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The remarkable transformation of nanoripples in glass-metal nanocomposite

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We report the linear-to-circular transformation of high spatial frequency (HSF) ripples formed on the surface of a glass with embedded silver nanoparticles under irradiation with 120 fs long pulses at the wavelength of 800 nm. In the experiments, at the ablation threshold of 1.28 J/cm², the HSF ripples with the period of ∼300 nm were oriented along the polarization of the laser beam. However, we found that the nanoripples pattern is gradually transforming from linear to an untypical circular one when the pulse energy increases. The ripples take nearly perfect circular shape at the pulse energy of ∼8.0 µJ, which corresponds to the fluence of 1.5 J/cm². © 2018 Author(s).

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INTRODUCTION

Material processing with ultrafast lasers1–3 has become a powerful tool for a number of promising applications including optical memory,4 microfluidics,5 and surface wettability control.6 They rely on the self-organization processes, which can result in the formation of periodic structures on the surface7 and in the bulk8 under the irradiation with tightly focused femtosecond pulses. The laser-induced periodic surface structures are often termed ripples, which can be either parallel or perpendicular to the polarization of the laser beam. High spatial frequency (HSF) ripples have a period of about 100 nm, while periodicity of low spatial frequency (LSF) ripples is close to the laser wavelength.7 There is a common belief that ripples are formed due to coupling of the incident radiation with the light scattered on collective oscillations of free carriers in the irradiated area7 that enable efficient energy transfer into the subsurface layer of the material.9

Here we consider the ripples formation on the surface of a soda-lime glass embedded with silver nanoparticles. Optical properties of this glass-metal nanocomposite (GMN) are strongly influenced by the surface plasmon resonance (SPR) at the wavelength of 428 nm that is originated from collective oscillations of conduction electrons in silver nanoparticles.10 In the studies of femtosecond modification of GMNs,3,11,12 it has been shown that at the excitation wavelength of 400 nm, the ablation of the GMN is accompanied by the formation of LSF7 directed perpendicular to the polarization of the laser beam.11 In contrast, at the excitation wavelength of 532 nm12 falling out of the SPR region, LSF ripples oriented along the laser beam polarization are formed. It is worth noting that the non-resonant excitation of the GMN with essentially longer nanosecond pulses at λ = 1064 nm resulted in shaping and in redistribution of silver nanoparticles rather than in ripples formation.13,14 This is partially because the light absorption in the subsurface layer of GMN is governed by metal nanoparticles, which were melted before transferring energy to the surrounding glass.

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In this paper, we report HSF ripples in silver-based GMN under the irradiation by femtosecond pulses at the wavelength of 800 nm. We demonstrate for the first time that when the laser fluence exceeds the ablation threshold the ripple pattern on the GMN surface transforms from the linear to the circular.

EXPERIMENTAL

Silver nanoparticles were formed in the subsurface layer of 1 mm thick soda-lime glass slides using Ag⁺-Na⁺ ion exchange technique\textsuperscript{15,16} in the Ag\textsubscript{0.5}Na\textsubscript{0.95}NO\textsubscript{3} bath at the temperature of 325°C for 20 minutes. After the ion exchange, the samples were annealed in hydrogen at atmospheric pressure for 10 minutes at 250°C. During the annealing, the silver ions in the subsurface region of the glass were reduced to neutral atoms, which aggregated into nanoparticles\textsuperscript{17,18} with the diameter of a few nanometers. The thickness of the GMN layer beneath the glass surface was about 100-200 nm (see Fig. 1).\textsuperscript{19} The transmission spectrum of the fabricated sample showed that the SPR wavelength was 428 nm, while the optical density at 800 nm was about 0.2.

In the experiment, we studied the transmittance of the GMN at the wavelength of 800 nm as a function of the incident pulse energy using a nonlinear transmittance measurement setup shown

![FIG. 1. TEM image of the GMN sample cross-section.](image1)

![FIG. 2. Experimental setup.](image2)
The pulse energy in the linear (horizontally) polarized beam of the Ti: Sapphire laser (pulse duration of 120 fs at 1 kHz repetition rate) was varied from zero to 9 µJ by rotating the half-wave plate (2) placed before the Glan polarizer (3). The beam splitter (4) divided the laser beam into the signal and reference beams. The reference photodetector (5) was used to register the laser pulse energy. The Glan polarizer (6) in the signal leg allowed us to avoid depolarization of the beam after the beam splitter. By rotating the half-wave plate (7) we controlled the polarization of the laser beam, which was focused on the GMN sample (9) by a lens with a focal length of \( f = 75 \text{ mm} \). The beam diameter on the sample surface was \( 2w_0 \approx 26 \mu \text{m} \). The signal detector (10) registered the energy of the transmitted pulse.

