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Laser-Induced, Polarization Dependent Shape Transformation of Au/Ag Nanoparticles in Glass

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Abstract Bimetallic, initially spherical Ag/Au nanoparticles in glass prepared by ion implantation have been irradiated with intense femtosecond laser pulses at intensities still below the damage threshold of the material surface. This high-intensity laser processing produces dichroism in the irradiated region, which can be assigned to the observed anisotropic nanoparticle shapes with preferential orientation of the longer particle axis along the direction of laser polarization. In addition, the particle sizes have considerably been increased upon processing.

Keywords Alloy nanoparticles · Glass · Laser irradiation · Femtosecond laser processing · Dichroism

Nano-sized metal particles embedded in glass are of great interest because of their potential application as non-linear material for photonic devices [1, 2]. The non-linear properties of nanocomposite glasses equipped with such particles are induced by the surface plasmon resonance at the interface between particles and glass matrix. This means that the optical effects in the spectral region around the surface plasmon resonance result from an electric field enhancement or a quantum confinement. Thus, applications are possible as in integrated photonic networks, in nanoelectronics, for surface enhanced Raman scattering, for upconversion processes and laser materials. Recently, the preparation of specific bimetallic nanoparticles like core-shell structures has been intensively investigated because of the far-reaching possibilities to modify the macroscopic properties [3–6]. A special way to extend the range of manipulating the optical properties of such nanocomposite glasses can be achieved by a development of central voids within the particles. There are known some first examples for hollow nanoparticles in glass that were prepared by sequential implantation of two different metal ions [6–8].

A further degree of freedom introducing anisotropic optical properties is the method of femtosecond laser pulse-induced shape transformation of the nanoparticles which has been studied intensively in recent years [9–11]. Depending on the actual irradiation parameters, uniformly oriented prolate or oblate nanoparticles can be prepared, whose orientation is controlled by the laser polarization [12]. So far these effects have been demonstrated for Ag nanoparticles at low concentration. In this Letter, we will demonstrate that a similar shape modification of initially spherical bimetallic and hollow Ag/Au nanoparticles in soda-lime glasses is possible by irradiation with femtosecond laser pulses at high intensity, but below damage threshold; in particular, it will be shown that anisotropic particle shapes or nearly linear arrangements of nanoparticles with preferential orientation along the direction of laser polarization can be fabricated with the help of this irradiation technique.

The samples used for this study were sheets of soda-lime glass containing (in mol%) 72.4% SiO_2 and 14.4% Na_2O as main components, which were exposed subsequently to Au^+ (150 keV) and Ag^+ (100 keV) ion implantation at

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room temperature. By this sequential high-dose ion implantation of Ag^+ and Au^+, metal particles have been formed in a surface-near region of the soda-lime silicate glass. The dose of implanted ions was 4×10^{16} ions/cm^2 for each type of ions (for further details see [8]). To characterize the surface plasmon resonance due to the metal nanoparticles formed in the implanted areas the optical density of glass samples was recorded by means of a Perkin-Elmer spectrometer in the wavelength range of 250–900 nm. These samples were irradiated by linearly polarized laser pulses of 150 fs temporal width at a wavelength $\lambda = 550$ nm. This wavelength is the sum frequency of a 1 kHz repetition rate Ti:Sapphire laser at $\lambda = 800$ nm and the idler ($\lambda = 1{,}760$ nm) of a Travelling-wave Optical Parametric Amplifier of Superfluorescence (TOPAS). The laser beam was focused on the sample to a spot size of ~ 100 μm. Moving the sample continuously on a motorized X–Y translation stage, several parallel lines of ~ 1.5 mm length and 150 μm lateral distance have been inscribed in the glass at a velocity of 0.5 mm/s, corresponding to, on average, 200 laser pulses hitting each spot within the lines. The polarization direction of the laser was parallel to the lines (writing direction).

The effect of irradiating the sample in the described way with average single pulse energy of 20 μJ is shown in Figs. 1 (microscope images) and 2 (optical absorption spectra). The lines prepared by high intensity fs laser irradiation exhibit a certain subdivision into a few parallel traces of decoloration as well as, at a few positions along the line center, some damage at the very glass surface. In the central region (width ~ 50 μm) the lines clearly show dichroism (see Figs. 1, 2). In the outer regions of the lines there is still a color change visible, but the dichroism decreases continuously to that of the original glass region.

