Femtosecond laser modification of the optical properties of glass containing noble-metal nanoparticles

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Abstract. The paper presents results on femtosecond laser irradiation-induced modification of the optical properties of a composite material – gold nanoparticles embedded into a borosilicate glass host. The process is initiated by laser pulses delivered by a Ti:sapphire laser system with pulse duration of 35 fs. The glass samples are prepared by melt quenching with gold added as hydrogen tetrachloroaurate (III) hydrate to the initial composition. Post-fabrication annealing leads to a homogeneous formation of nanoparticles in the glass; varying the annealing parameters results in producing nanoparticles with different sizes and shapes. The laser irradiation of the samples induces significant modification of the optical spectra of the glass through changes of the nanoparticles characteristics. The effects are studied of the laser fluence, laser wavelength and laser pulses number. The heat diffusion equation is applied to estimate the temperature evolution and explain the modifications observed. The results demonstrate this technique’s efficiency in modifying the nanoparticles properties with a high 3D spatial resolution, which can be useful in fabrication of integrated optical systems.

1. Introduction
The recent trend in the studies and applications of noble-metal nanoparticles includes more complex systems, such as ensembles of nanoparticles and nanoparticles-containing composite materials. The experiments make use of the strong dependence of the plasmon excitation characteristics on the properties of the arrays of nanoparticles and may open possibilities of tuning the optical properties of the composite system [1, 2]. Incorporating noble-metal nanoparticles into a dielectric matrix can define the optical properties not only as a simple additive effect, but it can result in the appearance of novel features. For example, Au nanoparticles embedded into SiO₂ and Al₂O₃ thin films enhance significantly the third-order nonlinear susceptibility compared to the native oxides [3, 4]. Although different techniques have been proposed for glass fabrication, e.g., classical melt quenching with appropriate choice of glass composition and annealing [5, 6], ion implantation [7], co-deposition [8],

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and different chemical approaches [9, 10], all of them offer fabrication of composite materials that consists of a transparent matrix and nanoparticles with a homogeneous distribution in the volume or in a surface layer. Laser treatment is among the powerful methods for fabrication of nanoparticle or modification of their characteristics with high spatial resolution [11, 12]. In the first type of space selective composite fabrication, nanoparticles can be formed after selective reduction of metal ions induced by laser radiation. In the second type, in a material that already contains of nanoparticles, their properties can be efficiently modified locally. Mechanisms as fragmentation, melting, ionization and Coulomb explosion based on laser treatment have been proposed to induce efficient optical properties modifications [13-15]. The application of ultrashort laser pulse interaction [16, 17] has been shown to alter the shape of the nanoparticles from sphere to ellipsoid with orientation of the long axis along the laser polarization direction. The studies performed have been mainly focused on thin film composites, while the method offers the capability of focusing the laser radiation inside the material giving potential for application of the technique to real 3D manipulation. This configuration and the involved effects have not been studied in detail due to the complex interplay of different processes, including initial nanoparticle properties, energy absorption, and shape modification in the presence of a dense surrounding. Furthermore, most of the studies have been focused on altering the nanoparticle’s shape by ultrashort laser pulses, while in fact a process of particles decomposition also takes place and needs more detailed studies.

This work presents results on modifications induced by ultrashort laser pulses of borosilicate glass containing Au nanoparticles. This glass type possesses high stability to temperature gradients and is often used as a base material for optical elements. We studied the influence of the laser treatment conditions on the process of altering the glass’ optical properties. This is considered in the context of a change of the geometrical characteristics of the nanoparticles. Further, the mechanism of nanoparticle modification is discussed. The results obtained provide a new insight on the process and can be used in the fabrication of novel complex optical elements.

2. Materials and methods
The base material in this study is borosilicate glass with composition 50% SiO₂, 20% Al₂O₃, 20% B₂O₃, 5% CaO, 2% Li₂O, 3% MgO in wt % prepared by the classical melt quenching method. The basic components were mixed and hydrogen tetrachloroaurate (III) hydrate was added to achieve Au doping. The material was melted in a Pt crucible and kept at a temperature of 1450 °C for 3 hours. The glass used in these work contained 0.015 w % Au. The fabricated sample was transparent and colorless. The glass samples were then annealed, whereby the heat-induced Au-ion reduction favored by the presence of a reducing agent (Li) produces Au atoms which coalesce into nanoparticles. By changing the annealing temperature or annealing time, one can prepare samples with nanoparticles with different size. The results presented here are related to two sample types: i) annealed at a temperature of 700 °C for 30 min, and ii) annealed at 1400 °C for 30 min. The samples were irradiated by a Ti:Sapphire laser system (Spectra Physics) generating laser pulses with a duration of 35 fs at a repetition rate of 1 kHz and a wavelength of 800 nm. The system is equipped with an optical parametric amplifier, which allows irradiation at wavelengths in the range 200 – 2000 nm. The laser beam was focused on the sample surface at a spot with a diameter of 100 μm. The transmission spectra of the samples before and after laser treatment were recorded in the range 200 – 1000 nm by an optical spectrometer equipped with a white light source (Ocean optics, HR 4000). The composition and the structure of the irradiated areas were estimated using TEM (JEOL JEM 2100) analysis. The modifications induced by the laser treatment were visualized by an optical microscope (Optica B-150) in transmission mode.

