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Optical absorption and Raman scattering mapping of nanoparticles patterns formed in glass by nanosecond laser in UV, VIS and IR

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Abstract. The paper is devoted to optical study of silver nanoparticles formed in a glass enriched with silver ions upon irradiation with nanosecond laser in UV, VIS and IR. The silver ions were introduced in glass by ion-exchange procedure. The silver nanoparticles were patterned to form spot-like (irradiation with individual laser pulses) and lines-like (laser pulses overlap on the glass surface) ensembles. Obtained optical absorption maps of spot-like and lines-like ensembles subjected to additional chemical etching of the glass reveal the impact of laser wavelength, fluence and pulse frequency on the spatial (lateral and depth) arrangement of the nanoparticles in the ensembles. The applicability of the etched and non-etched spot-like and lines-like ensembles in surface enhanced Raman scattering spectroscopy was demonstrated, and Raman scattering maps of the ensembles were obtained. The homogeneity of the signal along the ensembles and Raman enhancement factor were evaluated and compared with ones of silver nanostructures formed by other techniques.

Keywords: silver nanoparticles, glass, nanosecond laser

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Материалы конференции
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Оптическое и рамановское картирование структур из наночастиц, сформированных в стекле под действием наносекундного УФ, ВИД и ИК лазерного излучения

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Аннотация. Работа посвящена разработке и исследованию серебряных наночастиц, сформированных в обогащенном ионами серебра стекле под действием наносекундного лазерного излучения. Установлено влияние длины волны и плотности энергии лазерного излучения, а также частоты следования импульсов, на пространственное распределение

и оптические характеристики формируемых частиц. Продемонстрирована возможность применения наночастиц в спектроскопии поверхностно-усиленного рамановского рассеяния света.

Ключевые слова: серебряные наночастицы, стекло, наносекундный лазер

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Introduction

Metal nanoparticles (NPs) are known for their extraordinary optical properties. Their resonance light absorption at the wavelength of localized surface plasmon resonance (LSPR) is accompanied by giant enhancement of electric field nearby surface. This enhancement intensifies light-matter interaction allowing, in particular, detection of single molecules via surface enhanced Raman scattering (SERS) [1]. The developing approach to the formation of NPs is reduction of metal ions, which are embedded into a glass, by irradiation of UV-IR short pulse lasers. Commonly, silver ions are introduced in glass via ion-exchange [2] or ion implantation [3]. The laser irradiation reduces embedded silver ions due to the glass heating by absorbed light [4] (similarly to the reduction of silver ions in thermally heated glasses [5]) and generation of free electrons by multiphoton absorption or avalanche ionization followed by the reaction $Ag^+ + e^- \rightarrow Ag^0$ [6]. Clustering of silver atoms in heated/softened glass results in the formation of silver NPs. One of the advantages of the described approach, similarly to using profiled electrodes and thermal poling [7] is patterning of NPs distribution according to a given template, which opens up possibilities to integrate NPs in microfluidic chips and create lab-on chip devices based on SERS [8]. However, to imply NPs in SERS one should ensure that they meet criteria of sufficient Raman enhancement and homogenous signal distribution along the active area. In this study, we reveal impact of laser wavelength, fluence and pulse frequency on spatial arrangement and SERS-activity of silver NPs ensembles laser-drawn on the glass surface.

Materials and Methods

In the experiments we used soda-lime silicate glass and introduced silver ions in the subsurface glass layer via $Na^+ \leftrightarrow Ag^+$ ion-exchange [9]: the glass was immersed into the melt of $(AgNO_3)_{5wt.\%}(NaNO_3)_{95wt.\%}$ at 325 °C for 20 min. We irradiated the glass with 6 ns pulses of Nd:YAG laser (Litron Nano L) at wavelength, λ, of 1.06, 0.53 and 0.35 μm. Moving the glass in the plane perpendicular to the laser beam at the speed of 200 μm/s and varying laser pulse frequency we patterned NPs to draw “lines” (pulses overlapping on the glass surface) and “spots” (individual pulses). The frequencies were chosen for each wavelength individually considering the diameter of the laser beam, which was 90, 160 and 250 μm for $\lambda = 0.35$, 0.53 and 1.06 μm, respectively. The parameters of the pattering are presented in Table 1.

