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Ultrashort laser induced spatial redistribution of silver species and nano-patterning of etching selectivity in silver-containing glasses

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Abstract: Femtosecond laser-induced spatial redistribution of silver species (ions, clusters, and hole centers) in a silver-containing phosphate glass is investigated by correlative means of near-field scanning optical microscopy (NSOM) images, numerical simulations, chemical micro-probe analysis, and nanoscale spatial profiles after soft etching. In particular, we found that the chemical etching selectivity for nanoscale patterning is strongly dependent upon the irradiation of femtosecond laser due to the spatial redistribution of silver species within the affected area. These results strongly indicate that controlling the distribution of silver species by femtosecond laser irradiation may open new routes for surface nanoscale chemical and/or spatial patterning for the fabrication of 2D surface photonic crystals.

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1. Introduction

Femtosecond (fs) laser modification technology of materials has made tremendous progress over the past decade, to access a large panel of applications that require special optical, physical and/or chemical properties associated with integrated bulk or surface functionalities [1]. While considering laser-induced element redistribution, most of the reported literature deals with processes in thermal regime with temperature increase above glass fusion [2,3]. Additional potentialities rely on the innovative synthesis of prepared materials with photosensitive agents [4]. In this framework, controlling the photosensitive agents under laser irradiation in a non-thermal regime, as well as the spatial redistribution and chemical evolution due to activated chemical reactivity, is of prime importance to achieve reliable nano- and micro-scale material changes with high optical quality. Such control and understanding is highly challenging since it involves multi-scale material changes, which requires correlative investigation approaches.

In this work, we present the correlative description of fs laser-induced spatial redistribution of silver species of our photosensitive silver-containing phosphate glasses, based on near-field scanning optical microscopy (NSOM) images, chemical micro-probe analysis, spatial profile after soft etching, and numerical simulations of the silver species redistribution. These results corroborate each other, and have led us to retrieve for the first time the nanoscale spatial profile of soft chemical etching rate of laser-induced modifications.

2. Experimental methods: glass preparation, laser irradiation and analyses

We have developed a silver-containing zinc phosphate glass $55\text{ZnO}/40\text{P}_2\text{O}_5/4\text{Ag}_2\text{O}/1\text{Ga}_2\text{O}_3$ (in mol. %), as previously detailed [5]. Direct laser writing (DLW) was carried out with a Yb

fs oscillator (Amplitude Systèmes, T-pulse 500, 9.1 MHz, 1030 nm, 390 fs FWHM), focused with a microscope objective (Mitutoyo, M Plan Apo NIR, 20 × N.A. 0.4) [5].

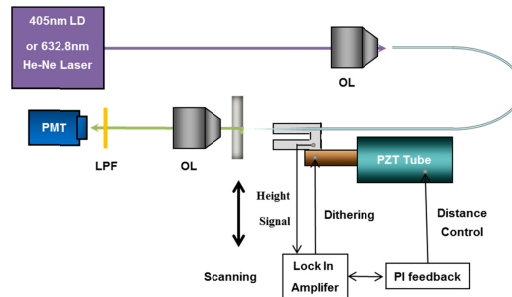


Fig. 1. NSOM setup in illumination mode, with light injection from a tapered optical fiber probe tip (100 nm aperture). LD: laser diode, objective lenses OL (focusing (20 × , 0.40NA) and imaging (40 × , 0.60NA)), LPF: long pass filter, PMT: photomultiplier detector.

DLW was performed to create a structure with a length of 400 μm by longitudinally translating the glass sample along the laser beam propagation. Sample velocity was 100 $\mu\text{m/s}$ and laser irradiance was 5-10 TW/cm^2 , typically. The irradiated sample was then re-polished perpendicularly to these fluorescent structures, to make them intersect the glass interface.

NSOM experiments were performed on the sample in illumination mode [6], where point-like light injection was achieved with a tapered optical fiber probe tip (100 nm aperture), as shown in Fig. 1. A nano-positioning stage allowed for ultrafine lateral scanning of regions of interest. The distance between the tip and the sample surface was stabilized by feedback control of a shear force detection system based on a quartz crystal tuning fork (resonance frequency of 32.768 kHz). The collection part of the setup (with a low NA objective and a single channel PMT detector) is a wide field collection. The spatial resolution of light injection results from the point-by-point scanning of the surface sample with the tapered optical fiber tip. Two wavelengths were considered, at 405 nm and 632.8 nm, to respectively achieve resonant and non-resonant evanescent coupling of the non-radiating light field from the output of the tapered optical fiber tip into free-optics propagation in the glass substrate.