We measured the energy of the transmitted pulse as a function of the incident pulse energy by averaging data over 25 laser pulses. We increased gradually the laser fluence at the irradiated area, which underwent modification as soon as the pulse energy reached the threshold value. In our experimental conditions, the ablation was observed at the threshold incident pulse energy of 6.8 µJ (laser fluence of 1.28 J/cm\(^2\)). The surface of the processed samples was characterized with an optical microscope and scanning electron microscope Leo 1550 (Gemini).

**RESULTS AND DISCUSSION**

The dependence of the energy of transmitted pulse as a function of the incident pulse energy is shown in Fig. 3. One can see that below the ablation threshold of 6.8 µJ (1.28 J/cm\(^2\)), the energy of the transmitted pulse, \( W_t \), is a monotonous function of the energy of the incident pulse, \( W_{in} \). At \( W_{in} < 3 \mu J \) (0.57 J/cm\(^2\)), \( W_t \) is a linear function of \( W_{in} \). However, within the incident pulse energy range from 3 µJ up to 4.5 µJ (i.e. in the fluence range from 0.57 to 0.85 J/cm\(^2\)), the slope of the \( W_t (W_{in}) \) decreases. This is a signature of the reverse saturable absorption, which manifests itself as an increase of the absorption coefficient of the nanocomposite. It is worth noting that at the excitation wavelength of 400 nm, which is close to SPR, similar nonlinear behavior has been observed at three orders of magnitude lower fluence.\(^{21}\) According to our estimations, in the silver-based GMN, the local field strength at the SPR frequency is about 3.5 times higher than that at 800 nm giving rise to the observed difference in the nonlinear transmittance.

Importantly, at 3 µJ \(< W_{in} < 4.5 \mu J \), the energy of the transmitted pulse did not depend on whether we increased or decreased \( W_{in} \). This indicates that within this range, the femtosecond excitation does not produce irreversible modification of the GMN, i.e. no changes in metal concentration or in nanoparticles shape in the GMN subsurface layer take place.

When we increase the pulse energy further, the slope of the \( W_t (W_{in}) \) increases again and remains unchanged until \( W_{in} \approx 6.8 \mu J \) (1.28 J/cm\(^2\)) (see Fig. 3). However, at \( W_{in} > 4.5 \mu J \) (0.85 J/cm\(^2\)) the
FIG. 4. Low (a) and high (b) spatial resolution SEM images of the irradiated surface area of the GMN at the incident pulse energy of 6.7 µJ (1.26 J/cm²).

energy of the transmitted pulse depends on whether we increase or decrease $W_{in}$. Specifically, one can observe in Fig. 3 that the transmitted pulse energy is slightly lower when we decrease the energy (blue arrows) of the incident pulse from 6.8 µJ (1.28 J/cm²) down to zero. This indicates that in this energy range, the GMN undergoes irreversible modification that does not significantly change its transmittance.

Such a conclusion is confirmed by examining the GMN surface with the scanning electron microscope (SEM). Figure 4 shows that when the fluence is below the ablation threshold of 1.28 J/cm² the irradiation with femtosecond laser pulses results in the redistribution of the metallic silver in the subsurface layer. Specifically, nanoparticles move towards the surface from the inner subsurface regions. A similar effect has been observed at the irradiation of GMN surface with nanosecond laser pulses.\textsuperscript{13,14}

When the incident pulse energy exceeds 6.8 µJ (1.28 J/cm²), one can observe a sharp transmittance fall, i.e. $W_t$ is no longer a monotonous function of $W_{in}$ (see Fig. 5). Moreover, starting from $W_{in} = 6.8$ µJ, the energy of the transmitted pulse strongly depends on whether we increase or decrease $W_{in}$. This is a clear evidence that the incident pulse energy of $W_{in} = 6.8$ µJ corresponds to the GMN femtosecond ablation threshold. The whole measurement circle shown in Fig. 5 demonstrates that the modification of the GMN results in 1.5 times drop of the transmittance.