Both “lines” and “spots” showed characteristic yellowish coloration induced by optical absorption at ~ 450 nm (silver NPs LSPR [10]). To map the LSPR intensity distribution we used homemade setup that included a halogen lamp (Ocean Optics HL-2000-FHSA-LL), a modular spectrometer (Solar LS SC82), a translation stage and a camera. Normally incident white light was focused by 10x/0.25 objective on the glass surface to the spot of the diameter of 80 μm, 90% of the light passed through the glass was collected by a second 10x/0.25 objective and analyzed

Table 1

The parameters of the laser pattering of silver ions-enriched glass

Laser wavelength, μm	Laser fluence, J/cm^2		
	5.4	10.3	12.6
1.06	–	0.5 Hz / 2 Hz	0.5 Hz / 2 Hz
0.53	–	1 Hz / 2 Hz	1 Hz / 2 Hz
0.35	1 Hz / 3 Hz	1 Hz / 3 Hz	–

with the spectrometer, while 10% was directed to the camera, which allowed precise positioning of the glass using the stage. Absorption spectra were measured along the "lines" and "spots" with 40 μm step by moving the stage in the plane perpendicular to optical axis of the setup.

To reveal NPs spatial arrangement we obtained LSPR intensity distributions for the glass subjected to the laser irradiation and additional chemical etching in HF(5μl):NH_4F(5g):H_2O(40g) for 2, 4, 6 and 8 min. We characterized the glass surface with optical profilometer (Zygo NewView 6000) before and after 8 min etching.

Etched and non-etched laser-irradiated glasses were tested in SERS of 1,2-di(4-pyridyl) ethylene (BPE) using confocal Raman microscope (Witec Alpha 300R) with 10x/0.25 objective and 532 nm excitation laser. The droplet of BPE water solution was dried on the glass surface, the molecular coverage being several monolayers, ~ 10^{-11} mol/mm^2. To evaluate Raman enhancement we also tested BPE crystallites (~ 10^{-8} mol/mm^2) placed on the surface of the virgin glass (plain Raman measurements). The spectra acquisition time was 1 s and laser power was 0.7 and 33 mW for SERS and Raman measurements, respectively.

Result and discussion

The glass surface characterization demonstrated that the laser drawing of "lines" and "spots" results in formation of craters which lateral size corresponds to the size of laser spot. The crater profile does not change in the course of the etching, and therefore, etching rate of the laser-irradiated glass corresponds to one of the pristine glass, being ~ 23 nm/min. Considering this, we analyzed optical and SERS maps obtained for the glass subjected to the laser irradiation and additional 2–8 min etching.

Typical LSPR intensity distribution across laser-drawn "spot" before and after the etching is illustrated with Fig. 1, *a*. One can see, the maximal absorption corresponds to the center of the "spot", which evidences formation of higher number of silver NPs in this region. The absorption decreases in the course of the etching, which indicates removal of NPs. The derivatives of functions of maximal absorption on thickness of the etched glass layer for the "spots" irradiated at different laser wavelengths and laser fluencies are presented in Fig. 1, *b–d*. One can see, NPs form within thin subsurface glass layer, < 150 nm, the maximal concentration being at ~ 50–100 nm under the surface for all the wavelengths. Note, for λ = 1.06 μm the increase in the laser fluence results in the appearance of two regions enriched with NPs - they form near the surface and deeper in the glass bulk (see Fig. 1, *b*) that is two-layer ensemble. For λ = 0.35 and 0.53 μm (Fig. 1, *c*, *d*) the increase in the laser fluence results in formation of NPs deeper in glass and closer to the surface, respectively.