3. Results and discussion

During NSOM experiment, the feedback control on the shear force positioning system showed no surface height modification while scanning a laser induced structure, indicating a truly flat surface at the structures after polishing, which excludes any topological artifact. Indeed, by injecting a laser diode excitation source at 405 nm and collecting light above 435 nm after a long-pass filter (Edmund GG-435), the high-resolution image of the transverse distribution of fluorescent silvers at the surface was obtained (see Fig. 2(a)). The horizontal cross section along the diameter of the fluorescent tubes is given by Fig. 2(c) (green curve). Similarly to confocal fluorescent imaging (not shown here), NSOM shows the clear annular distribution of silver clusters, the larger fluorescence pedestal coming from the concomitant excitation and fluorescence collection from planes below surface.

While injecting a He-Ne laser source at 632.8 nm and collecting light with a long-pass filter (665 nm, Edmund RG-665), the NSOM image (Fig. 2(b)) led to a non-zero background signal and a weakly brighter double-ring distribution (6% increase) that typically matches the position of the fluorescent ring image from Fig. 2(a), and to a darker distribution (17% decrease) inside the annular silver cluster distribution (Fig. 2(c), red curve). Similar NSOM image had also been obtained while collecting without the RG-665 long-pass filter: since the fluorescence excitation of both the randomly distributed Ag^+ ions and the 3D localized silver clusters is extremely weak while excited at 632.8 nm [7], we thus believe that measurements (Figs. 2(b) and 2(c), red curve) are mostly from the 632.8 nm residual background, after the non-resonant evanescent coupling.

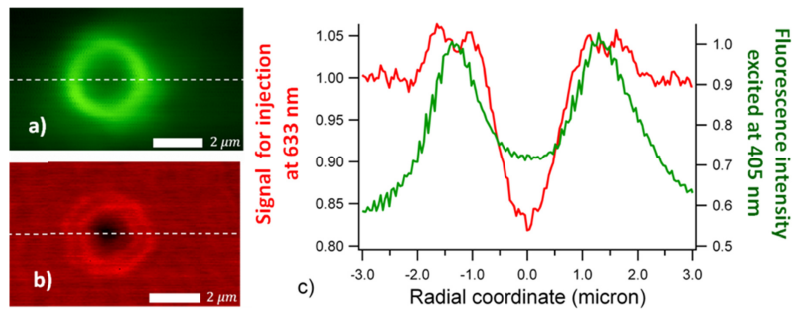


Fig. 2. (a,b) NSOM images with 405 nm and 633nm laser injections; (c) associated line profiles.

NSOM image with the He-Ne injection remarkably gave access to new insight concerning the laser-induced silver-mediated material modification, comparatively to the UV-excited counterpart. The proposed interpretation of the observed spatial distribution at 632.8 nm (Figs. 2(b) and 2(c)) is that it corresponds to a direct image of the local redistribution of silver element (ions and clusters) after DLW, as discussed hereafter. *First*, our phosphate glass typically shows a linear correlation between the refractive index of non-structured bulk samples and their silver content. *Second*, several reports evidence of the laser-induced migration of silver elements over mesoscopic scales (larger than 100 nm) during laser irradiation: *Bellec et al.* have shown by high-resolution electron scanning microscopy the enhancement of silver elements correlatively located at the position of the silver clusters [8]; by chemical analysis from electron microprobe, *Desmoulin et al.* have observed the partial depletion of the silver reservoir (about 10-20%) in the center of laser-induced silver-based annular structures (same structures as those of the present study) [9]; *Marquestaut et al.* have reported by back-scattered electron scanning microscopy that the created silver cluster distributions could further be thermally developed into 3D-localized plasmonic metallic silver nanoparticles [10]; *Third*, local index change can result from both a local density change and/or the local creation of new polarizable chemical bounds (as occurring for the creation of silver clusters). *Abou Khalil et al.* recently reported the direct correlation between spatial distributions of silver clusters and associated refractive index change [11]. Thus, light interaction at 632.8 nm with silver elements is mostly non-resonant. Any correlation between a local index change and the 3D distribution of silver elements can mostly be related to density aspects, thus to the local of silver element concentration (ions and clusters). Thus, non-resonant NSOM coupling efficiency appears as directly depending on the local refractive index experienced by the light field in the sub-wavelength regime at the glass surface, at the output of the tapered optical fiber tip. Thus, it directly depicts the spatial redistribution of silver elements (silver ions and clusters), as shown in Figs. 2(b) and 2(c).