To evaluate the nanoscopic background of the observed optical changes, the parameters mean size, size distribution, shape, and penetration depth of the metal particles have been examined by transmission electron microscopy (TEM) using

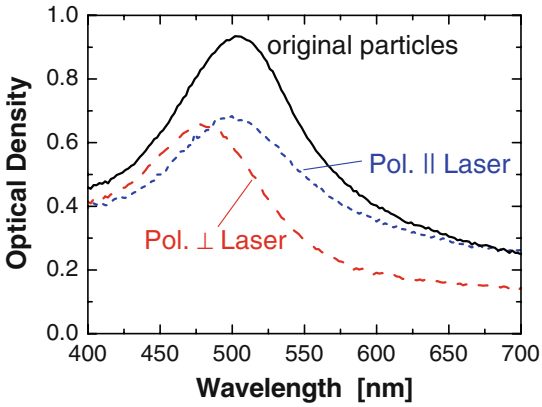

Fig. 2 Optical density within the central region of irradiated glass measured before (original glass, *solid line*) and after laser irradiation with polarized light, parallel (*dotted*) or perpendicular (*dashed*) with respect to laser pulse polarization and line direction (see Fig. 1). The spectra of non-irradiated samples are identical for parallel and perpendicular polarization

a JEM 1010 operating at 100 kV and a JEM 4010 operating at 400 kV. For this purpose, planar and cross-section preparation were applied including mechanical grinding, polishing and argon ion-beam etching followed by deposition of a thin carbon film on both sides. For the samples of this study, prepared by applying an ion dose of 4×10^{16}/cm^2 for both of the metals, a particle-containing region has been obtained that extends from the very glass surface to a depth of about 135 nm. TEM imaging of cross-section samples reveals that this particle layer exhibits a non-uniform spatial distribution of particles as already reported earlier [8]. In the middle of the particle layer mainly larger particles are situated whose anomalous image contrasts point to the presence of voids in their interior as may be recognized from the TEM image of a planar preparation sample shown in Fig. 3. While for the entire set of particles present in the layer a mean size of 5.34 ± 3.89 nm has been determined, the mean outer diameter of the void-containing particles amounts to 16.2 nm. Altogether the particle sizes range from

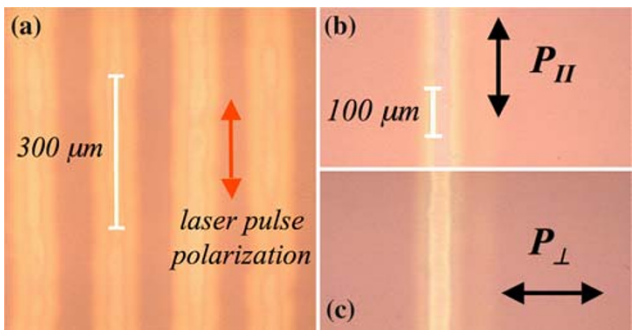

Fig. 1 Optical micrographs of the Au/Ag nanoparticles containing glass after laser irradiation recorded using **a** non-polarized, and **b**, **c** polarized light, respectively

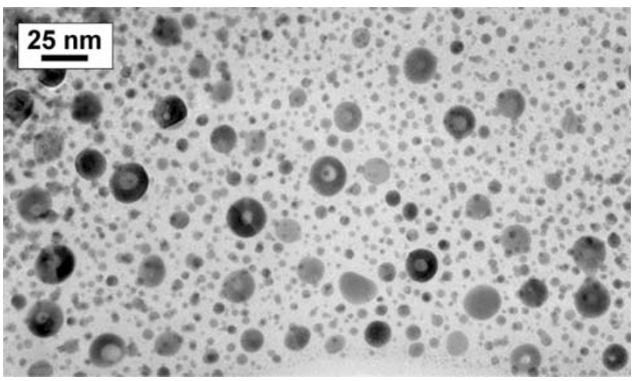

Fig. 3 TEM micrograph of the 4×10^{16}/cm^2 Ag^+ and 4×10^{16}/cm^2 Au^+ ion implanted sample

about 1.5–24 nm. The frequency of the surface plasmon resonance of the non-irradiated glass (see Fig. 2) appearing between those of pure Ag and Au particles demonstrates the formation of Ag–Au alloy nanoparticles. The relation of concentrations of both elements incorporated into the nanoparticles should be ~1:1 corresponding to calculations of theoretical spectra [13] and to experiments by anomalous small angle X-ray scattering [14].