3. Results and discussion
The annealing of the as-fabricated glass at the temperatures of 700 °C and 1400 °C resulted in coloration of the glass – red and blue, respectively. Figure 1 shows the transmission spectra of these samples. For the sample annealed at 700 °C, there is a clear transmission minimum at about 550 nm.
This optical spectrum is related to the formation of nanoparticles, with the dip representing a plasmon resonance. The spectrum of the sample annealed at the temperature of 1400 °C has more complex features, as two minima can be clearly observed, one at about 530 nm and a second one at 595 nm. Based on the theoretical and experimental study presented below, such spectra can be related to the formation of large particles (size of about 100 nm) [18], or of non-spherical ones [1].

Figure 2 shows TEM images of the two glass samples, which confirm the formation of gold nanoparticles; in the case of the sample annealed at 700 °C (figure 2 a), their size is estimated at few nanometers. In the case of the sample annealed at the higher temperature (figure 2 b), metallic gold-composed areas with irregular shape and bigger size can be observed. We speculate that multi-domain structures are formed that behave as single particles [19]. They may have sizes of few tens of nanometers and irregular shapes.

Figure 3 presents the transmission spectra of the sample glass annealed at temperature of 700 °C and irradiated by 30 000 laser pulses at wavelength of 800 nm and different fluences. It is clearly seen...
that the laser radiation causes significant changes in the transmission spectra, namely, an increase of the transmission at the plasmon resonance and a blue shift of the resonance position.

The fluence dependence of the sample annealed at 1400 °C is shown in figure 4. It is also seen that the laser irradiation increases the transparency in the spectral range of the plasmon resonance.

The further increase of the laser fluence for this sample (figure 5) results in the appearance of additional features in the transmission spectra. At a fluence of 3.8 J/cm², another dip appears at 670 nm. At the highest fluence used (4.8 J/cm²) this dip shifts to about 710 nm. The effect could be related to formation of elongated nanoparticles, as observed previously [13].

Varying the number of laser pulse applied results in a similar behavior of the sample transmission as the laser fluence. In figure 6 we show this dependence at laser radiation wavelengths of 800 nm – a), and b) at 595 nm. The latter is chosen as corresponding to the maximal absorption of the glass as can be seen in figure 1. In both cases, the transmission increases after irradiation and with increasing the pulse number. In the case of irradiation at 595 nm, a stronger shift in the plasmon band position is observed. Radiation with this wavelength interacts most efficiently with the nanoparticles and even at a low fluence (as used here) modifies their properties.

It should be mentioned that laser irradiation can lead to a complete transparency of the irradiated area. Since in the presented configuration the irradiated spot is smaller than the minimal size that the spectrometer system can measure, part of the non-treated material gives contribution to the measured spectra.

The changes presented in the optical properties of glasses with embedded nanoparticles are related to modification of the nanoparticles’ properties. The increased transparency caused by the laser treatment has to do with the decomposition of the nanoparticles to atoms and small non-plasmonic clusters. The effects could be considered as thermal in nature – the particles are heated to a high temperature which induces atom diffusion into the glass matrix and reduces their size.

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**Figure 5.** Transmission spectra of glass sample annealed at temperature of 1400 °C before and after irradiation with different laser fluences. The pulse number is \( n = 30\,000 \). The wavelength of the laser radiation is 800 nm.