Remarkably, the NSOM experience at 632.8 nm seems to be the first direct optically-based imaging (instead of electron beam approaches [8–10]) of the laser-induced reservoir depletion of silver ions and silver element redistribution. Although qualitative, the NSOM method appears as a unique imaging approach since it provides a great sensitivity to local composition dependences, while the chemical micro-probe analysis (although fully quantitative) generally shows a limited sensitivity of 1-2%: *Desmoulin et al.* had seen only the reservoir depletion of silver ions, but not the creation of silver clusters (see Fig. 3 from [9]). Consequently, NSOM and electron microprobe appear as highly complementary tools.

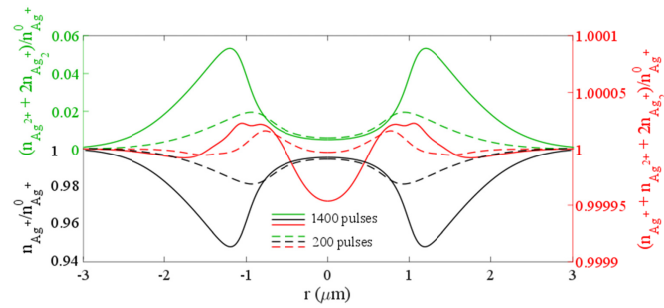


Fig. 3. Numerical modeling of the laser-induced redistribution of silver species (8.8 TW/cm², $N_{\text{pulses}} = 200$ or 1400), showing the profiles of the silver ions (black curve), the induced silver clusters and hole centers (red curve) and the overall silver elements (green curve).

To support the interpretation of non-resonant NSOM, numerical investigations were performed with our multi-scale multi-pulse multi-physics numerical model of laser-activated silver ion migration and photochemistry [12], considering similar laser irradiation parameters and silver-containing glass (intensity = 8.8 TW/cm², $N_{\text{pulses}} = 200$ or 1400, beam radius at the focal plane $r_0 = 2.5$ μm). The full calculated redistribution of silver species was extracted, including the silver ions (Ag^+), the induced silver clusters (Ag_2^+) and the remaining hole centers (Ag_2^{2+}). Figure 3 shows the normalized calculated silver element distributions: the Ag^+ ions (black curve), the total silver elements (red curve: $n_{\text{Ag}^+} + n_{\text{Ag}_2^{2+}} + 2n_{\text{Ag}_2^+}$), and the induced clusters and holes (green curve: $n_{\text{Ag}_2^{2+}} + 2n_{\text{Ag}_2^+}$). The numerical model obeys the overall conservation of silver elements. The Ag^+ distribution (black curve) shows both the central Ag^+ depletion due to their radial outward diffusion, but also their reduction at the periphery of the irradiated spot by chemical consumption to create the silver clusters (as observed also with the red curve of silver cluster and hole distributions). Still, the overall silver element distribution (red curve) confirms both the central depletion due to ion migration and the accumulation at the periphery due to the chemical precipitation and stabilization with silver clusters. Such silver element distribution (red curve of Fig. 3) remarkably matches the 1D cross-section of the He-Ne injected NSOM experiment (Fig. 2(c)), especially for $N_{\text{pulses}} = 1400$. The silver element redistribution (Fig. 3, red curve) shows a slightly smaller ring diameter than that of the simulated silver clusters (Fig. 3, green curve), possibly corresponding to the non-resonant NSOM double-ring structure (Fig. 2(c), red curve). This corroborates the interpretation of the NSOM approach, strengthening our description of laser-activated mechanisms of silver-containing glasses in an athermal regime.