The above-described ultrashort laser pulse processing of this sample resulted in a totally different appearance of the structural characteristics of this particles-in-glass composite material which, however, is restricted to those regions where the laser lines have been inscribed into the particle layer. By careful target preparation we achieved to place the position of the hole at the edge of one of these lines; this allowed us to image within one specimen regions without laser irradiation as well as regions where the maximum laser pulse intensity had been applied. The TEM examination reveals that ultrashort laser pulse processing causes fundamental changes in size, shape, arrangement and configuration of the metal nanoparticles in the irradiated regions (see Fig. 4), whereas no changes can be observed in non-irradiated regions. In the center of the irradiated regions the particles exhibit distinctly increased size, but none of them contains a void. Most of the larger particles are elongated nearly along a common direction parallel to the laser lines inscribed (and thus along the laser polarization vector). The elongated particle shapes may be described as spheroidal, but with a certain degree of irregularity. Altogether the particle dimensions range from about 4.4 to 52.6 nm for the minor axis (mean value 16.68 ± 8.69) and from 5.6 to 79.6 nm for the major axis (mean value 20.98 ± 13.47). The aspect ratio (i.e., the ratio of major to minor axes lengths) of the particles increases nearly linearly from a value of 1 for particles of about 4.7 nm diameter to a value of 1.5 for particles of about 60.4 nm diameter (these diameters refer to spheres of the same volume as the spheroids have). The total increase in particle size compared to the initial situation in the sample before irradiation corresponds to a more than ten-fold volume increase for the individual particle. So, the laser processing resulted in a totally different appearance, not only the particle dimensions have increased by a factor of 3, but also the size distribution has become a little bit narrower and lost part of its asymmetry, and, what is the important issue in this result, shape and arrangement of the particles deviate from the previous isotropic appearance. On the other hand the optical absorption remains fairly constant or even decreases indicating that the total amount of silver and gold does not grow. So it can be concluded that the volume increase of the particles is compensated by a simultaneous decrease of their number. The optical spectra also show that the composition of alloy nanoparticles should be similar to that before the irradiation. There are only slight shifts due to variations in sizes of particles and concentrations of elements within the particles.

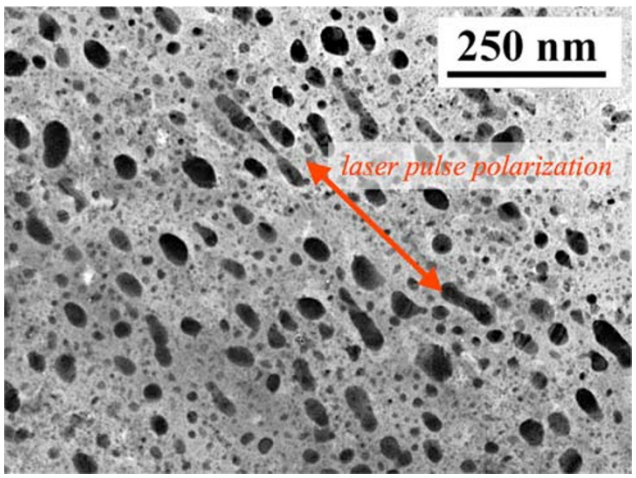

Fig. 4 TEM micrograph of the above sample upon ultrashort laser pulse irradiation