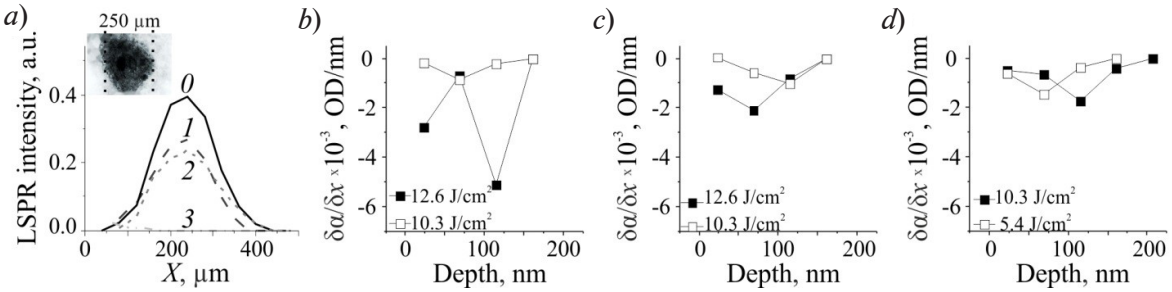

Fig. 1. Typical LSPR intensity distribution across laser-drawn "spot" before (0) and after etching off 45 (1), 90 (2) and 140 nm (3) of glass (*a*). The derivatives of functions of maximal absorption on thickness of etched glass $\delta\alpha/\delta x$ for the "spots" irradiated at 1.06 (*b*), 0.53 (*c*) and 0.35 μm (*d*) laser wavelengths

Fig. 1, *a* corresponds to the "spot" formed at 1.06 μm, 12.6 J/cm^2 and 0.5 Hz.

Fig. 2, *a* presents typical LSPR intensity distribution along etched and non-etched laser-drawn "line". One can see, the overlapping of the laser pulses on the glass surface results in formation of silver NPs that are uniformly distributed along the "line" - the relative standard deviation (RSD) of the absorption is only 6% for the non-etched "line" presented in Fig. 2, *a*. For λ = 1.06 and 0.35 μm the derivatives of functions of the average absorption on thickness of the etched off glass layer demonstrate relatively uniform depth distribution of NPs within ~ 200 nm (see Fig. 2, *b*, *d*). For λ = 0.53 μm NPs concentrated at ~ 50 nm under the glass surface (see Fig. 2, *c*).

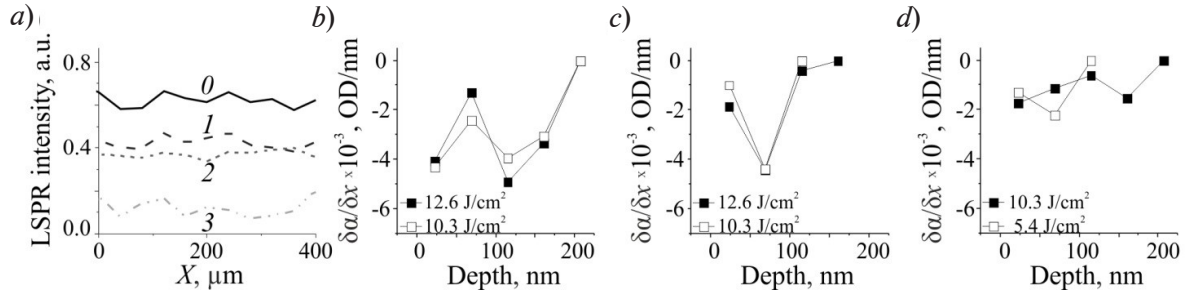

Fig. 2. Typical LSPR intensity distribution across laser-drawn "line" before (0) and after etching off 45 (1), 90 (2) and 140 nm (3) of glass (*a*). The derivatives of functions of average absorption on thickness of etched glass $\delta\alpha/\delta x$ for the "lines" irradiated at 1.06 (*b*), 0.53 (*c*) and 0.35 μm (*d*) laser wavelengths.
Fig. 1, *a* corresponds to the "line" formed at 1.06 μm, 12.6 J/cm² and 2 Hz

Thus, in most cases of laser-drawing, concentration of NPs is maximal at ~ 50 nm under the glass surface. Indeed, NPs formation is governed by glass heating [4], and the heat penetration depth determined by laser pulse duration and glass thermal diffusivity [11] is ~ 55 nm.

