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Nanosecond Laser Surface Silver Metallization of Wet Ion Exchanged Glasses

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Abstract. Silver ions are embedded in glass slides by a traditional "wet" ion exchange technique. The glass slides irradiation by 10 ns laser pulses at 355 nm wavelength leads to the formation of metal-like film at the surface. Scanning electron microscopy shows that the films presents a dense layer of silver nanoparticles about the same size and separation. Varying the irradiation parameters results in a significant difference in the transmission spectra of the slides. Particle size grows when the laser power increases.

Introduction

Noble metal nanoparticles are interesting due to their unique nonlinear optical properties [1–3]. The optical properties of a glass embedded with silver nanoparticles can be controlled via varying physical properties of nanoparticles, and this makes the glass-metal nanocomposites promising candidates for numerous applications in optoelectronics [4] and sensing [5]. The optical properties of these glassy composites are dominated by the SPRs which are specific for different metals and different types of surrounding matrix, size, shape, spatial distribution and concentration of the metal inclusions. The manipulation of physical properties of nanoparticles changes their surface plasmon resonance (SPR) position and, respectively, optical properties of the composites.
Controllable two-step fabrication of silver-glass composite by dry field-assisted ion-exchange with subsequent laser irradiation has been reported [6]. The main aim of this work is the study of the composite formation as the result of the interaction between ns-pulsed laser and silver ions embedded to the glass slide using "wet" silver-sodium ion-exchange. In this paper, we present the optical and structural properties of the nanocomposite.

Experimental methods

To embed silver ions into glass matrix, soda-lime glass slides were ion-exchanged in silver-sodium melt solution: $_{5\%wt.}AgNO_3$: $_{95\%wt.}NaNO_3$ for 20 min at 325°C. In the process sodium ions were replaced by silver ions in several microns deep subsurface layer of the glass. Prepared samples were irradiated by

3rd harmonic of pulsed Nd:YVO_4 laser (pulse length τ = 10 ns) at λ = 355 nm wavelength (edge of absorption of the glass) in standard atmospheric environment (room temperature and normal pressure). The laser beam had a Gaussian intensity profile and was focused onto the sample surface using a flat-field scanning lens system. The diameter of the focused spot (φ) was about 60 µm. Samples were irradiated with laser pulse repetition frequency of 80 kHz, by scanning line-by-line with the speed of 1 mm/s (4800 pulse/spot). Laser output energy density (laser fluence) was varied from 332 to 197 mJ/cm^2. The irradiated areas were characterized using Specord 50 spectrophotometer, Leica digital microscope, and a LEO 1550 Gemini scanning electron microscope (SEM). The list of prepared samples is presented in Table 1.

Table 1. The list of parameters of prepared samples

Sample name	#1	#2	#3	#4
Energy per pulse, µJ	9.38	9.00	6.94	5.56
Laser fluence, mJ/cm^2	332	319	246	197

Results and discussions

Photographs of the prepared samples are presented in Figs. 1,2. As seen, only particles on the glass surface were formed by laser pulses with the energy below ~6 µJ. Starting from 7 µJ energy of the irradiating pulses, bulk nanoparticles formation in the glass volume occurred Increasing pulse energy resulted in stronger reflection. At 9 µJ pulse energy the films started to become rough because of overheat resulted in bubbles and cracks formation near the glass surface.

Figure 1. Photos of the laser modified areas of the sample. From left to right areas #1 - #4. The sizes of the squares are 2.4x2.4 mm^2. Images (a) and (b) were taken with different illumination.