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**Figure 6.** Effect of the laser pulse number on the spectra of glass samples. The wavelength of the laser radiation is 800 nm (a) and 595 nm (b). The corresponding laser fluences are 3.2 J/cm² (a) and 640 mJ/cm² (b).
In order to estimate the effect of heating the nanoparticles, we used a numerical model based on the two-temperature heat-diffusion equation:

\[ C_e \frac{\partial T_e}{\partial t} = -\gamma(T_e - T_t) + S \]

\[ C_i \frac{\partial T_i}{\partial t} = \gamma(T_e - T_i) \]

\[ S = \frac{IC_{abs}}{V_p} \]

In Eq. (1) \( T_{e, i} \) are the electron and lattice temperatures, respectively; \( I \) is the laser light intensity; \( V_p = 4/3\pi R^3 \) is the particle volume. Set (1) is solved using the classical finite-difference scheme and by taking into account the values for \( C_e, C_i, \) and \( \gamma \) from [20]. \( C_{abs} \) is the absorption cross-section of the particle. It is obtained from the Mie model developed as a numerical code by Xu et al. [21]. Considering particles with a size of 10 nm, the calculation show that the melting temperature is reached at a fluence of approximately 2 J/cm², the bulk gold melting temperature being 1604 °C. Bulk evaporation takes place at fluences higher than approximately 4.2 J/cm². Since these characteristic temperatures decrease with the decrease of the particle size, the melting and evaporation are realized at lower fluences. We thus conclude that the modifications observed in the optical spectra of the glass samples studied start with melting of the nanoparticles. This could lead to changes in their shape and diffusion of atoms into the glass matrix [15].

4. Conclusions
This work demonstrates femtosecond laser pulses modification of the optical properties of borosilicate glass containing gold nanoparticles. The induced modifications are expressed by an increase of the transmission, especially in the wavelength range of the plasmon resonance, and a shift of the resonance position. These effects can be controlled by the laser processing parameters – laser fluence and number of pulses. A new effect, namely, the appearance of an additional transmission dip with the increase of the laser fluence is also observed. The governing mechanism can be attributed to particle heating, melting and decomposition. The results can be applied to achieving a controlled tuning of the optical properties of composite materials containing noble metal nanoparticles.

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References
[1] Noguez C 2007 J. Phys. Chem. C 111 3806
[2] Kreibig U and Vollmer M 1995 Optical properties of metal clusters (Berlin: Springer)
[3] Liao H B, Xiao R F, Fu J S, Yu P, Wong G K L and Sheng P 1997 Appl. Phys. Lett. 70 1
[4] Liao H B, Xiao R F, Fu J S and Wong G K L 1997 Appl. Phys. B 65 673
[5] Rao Pr and Doremus R J 1996 Non-Crystalline Sol. 203 202
[6] Jimenez J A, Lysenko S, Zhang G and Liu H 2007 J. Electr. Mat. 36 812
[7] Stepanov A L, Hole D E, Bukharaev A A, Townsend P D and Nurgazizov N I 1998 Appl. Surf. Sci. 136 298
[8] Serna R, Suarez-Garcia A, Afonso C N and Babonneau D 2006 Nanotechnology 17 4588
[9] Almeida J M P, Tribuzi V, Fonseca R D, Otuka A J G, Ferreira P H D, Mastelaro V R, Brajato P, Hernandez A C, Dev A, Voss T, Correa D S and Mendonca C R 2013 Opt. Mater. 35 2643
[10] Mohapatra S 2014 J. Alloy. Compd. 598 11
[11] Nedyalkov N, Koleva M, Stankova N, Nikov R, Terakawa M, Nakajima Y, Aleksandrov L and Iordanova R 2017 Beilstein J. Nanotechn. 8 2454
[12] Nedyalkov N, Koleva M, Nikov R, Stankova N, Iordanova E, Yankov G, Aleksandrov L and Iordanova 2019 Appl. Surf. Sci. 463 968
[13] Doster J, Baraldi G, Gonzalo J, Solis J, Hernandez-Rueda J and Siegel J 2014 Appl. Phys. Lett. 104 153106
[14] Podlipensky A, Abdolvand A, Seifert G and Graener H 2005 Appl. Phys. A 80 1647
[15] Licea-Rodriguez J, Rocha-Mendoza I, Rangel-Rojo R, Rodriguez-Fernández L and Oliver A 2014 Opt. Mater. 36 682
[16] Kaempfe M, Rainer T, Berg K J, Seifert G, Graener H 1999 Appl. Phys. Lett. 74 1200
[17] Seifert G, Stalmashonak A, Hofmeister H, Haug J and Dubiel M 2009 Nanoscale Res. Lett. 4 1380
[18] Shah M, Badwaik V, Kherde Y, Waghwani H K, Modi T, Aguilar Z P, Rodgers H, Hamilton W, Marutharaj T, Webb C, Lawrenz M B and Dakshinamurthy R 2014 Front. Biosci. 19 1320
[19] Zheng J, Ding Y, Tian B, Lin Wang Z and Zhuang X 2008 J. Am. Chem. Soc. 130 10472
[20] Chowdhury I H and Xu X 2003 Numer. Heat Tr. A 44 219
[21] Xu Y 2003 Phys. Rev. E 67 046620