By examining SEM images of the GMN surface we discovered that the irreversible in the transmittance change was caused by femtosecond ablation, which is accompanied by the formation of

FIG. 5. Dependence of the energy of transmitted pulse on the energy of the incident pulse at $W_{in} < 8.0$ µJ. Blue, green, pink, and yellow areas correspond to the linear ($W_{in} < 3$ µJ), nonlinear (3 µJ < $W_{in} < 4.5$ µJ), modification (4.5 µJ < $W_{in} < 6.8$ µJ), and ablation ($W_{in} > 6.8$ µJ) regimes, respectively. Insets (1-5) show SEM images of the irradiated GMN surface for the above energy regions. Red and blue lines indicate the branches where measurements were performed at increasing and decreasing energy of the incident pulse, respectively.
FIG. 6. SEM images of the surface area irradiated by the horizontally polarized femtosecond laser beam with pulse energy of 6.9 µJ (a), 7.2 µJ (b) and 8 µJ (c).

nanoripples along the polarization of the laser beam. Figure 6 shows transformation of the ripples pattern from linear to circular when the incident fluence increases. The ripples oriented along the polarization of the laser beam (Fig. 6(a)) have been numerously observed (see review paper[7] for references). However, in our experiment, for the first time, we observe the change in the ripples pattern topology. The nanoripples are parallel to the beam polarization over the irradiated area when the pulse energy is slightly above ($W_{in} = 6.9$ µJ, fluence 1.3 J/cm$^2$) the ablation threshold (Fig. 6(a)). The increase of the pulse energy up to 7.2 µJ, (1.36 J/cm$^2$) is accompanied with the formation of the circular nanoripples pattern in the central area of the laser spot (Fig. 6(b)), and over nearly the complete irradiated area at $W_{in} = 8$ µJ (1.51 J/cm$^2$) shown in Fig. 6(c). One can observe from Fig. 6(c) that in the central area of the laser spot, the ripples take circular form, while in the periphery of the spot (where the laser fluence is lower) they remain parallel to the beam polarization.

The circular pattern in Fig. 6(c) resembles images of a plasmon-polariton wave excited on the metal surface by radially polarized laser beam.[22] Such resemblance may indicate that well above the ablation threshold, the injection of a dense electron plasma into a metal-enriched subsurface layer, which is produced by the focused femtosecond pulse, results in the excitation of plasmon polaritons in the GMN.[23–25]

Since the ablation crater depth was about 1 micron, one may expect that the metal nanoparticles were mainly ablated because they were formed in the 100-200 nm thick subsurface layer (see Fig. 1). This implies that in contrary to Ref. 11, the contrast in the SEM images (Fig. 6) originates from a finite height of the ripples. This is very different from the no-ablation regime when the drastic change in brightness of the SEM image of the GMN surface (compare insets 1 and 3 in Fig. 5) is due to the redistribution of the metal over the irradiated area.

To examine whether the modification of the GMN by horizontally polarized pulse resulted in optical anisotropy, we measured the transmittance of the modified area with a vertically polarized laser beam. We did not observe a measurable difference in the slope of the $W_t (W_{in})$, i.e. the circular HSF ripples shown in Fig. 6(c) did not result in a linear dichroism of the laser-modified GMN.

CONCLUSION

We show that in the non-resonant regime when the wavelength of the excitation pulse is away from the SPR, the irradiation of the glass-metal nanocomposite with femtosecond pulses, results in the formation of HSF ripples along the polarization of the laser beam. Surprisingly, increasing the pulse energy results in the evolution of the ripples pattern from the linear to the circular one. This experimental finding indicates that in our experimental conditions, the mechanism of the GMN modification is different from that in the resonant regime.[11] This new observation opens an exciting opportunity to employ transformation of the ripples topology for investigating the mechanisms of the interaction of the high-intensity laser beams with solids. The presence of metal inclusions makes GMN an attractive playground to study plasma-assisted processes driven by femtosecond optical pulses.
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