Formation of silver nanoparticles in ion-exchanged glass with nanosecond laser irradiation

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Abstract. We studied the irradiation of silver enriched soda-lime glass slides by 6 nanosecond long laser pulses at the wavelengths of 1064 and 532 nm. The extinction spectra of the irradiated glass regions after the laser exposition and after chemical and reactive ion etching (RIE) were compared. Independently on the wavelength, the irradiation resulted in the formation of silver nanoparticles demonstrating localized surface plasmon resonance (LSPR), which gradually disappeared with the etching of the samples. The dependence of the spectral position of LSPR on the etching time was significantly different for chemical etching and RIE. We relate this to the chemical interaction of silver with the gases used in RIE.

1. Introduction

Studies of glasses embedded with silver nanoparticles (SN) and containing the nanoparticles on their surface are being carried out during last decades. The reason of this interest is the possibility to use SN in multiple applications: as nucleation agent in glass ceramics formation, as Raman scattering and luminescence enhancing agents, as elements of optical polarizers and masks, in nonlinear optics, etc. In all cases, silver should be either introduced into the glasses or deposited onto the surface. Except the synthesis of silver-contacting glasses, a powerful tool to dope glasses with silver is ion exchange processing resulting in the replacement of sodium or other alkaline ions from the glass by silver ions from the melt of a silver-containing salt. These ions can be reduced to metal silver forming nanoparticles in the bulk or on the surface via the phase decomposition of the silver-glass solid solution. The reduction can be induced either by a reducing agent, like hydrogen penetrating into the glass [1], or by ions of variable valence introduced in the glass during its synthesis [2]. Formation of nanoparticles in silver-doped glass under heating was also reported [3]. Another approach to SN formation is to irradiate silver-containing glasses with powerful nanosecond lasers in visible or UV wavelength range [4], continuous UV radiation [5], or femtosecond IR radiation [6]. In addition to the appearance and growth of SN [7], their laser modification [8], dissolution [9] and structuring of glasses with formed SN [10] were reported. In this paper, we report the effect of exposure of a silver-doped glass by the fundamental and the second harmonic radiation of a nanosecond neodymium laser, and the results of chemical and reactive ion etching of the irradiated regions.
2. Experimental
We used a soda-lime glass containing 14.3 wt.% of sodium oxide. 1 mm thick glass slides were immersed in the melt of 0.05Ag NO₃ - 0.95NaNO₃ (in wt.%) at 350 °C for 20 min. This resulted in the enrichment of the subsurface layer of the glass with silver ions, maximal depth of their penetration (zero concentration level) being ~6 μm and maximal silver oxide concentration at the glass surface ~10.5 wt.% [11].

Ion-exchanged glass samples were irradiated with Litron Nano L Nd:YAG laser (wavelength of 1064 nm) providing 6-ns-long pulses with the maximal pulse energy of 14.0 mJ. Doubling of the radiation frequency provided pulses at 532 nm wavelength with the maximal pulse energy of 3.6 mJ. The radiation was focused on the sample surface using a lens with focal length of 125 mm that provided the focal spots ~130 and ~70 μm in size at 1064 and 532 nm wavelengths, respectively. Thus, the maximal achievable energy density was 105.5 J/cm² for the samples irradiated at the laser fundamental wavelength and 93.5 J/cm² for the irradiation at the second harmonic wavelength, however, in the experiments we mostly used lower energies. To characterize optical extinction of the irradiated glass regions we used homemade setup with QE65 Pro spectrometer (OceanOptics, USA), 50 μm collecting optical fiber and 5x/0.13 objective (~100 μm collection spot) and spectrophotometer Specord 50 (7x1 mm collection spot).

Chemical etching (CHE) of the samples was performed in HF(5 μl):NH₄F(5 g):H₂O(40 g) solution. We obtained the etching rate of the ion-exchanged glass by measuring the height of the step between the etched and protected (non-etched) parts of the sample surface after each minute of the etching, and found it to be ~6 nm/min. The samples were also subjected to reactive ion etching (RIE) with 10Ar-20CF₄ gas mixture. RIE of the samples was performed in PLASSYS MU400 station during 15, 45 and 90 s. In this case the etching rate of the ion-exchanged glass was essentially faster, ~40 nm/min.

3. Results and discussion
The optical extinction spectra presented in figure 1 demonstrate a resonance at the wavelength of ~450 nm after the irradiation at both wavelengths. This spectral position corresponds to the localized surface plasmon resonance (LSPR) in silver nanoparticles. The irradiated region is colored in yellow (see inset in figure 1), which is also typical for glasses containing silver nanoparticles. This allows concluding about the presence of such nanoparticles in the irradiated regions.