We tested formed NPs in SERS before and after removal of ~ 50 nm of glass. The SERS signal was undetectable for the non-etched samples, which evidences that NPs are completely covered with glass. Typical SERS signal distributions along etched "spot" and "line" are presented in Fig. 3, *a, b* respectively. One can see, SERS maps are similar to optical ones: maximal signal is detected in the center of the "spot", and signal is relatively uniform along the "line". Note, at the fixed laser fluence the decrease of the wavelength results in decreasing RSD of SERS signal along the "line" from 102% to 41%. For λ = 0.35 and 0.53 μm the increase in the fluence results in decreasing RSD, the minimal RSD being 29% for λ = 0.53 μm. The "line" drawn at 1.06 μm and high fluence demonstrates the highest RSD, 225%.

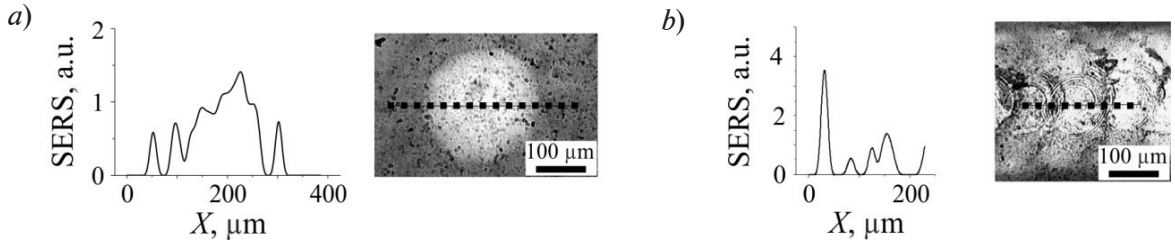

Fig. 3. Typical SERS signal distributions along etched "spot" (*a*) and "line" (*b*)
Fig. 1, *a, b* correspond to the "spot" and "line" formed at 1.06 μm, 12.8 J/cm², 0.5 and 2 Hz, respectively

We evaluated enhancement factor (EF) provided by NPs ensembles using the procedure described in Ref. [12]. We used maximal and average SERS signal for evaluation of "spot" and "line" EFs, respectively. The "spot" and "line" EFs are in ~ $2–4\cdot10^5$ and ~ $0.6–4\cdot10^5$ range, respectively. The maximal EF is for the "spot" drawn at 0.53 μm and 12.6 J/cm², and for the "line" drawn at 0.35 μm and 5.4 J/cm². The minimal EF is for the "spot" and "line" formed at 1.06 μm, 12.6 and 10.3 J/cm², respectively. The tendency is clear: the ensembles provided maximal EF have maximal concentration of NPs at ~ 50 nm under the surface (see Fig. 1 and 2). The patterns formed at 1.06 μm provide minimal EF because of the two-layer ensemble of NPs – the peaks of their concentrations are at ~ 25 and ~ 100 nm under the surface.

Thus, one can expect higher EF by etching NPs ensembles obtained at 1.06 μm shorter or longer time. Nevertheless, obtained EFs are comparable with ones demonstrated by nanostructures formed, for example, by laser nanostructuring of soda-lime glass with the subsequent deposition of thin silver film [13], by femtosecond laser sintering of silver NPs paste [14] or by femtosecond laser induced plasma assisted ablation of silicon wafer followed by deposition of thin silver film [15].

Conclusion

We demonstrated that the irradiation of silver ions-enriched soda-lime glass with 6 ns-long laser pulse at 1.06, 0.53 and 0.35 μm wavelength results in formation of silver nanoparticles in the area corresponded to the size of laser spot. The maximal concentration of nanoparticles is in the center of the spot, and ~ 50 nm under the glass surface for 0.35 and 0.53 μm irradiation and at ~ 25 nm and ~ 100 nm for 1.06 μm irradiation. The irradiation of the glass with the pulses overlapping on the glass surface ("line"), which was provided by moving the glass in the course of the irradiation, results in formation of nanoparticles that are uniformly distributed along the "line". After the removal of ~ 50 nm glass surface layer, formed ensembles of silver nanoparticles are applicable in SERS. The Raman enhancement provided by the nanoparticles is in ~ $6 \cdot 10^4$ – $4 \cdot 10^5$ range, depending on the laser wavelength, fluence and pulse frequency. Distribution of Raman signal along active area is close to uniform for the ensembles formed under 0.35 and 0.53 μm irradiation, the minimal relative standard deviation of signal being 29%.

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