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Reorganizing and shaping of embedded near-coalescence silver nanoparticles with off-resonance femtosecond laser pulses

G Baraldi, J Gonzalo, J Solis and J Siegel

Laser Processing Group, Instituto de Óptica, CSIC, Serrano 121, 28006 Madrid, Spain

E-mail: j.siegel@io.cfmac.csic.es

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Abstract

We demonstrate that 2D distributions of non-spherical near-coalescence silver nanoparticles (NPs) embedded in an ultrathin dielectric film can be reorganized, shaped and aligned by exposure to ultrashort laser pulses. As-grown samples prepared by pulsed laser deposition show a broad absorption band with a surface plasmon resonance (SPR) at 650 nm, which can be blue-shifted down to 440 nm and transformed to show polarization anisotropy. In situ white light probing of the spectral sample transmission allows control during irradiation of the position and polarization anisotropy of the SPR, effectively controlling particle reorganization and shaping. Using the high spatial resolution of the optical probe technique (better than 10 µm), the dependence of the nanoparticle shape and distribution on the local fluence can be studied in a single irradiated region. The results inferred from the spectral measurements have been confirmed by TEM studies, showing the formation of nanoparticles with prolate shape, preferential alignment along the polarization axis of the laser and a narrow size distribution. This simple and efficient approach for NP shaping and the straightforward extension to multilayer systems offer excellent perspectives for optical encoding, multidimensional data storage and fabrication of complex, polarization-sensitive spectral masks starting from thin films with near-coalescence distributions of NPs.

(Some figures may appear in colour only in the online journal)

1. Introduction

Metal nanoparticles (NPs) embedded in dielectric hosts form new material systems with exciting optical properties. In particular, the appearance of surface plasmon resonances (SPRs) in these materials related to the size, shape and separation of the NPs, amongst other factors, provides an opportunity to design devices with a tailored spectral response [1–3]. Among the different techniques for fabrication of nanostructured films, such as physical vapor deposition, sputtering and lithography, pulsed laser deposition (PLD) [4, 5] is a suitable technique for producing in a single-step process single and multilayer NP structures as well as columnar structures [4, 6]. However, it remains a challenge to produce NPs with well defined symmetry axes (e.g. oblate or prolate spheroids) and preferential alignment in order to exploit the resulting dichroic optical response. Different solutions have been proposed to overcome this limitation, that usually affects most of the fabrication techniques based on physical methods. One approach is based on the use of nanostructured substrates in order to achieve controlled growth of regular arrays of silver nanoparticle chains [7] or stripes [8]. A different approach, which is compatible with unpatterned substrates, has been demonstrated very recently, and is based on physical vapor deposition at glancing angle combined with post-treatment with a low power infrared nanosecond YAG laser [9]. The authors achieve alignment and shaping of NPs accompanied by the corresponding changes in the optical response (SPR shifts and polarization anisotropy). The role of the laser is to heat, preferentially melt and merge certain NPs. In all these cases, though, shaping is performed on NPs at the substrate surface exposed to air, which is especially problematic for silver since it is known to degrade via oxidation [10].
Kaempfe et al have introduced a method to change the shape of glass-embedded spherical silver NPs via irradiation with femtosecond (fs) laser pulses [11]. The authors observed a fluence-dependent broadening and red-shift in the extinction spectrum together with dichroism, which they demonstrated to be related to an increase in the particle diameter and a shape change from spheres to oblate spheroids. Despite being embedded in a matrix, the high peak intensities of ultrashort laser pulses enable NP reshaping. Other studies have built on this pioneering work and report, for instance, on the shaping into prolate spheroids with large aspect ratios [12] or into nanodisks [13], and on ex situ particle shape analysis via optical characterization [14]. In all cases, the initial state before irradiation corresponds to spherical NPs with a narrow size distribution embedded in a glass matrix produced by ion exchange followed by annealing in H₂.

In this paper we present results of very heterogeneous 2D distributions of highly non-spherical and randomly oriented NPs embedded in an ultrathin dielectric film produced in a single-step process by PLD at room temperature, which reshape and self-organize upon fs laser irradiation. We also demonstrate how a spectral monitoring system with high spatial resolution can be implemented to monitor in situ the final particle shape upon irradiation, providing information on the laser fluorescence dependence of the process.

2. Experimental details

The samples used in our experiment consisted of a single layer of Ag NPs embedded in amorphous Al₂O₃, deposited on fused silica or carbon-coated mica substrates, the latter being used for TEM studies. The samples were produced by alternate PLD (a-PLD) in vacuum (2 × 10⁻⁶ mbar) of polycrystalline Al₂O₃ and Ag rotating targets at room temperature using a focused ArF excimer laser (λ = 193 nm, τ = 25 ns full-width at half-maximum, E = 2.5 J cm⁻²). The use of a-PLD allows precise control of the size of the NPs as well as the thickness of the underneath and covering a-Al₂O₃ layers through the number of laser pulses on each target [15]. In the present case, the size of the Ag NPs was selected to be near coalescence and the thickness of the a-Al₂O₃ buffer and cover layers were 10 nm and 22 nm, respectively, achieving an overall film thickness of less than 50 nm. The use of a sandwich structure ensured the silver NPs were protected from degradation via atmospheric corrosion [10]. Further details of the preparation procedure can be found elsewhere [15]. Figure 1(a) shows a transmission electron microscopy (TEM) image of the NP film, illustrating the highly non-spherical shape and near-coalescence distribution of the NPs. The corresponding transmission spectrum for unpolarized light is also included in figure 1(a). It displays an SPR centered at λ_{SPR} = 650 nm with a broad tail reaching the near infrared region.

