanoparticles are embedded into a matrix they may drastically influence its optical response. It is found that noble metal nanoparticles incorporated into glasses, polymers and oxides may induce modification of the nonlinear optical parameters, luminescence signal and higher sensitivity of the plasmon resonance wavelength to change of the environment properties [9–12].

The technique for fabrication of composite glasses that consists of noble metal nanoparticle is known from centuries. The presence of gold nanoparticles gives the ruby color of the famous dichroic Lycurgus cup and is used in color glass decoration of cathedrals in the 17th century [13,14]. Recently it was shown that laser radiation can induce a space selective reduction of noble metal ions in glasses, oxides and polymers that may be used for further

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formation of nanoparticles [15–17]. The method usually includes two steps – ultrashort laser treatment that is believed to result in noble metal ion reduction and subsequent annealing where the formed atoms coalescence into nanoparticles. The use of ultrashort laser pulses can ensure nonlinear absorption at the standard for these systems wavelength of 800 nm and thus provides efficient energy absorption. It is also demonstrated that the use of high repetition rate femtosecond lasers may induce direct nanoparticle formation as the necessary heat for particle growth is provided by the heat accumulation during the laser irradiation [18,19]. The nanoparticle-composed glasses express novel properties that could be a basis for high efficient applications. Enhancement of the nonlinear properties of the composite material, change of the refractive index and modified luminescence properties has been observed for such composites. It is shown [9] that laser irradiation can induce sign reverse of the nonlinear refractive index in nanoparticle composed glass. Au nanoparticles/SiO_2 composites may express more than an order of magnitude larger third-order nonlinear susceptibility compared to native oxide [20]. On the basis of these properties fabrication of optical elements as filters, phase changing elements, generation of light at specific wavelengths and optical switchers can be designed. The combination of these materials with specific ions with strong luminescence that can be enhanced by the nanoparticles may lead to development of novel emitting and sensor elements and laser active medium [21]. It is also shown that in nanoparticle composed glasses laser pulses may induce particle shape modification and respectively modification of their optical response in a desired manner for application in integrated selective filters [22]. The extensive work on laser processing of glasses performed recently gave a methodology of precise fabrication of optical waveguides and fluidic channels [23]. In a combination with metal nanoparticles a development of complex analytical systems can also be considered. The presented results on the topic demonstrate that the method is unique in fabrication of three dimensional nanoparticle structures inside transparent materials. However, the complex dynamics of the involved processes still embarrassed the reveal of the full capacity of the method. There is a lack of data about the method realization using other wavelengths or nanosecond pulses. It is not still described the influence of the irradiation and annealing conditions on the nanoparticle characteristics. All these will contribute to understanding the underlying processes and to ability of exploitation of the method in novel applications.

In this work we present results on color changes in gold-ion-doped borosilicate glass after irradiation with nanosecond laser pulses and annealing. It is shown that at certain conditions nanoparticles can be formed as an efficient control of their properties can be achieved by the laser processing and annealing parameters. The mechanism of the influence of the processing conditions on the nanoparticle size is discussed and analyzed on the basis of a theoretical model. The work represents data about the process of nanoparticle formation for glass type that is rarely considered and for commercial nanosecond laser system which makes them valuable for efficient application of the method in photonics and for fundamental study of composite materials formation and properties. The focus is on borosilicate glass, an optical material with low coefficients of thermal expansion that ensure high stability of thermal shock, an important property when laser applications or laser based devices are considered.

2. Experimental

The modification of the optical properties of gold-doped borosilicate glass induced by laser irradiation and annealing is studied in this work. The glass samples are obtained by the classical melt quenching method. Its composition (in Wt.%) is 50% SiO_2, 20% Al_2O_3, 20%B_2O_3, 5% CaO, 2% Li_2O, 3% MgO. $HAuCl_4 \cdot 3H_2O$ is used as a gold donor material and it is added in the initial mixture. Three types of glass with different gold concentration of 0.015, 0.5, and 1 wt% are produced and used in the presented experiments. The mixed material is melted in Pt crucible and kept at temperature of 1450 °C for 3 h. Then it is removed from the oven and left to cool down to the room temperature when it is cut and polished at pieces with thickness of 2 mm. Borosilicate glass is chosen in this study as a material with low thermal expansion coefficient and resistivity against high thermal gradients that could be induced during the laser processing. The laser irradiation is performed by a nanosecond Nd:YAG laser systems (Lotis) that can operate at four wavelengths – 1064, 532, 355, and 266 nm. The pulse repetition rate is 10 Hz and the pulse duration is 12 ns. The laser radiation is focused by a fused silica lens with focal length of 200 mm on the sample surface. The laser parameters as applied fluence and pulse number for each wavelength are varied in order to study their influence on the glass optical properties. The thermal annealing of the glass samples is performed by a standard oven with controllable heating parameters in air, as the influence of the annealing time and temperature is studied. After each step of processing (laser radiation and annealing) the optical properties of the samples are studied on the basis of the transmission spectra taken by spectrometer (Ocean optics, HR 4000) in the range 200–1000 nm. For structure characterization of the samples a TEM (JEOL JEM 2100) is used. The EMCAT/EMFIT computer program [24] is used to interpret the selected area electron diffraction (SAED) patterns and to identify the phase composition of the samples. Optical images of the processed areas are obtained by optical microscope (Optica B-150).

3. Results and discussion

The glass used in the presented experiments is opaque at wavelengths lower than approximately 300 nm. Fig. 1 shows the transmission spectra of samples with different gold concentration. It is clear that presence of gold does not influence the transmission spectra of the samples. The irradiation of the samples by nanosecond laser pulses at wavelength of 355, 532, and 1064 nm does not induce modification of the optical spectra at fluences lower than the damage threshold. It is defined as fluence where microscopically observed permanent damages are formed in the glass after laser irradiation. When such modifications are formed the

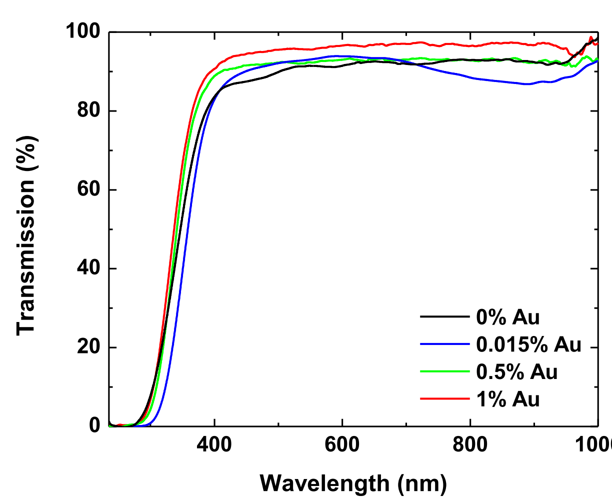

Fig. 1. Transmission spectra of borosilicate glass samples with different gold concentrations.