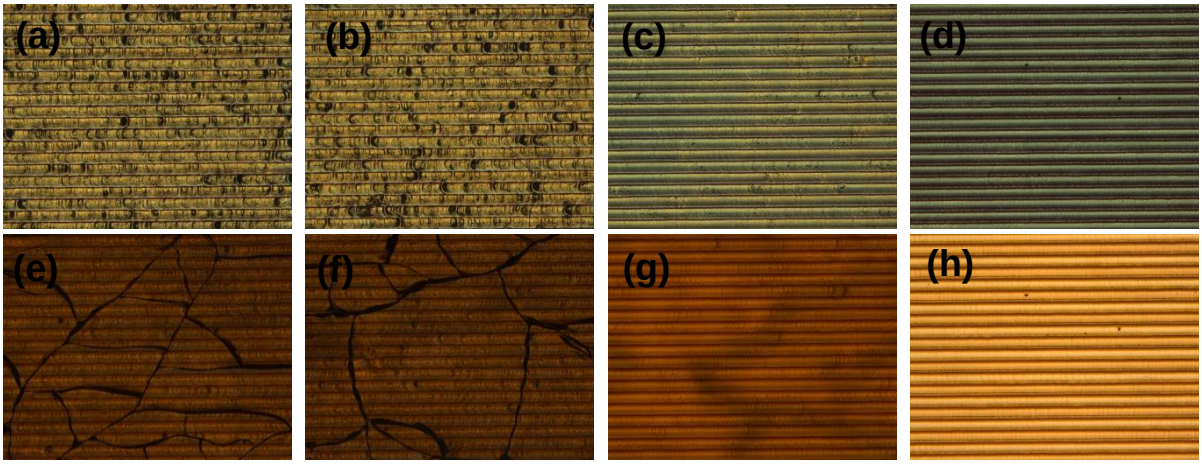

Figure 2. Optical microscopy images of the samples taken with 5x magnification. Images (a-d) and (e-h) correspond to the samples #1 - #4. Images (a-d) were obtained in reflection mode and images (e-h) correspond to the transmission mode. The lines result from the scanning of the laser beam.

Optical absorption spectra of the irradiated areas are shown in Fig. 3. Optical density increases for higher irradiation laser power, which is also in accordance with Figs. 1,2. It is important to note that the peak of the absorption spectra lies at 440 nm wavelength, which is typical for spherical silver nanoparticles. Increase of the absorption means bigger amount of nanoparticles, while broadening of the absorption peak indicates broadening of the nanoparticles size distribution or an increase in their volume fraction.

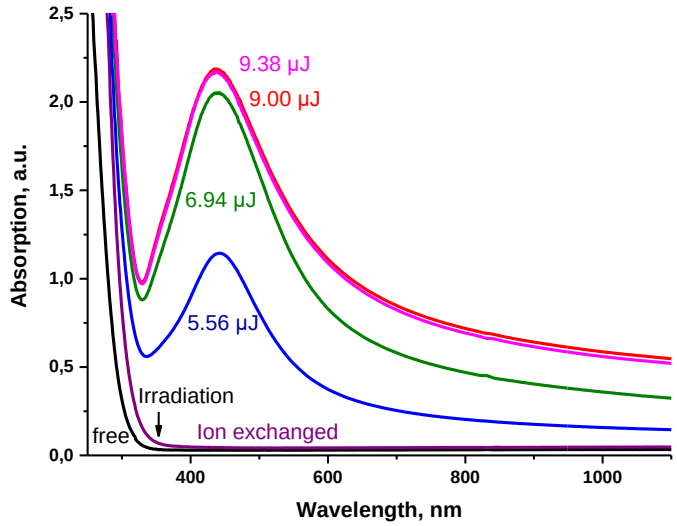

Figure 3. Optical absorption spectra. Figures near corresponding spectra indicate laser pulse energy.

SEM images taken in the centre of the irradiated lines show that under decreasing the laser power the average silver nanoparticle size drops from 15 to 10 nm. This is well correlated with optical spectroscopy data presented in Fig. 3.

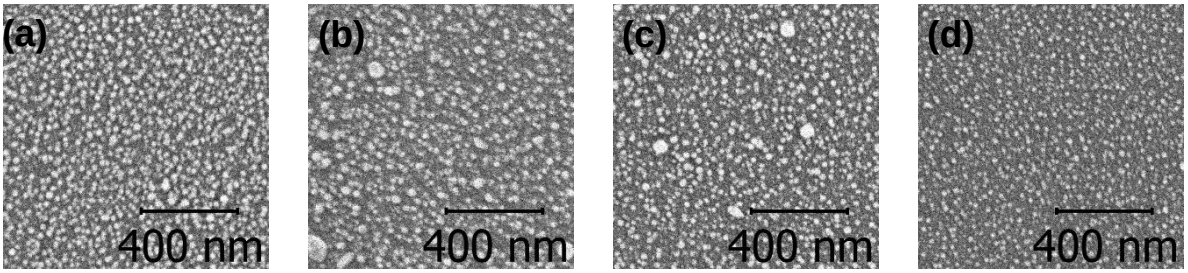

Figure 4. SEM images of the samples taken in the center of the irradiated lines. Images (a-d) correspond to the samples #1 - #4.