To go further, spatially-distributed etching rates have been investigated, by correlatively considering the spatial distribution of silver elements from micro-probe measurements [9] and the present NSOM data. Figure 4(a) depicts the experimental surface morphology of the laser-modified area revealed after 6 minutes soft etching with deionized water (blue curve, from [9]). Spatial etching rate distributions have been designed (Fig. 4(a), green curve) [13], so that the simulation of the associated simulated etching process leads to a surface profile (Fig. 4(a), red curve) in very good agreement with the experimental surface profile (Fig. 4(a), blue curve). The optimized etching rate profile shows the normalized behavior of the pristine glass at the periphery of the laser-modified area (typically corresponding to 0.22 nm/s for the considered soft etching conditions). At the position of silver clusters, the etching rate strongly drops by a factor of 20.6, corresponding to a chemically hardened area of the laser-modified glass. Between the silver cluster localization, the etching rate shows a Gaussian-like distribution (FWHM = 310 nm), with central and pedestal values being 2.5 times larger and 1.8 times smaller, respectively, than that of the pristine glass. This shows a very strong chemically-sensitive material modification highly located in the center of the laser irradiation, with non-trivial etching sensitivity distributions. Figure 4(b) provides then the comparison of such etching rate distribution (green curve) with the micro-probe measurement of the silver

element distribution (blue curve, from [11]) and the present non-resonant NSOM measurement interpreted as the refractive index spatial distribution (red curve), independently revealing the presence of the three same laser-affected areas.

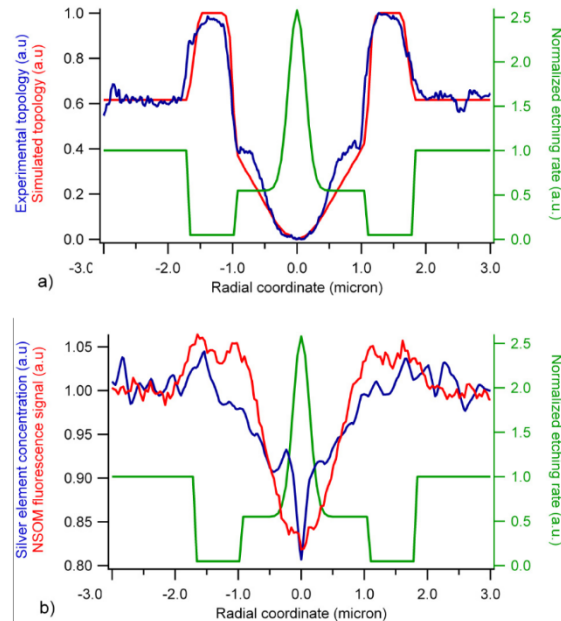


Fig. 4. (a) Experimental topological profile (blue curve) and simulated etching-induced topological profile (red curve) adjusted by optimizing the normalized etching rate distribution (green curve). (b) Silver element distribution by micro-probe measurement (blue curve, from [9]) and NSOM measurement (red curve, from Fig. 3(d)) with respect to the optimized normalized etching rate distribution (green curve).

Indeed, the NSOM measurements of silver element accumulation and cluster creation correlate with a very low etching rate (radius between 1 to 1.8 μm). Moreover, the silver reservoir depletion is independently shown by NSOM and electron micro-probe. Finally, the estimation of a very strong on-axis etching rate (240 nm, FWHM, green curve) corroborates the very narrow on-axis silver depletion (sub-200 nm, FWHM, blue curve), which may even be seen in the on-axis NSOM trace (red curve). Thus, laser-induced index change distributions [11] as well as the spatially-distributed etching rate depend here on the local concentration and nature of silver species [14], and on additional glass matrix rearrangements such as release of molecular oxygen to ensure charge compensation and material stabilization, as reported in thermal poling [15] or for glass irradiations in a thermal regime [16].

4. Conclusion

In conclusion, we have reported for the first time the correlative description of laser-induced silver redistribution in terms of chemical micro-probe, NSOM and numerical modeling. The results significantly strengthen the understanding of material modifications in such glasses in a non-thermal interaction regime. In particular, it has been found that the spatial distribution of species in silver-containing glasses produced by femtosecond laser irradiation has a significant effect on chemical etching selectivity. This should help for future development of nanoscale surface chemical patterning, such as for 2D photonics crystal applications [17].

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