Finally, we want to discuss briefly which physical mechanisms may lead to the observed shape changes of bimetallic nanoparticles upon intense fs laser irradiation, in particular explaining the preferential orientation of elongated particles more or less arranged parallel to the laser polarization. The shape changes observed here can be compared to similar previous results obtained on two quite different types of metal-dielectric nanocomposites. The first type of material is glass containing low concentration of Ag nanoparticles. For such systems it has been found that only the individual particle and its immediate surroundings are affected by laser-induced modifications. The sequence of processes there starts with field-driven electron emission from the particle, followed by electron trapping in the glass matrix, ion emission, their local recombination with trapped electrons, and diffusion and precipitation of Ag atoms at the poles of the particle in the transiently heated nearest shell of the matrix [11]. The second type of material studied previously is plasma polymer embedding a quasi 2-dimensional metal island film. Irradiating these systems with similar parameters as in this work, a grating-like superstructure oriented along the laser polarization with a typical period of 2/3 of the laser wavelength has been observed, where stripes of unchanged metal nanostructure (percolation region) are alternating with stripes of coagulated larger, spherical particles [15]. The explanation for these self-organized structures comprises spatially modulated energy input in the metal layer by interference of the incoming laser light with the scattered surface wave, where statistical inhomogeneities of the sample provide a feedback, so that the structures are becoming more pronounced and regular shot by shot.

The shape changes reported here are somehow intermediate between the abovementioned limiting cases. Comparing the situation with the plasma polymer samples, we here also observe a large increase of particle sizes, but no regular superstructure. Comparing with isolated Ag nanoparticles in glass, we also find individual non-spherical shapes with the long axes oriented preferentially along the laser polarization; but, in addition, particles are growing and sometimes merging, preferentially in situations where together they form a coagulated particle with longer axis along the laser polarization.

From these considerations we conclude that the laser-induced shape changes of bimetallic nanoparticles are initiated by the same mechanisms as in the case of low-concentrated Ag nanoparticles, i.e., directional electron emission and capture in the glass matrix, followed by the processes listed above. The main difference appears to come from the higher metal concentration leading to spatially and temporally more extended regions of high temperature around metal particles in the matrix, enabling much larger diffusion distances of electrons and metal ions or atoms. It cannot be decided at present if, in addition to the basic mechanism of particle reshaping during laser irradiation (migration of individual atoms or ions), also processes like migration and coalescence of very small particles contribute to the observed particle growth. The reason is that all processes are started by an $\sim$100 fs laser pulse; then the surrounding glass is heated within a few *ps* and cools down again by heat conduction within a few *ns* [16]. Particle formation or growth under such strongly non-equilibrium conditions has, to the best of our knowledge, so far not been modeled theoretically.

Still, however, the local trapping sites for electrons in glass are obviously a necessary prerequisite for shape anisotropy of the particles. This is confirmed by the lack of similar shape anisotropy of the metal particles after fs irradiation in plasma polymers. Furthermore, the temperature increase during laser irradiation within the particle regions explains the transformation of hollow particles into solid ones because of their thermal instability [17, 18]. The vacancies leave the central void toward the outer surface and the hollow region disappears at elevated temperatures. The laser-induced changes of shape and configuration of nanoparticles described above can also explain the slight blue shift of the surface plasmon resonance observed for perpendicularly polarized light as well as the lacking red-shift for parallel polarization (as shown in Fig. 3). From the reduced total optical density after laser treatment, one can conclude a reduced concentration of precipitated particles compared with the nanocomposites before irradiation. That is, obviously the recombination of emitted ions with trapped electrons is not completed. While, however, the probability for emission during interaction with an ultrashort laser pulse is the same for Au and Ag ions, the mobility of Au in the glass matrix is considerably less than that of Ag species. This difference should also affect the amount of both elements being incorporated into the particles again; so in the end the concentration ratio in the particles will be shifted toward Ag atoms, and this will shift their plasmon resonances toward shorter wavelengths.

In conclusion, we have shown that spherical, bimetallic Au/Ag nanoparticles in glass at high concentration can be transformed to anisotropic shapes (accompanied by size increase) preferentially oriented along the direction of the linear laser polarization. The mechanism appears to be similar to that observed for silver nanoparticles in glass at low concentration, but with additional effects like coalescence caused by the close proximity of the particles. Overall, the demonstrated high-intensity laser processing is a promising and flexible technique to design the linear and nonlinear optical properties of metal-glass nanocomposites.

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