![Figure 1](image_url)  
**Figure 1.** Spectra of the glass regions irradiated with 532 nm laser pulses at different energy densities.  
**Inset:** microphotograph of a glass region irradiated by a single laser pulse. Yellow coloration indicates the LSPR of silver nanoparticles.

Comparing the extinction spectra in figure 1, one can see that increasing the pulse energy density results in higher LSPR peak (see figure 2a also). This trend was observed for both wavelengths used in the experiment. The growth of the LSPR peak could be due to an increase in the number of the nanoparticles and/or in their size. The latter should manifest itself in the shifting of the LSPR spectral
position to longer wavelengths [12], however, the experiments do not show any red-shift of the resonance which is evidenced by figure 2b. Oppositely, one can see in figure 2b a blue-shift in the beginning of the curve followed by the constant LSPR wavelength.

![Figure 2. LSPR peak amplitude (a) and spectral position (b) for different pulse energy densities. Irradiation wavelength 532 nm.](image)

Etching of the samples allowed us to follow the magnitude of the LSPR peak and evaluate the depth distribution of the laser-formed nanoparticles. Since the formation of nanoparticles likely occurs in a similar way under the irradiation at both laser wavelengths, we studied etching of the samples irradiated by 1064 nm laser pulses only. Local extinction spectra of the samples subjected to CHE and RIE are presented in figure 3a and figure 3b, correspondingly. Spectra are normalized by the initial LSPR peak amplitude.

![Figure 3. Optical extinction spectra of the samples irradiated at 1064 nm laser wavelength after different time of (a) chemical etching, (b) reactive ion etching.](image)
We studied the extinction spectra of the samples irradiated with 1064 nm laser pulses before and after the removal of nanometers-thick glass layers using CHE and RIE. Processing of these data provided us with the dependence of the LSPR peak amplitude and spectral position on the etching time, which are presented in figure 4 a-d. One can see that the LSPR peak gradually changes during the first 6 min of CHE (figure 4a,b), then a rapid decrease in the amplitude occurs, which is accompanied by a blue-shift of the LSPR. After 10 min of the etching only small quantity of SN rests in the sample. Taking into account that the etching rate is ~ 6 nm/min in CHE, the most nanoparticles should be in ~ 60 nm subsurface layer of the glass.

In RIE, LSPR peak amplitude drastically drops by almost 2 times after the first 15 sec (figure 4d), and following increase in the etching time results in linear decrease of the peak. The LSPR drop off evidences the decrease of number of silver nanoparticles, therefore, most of the nanoparticles are on the surface or in the subsurface 5-10 nm layer of the glass. The rest of the nanoparticles are uniformly distributed within ~ 60 nm thick glass layer under the surface, which is evidenced by 5 times drop of the LSPR peak after 90 sec of RIE. The former corresponds well with the data obtained by chemical etching.

Figure 4c also demonstrates that LSPR red-shifts by ~10 nm in the course of RIE. This dynamic differs from one observed in CHE, when LSPR blue-shifts when the sample was etched (figure 4a). Spectral position of LSPR changes if size or form of nanoparticles change, or dielectric constant of the surrounding media varies. We attribute the blue-shift observed in CHE to a change in size of SN; smaller nanoparticles are deeper in the glass and thus are removed the last. But why a red-shift occurs in RIE? There is no reason for a difference in the distribution, size or form of silver nanoparticles in the samples etched in HF solution or by RIE, for they were formed at the same conditions. Thus, the only reason of LSPR red-shift during RIE could be an increase in the dielectric constant of the surrounding media. RIE with 10Ar - 20CF₄ gas mixture could result in the formation of thin AgF layer on silver surface [13, 14]. Dielectric constant of AgF ε_{AgF}=3.2 [15] is essentially higher than that of silicate glass, ε_{glass}=2.3. Thus, SN surrounded by AgF layer will demonstrate a red-shift in LSPR if compared with SN in a glass. As for CHE, there is no chemical alteration of the surface during HF etching [16].

4. Conclusions
Presented results allow us concluding that the irradiation of the glass enriched with silver ions by nanosecond laser pulses at the wavelengths of 1064 and 532 nm results in the formation of silver nanoparticles. Nanoparticles are distributed within ~ 60 nm subsurface layer, the bigger ones being ~ 5-10 nm under the surface or on the surface. The number of the nanoparticles rises with the increase...
of the pulse energy. Etching of the glasses with silver nanoparticles removes them, the rate of etching being ~ 6 nm/min for chemical etching, and ~ 40 nm/min for reactive ion etching. Besides, RIE with 10Ar - 20CF\textsubscript{4} gas mixture is accompanied by a change of the nearest environment of the nanoparticles. Most likely, this is the formation of AgF. Chemical etching in diluted HF does not lead to any chemical reactions. Thus, if one needs to obtain “bare” nanoparticles on the surface, for example, for surface-enhanced Raman spectroscopy, it is more preferable to use chemical etching.

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