The laser beam focused on the glass surface with the spot size of 60 μm creates ~60 μm wide line of nanoparticles when scanned. Silver nanoparticles up to 500 nm in size were grown at the border of this line. In Fig. 5 one can see the presence of nanoparticles outside the irradiated line. This line broadening is caused by laser heating of the glass surface, which results in the formation of silver nanoparticles in the glass bulk (about 60 μm deep region – see Fig. 6) and on the glass surface near the irradiated area. The broadening of the line is about 30 μm from each side of the line. The size of silver nanoparticles outside the line is about 1.5-2 times bigger, and the nanoparticles are denser then inside of the irradiated area. This effect should be taken in account for line-by-line metallisation of a glass.

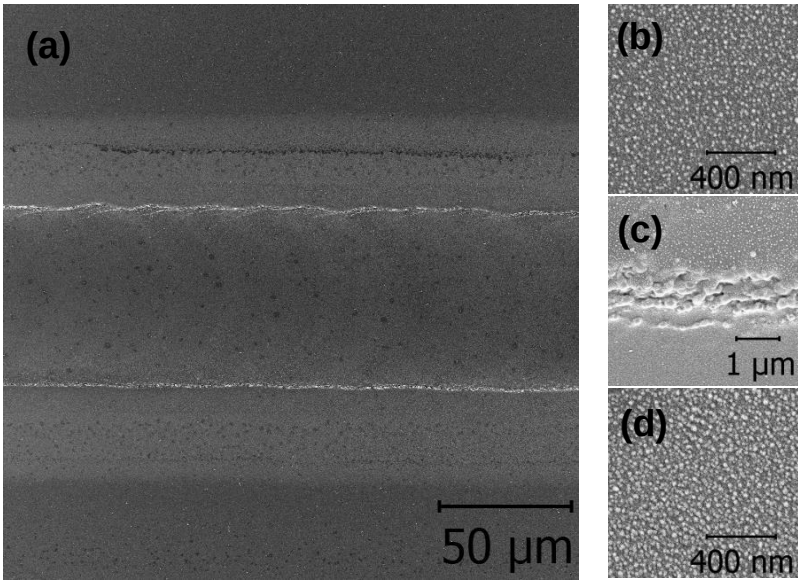

Figure 5. SEM of individual 60 μm-wide line drown by the laser on the sample #4 surface (a). Images taken inside the line (b), at the border of the line (c) and outside (d) the line.

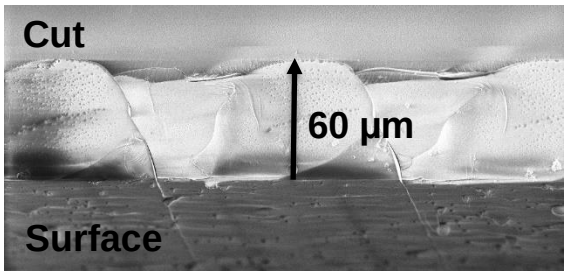

Figure 6. SEM of the chipped glass (side view). One can see 60 microns thick region enriched with the nanoparticles.

Conclusion

The formation of silver nanoparticles in the glass embedded silver ions via classic wet ion-exchange under nanosecond (10 ns) pulsed Nd:YVO_4 laser irradiation at 355 nm wavelength is demonstrated. Increase of the laser power resulted in the growth of the average nanoparticle size. This technique of controlled local formation of the nanoparticles by pulsed laser irradiation allows one to create complex patterns of closely-positioned nanoparticles in glasses containing silver ions.

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