The experimental setup used for NP reshaping consisted of a three axis motorized sample stage, a focused laser beam incident at 53°, an in situ microscope with 400 nm LED illumination installed normal to the sample surface (z-axis) and a white light illumination point probing of the region exposed to the laser, whose transmission was detected by a fiber spectrometer. The laser used was an amplified Ti:Sa laser with 800 nm wavelength, 100 fs pulse duration and a repetition rate of 100 Hz, s polarized and frequency doubled to λ_{irr} = 400 nm before focusing it with a 150 mm lens. It is worth noting that the use of 400 nm wavelength for irradiation implies off-resonance excitation of NPs, as opposed to the standard approach of resonant excitation by other groups [11, 12, 14]. We have chosen s polarization in order to set the polarization vector in the surface plane. For p- or other polarization configurations, the polarization vector would have had components along the film depth, due to the 53° angle of incidence, which would make the interpretation of transmission spectra non-trivial. The intensity distribution at the sample plane was measured to be Gaussian with a spot size of 98.4 μm × 59.2 μm (1/e² diameter). A half-wave plate was used to ensure that the polarization of the 400 nm light was along the y-axis, i.e. perpendicular to the plane of incidence. Following the observations of other groups that irradiation with hundreds of low energy pulses has a stronger effect on the NP shape than a single pulse of high energy [11, 12, 14], we used a constant pulse number of n = 200 in the present study.

Figure 1. (a) TEM image of the embedded Ag nanoparticle layer before irradiation and corresponding optical transmission spectrum with unpolarized light (inset). (b) Sketch of the fs laser irradiation (400 nm) and transmission point probe (white light) setup. Two different positions of the probe beam are drawn, inside and outside the laser-irradiated spot, in order to highlight the strong change in the optical response induced.
The central region of the laser-exposed region has been probed by a focused white light beam incident from the back of the sample (z-direction), as schematically shown in figure 1(b). In order to achieve a small white light spot, we placed a circular aperture with a diameter of 550 µm in front of the fiber bundle connected to the source (Hamamatsu Lightningcure 200) and imaged this aperture onto the front surface of the sample using an 80× long working distance objective lens. Care was taken to achieve a sharp image of the aperture at the sample plane with help of the in situ microscope, which also enabled us to position the white light probe in the center of the irradiated area. The nominal white light spot size is 7 µm, and we measured it to be less than 10 µm. The transmitted light was collimated by the objective lens of the in situ microscope and focused onto the end face of a fiber connected to a spectrometer. A linear polarizer in front of the 80× lens allowed rotation of the polarization of the incident probe light between the x- and y-axes (perpendicular and parallel to the laser polarization, respectively).

Ex situ characterization of the laser-irradiated regions has been performed using an optical microscope with a 100× objective lens (N.A. = 0.9) employing white light illumination. Optical micrographs have been recorded in both reflection and transmission with a color digital camera. The size, morphology and organization of the embedded Ag NPs, both in laser-irradiated regions and in unexposed regions, have been investigated by transmission electron microscopy (TEM) in plan-view configuration using a LEO 910 operating at 120 kV. The samples were prepared by depositing laser-irradiated films from carbon-coated mica substrates on deionized water and picking them up on Cu grids.

3. Results and discussion

We have performed a series of irradiations with fs laser pulses at increasing fluence, using a constant pulse number n = 200 for each fluence. The in situ microscope allowed us to monitor in situ visible laser-induced reflectivity changes in the sample. In particular, a slight reflectivity increase was observed when the laser fluence increased above 31 mJ cm$^{-2}$, and a strong increase for energies above 52 mJ cm$^{-2}$. After irradiation the exposed regions have been studied ex situ in reflection with white light illumination and a color digital camera. Figure 2(a) shows an optical micrograph of a region of the sample grown on fused silica after exposure to 200 pulses at 66 mJ cm$^{-2}$.

A strong color change is observed in the laser-exposed region, ranging from orange for the unexposed region over black at the spot border to green at the spot center. For comparison, figure 2(b) displays a transmission micrograph of the same region, which shows essentially the opposite behavior, changing from greenish for the unexposed region over yellow at the spot border to orange at the spot center. These images beautifully demonstrate the laser-induced strong change in the optical response. It is worth noting that the high reflectivity (for green light) in the spot center (figure 2(a)) demonstrates that the film has experienced no ablation but a change in its optical properties. Since the anular region has experienced a lower local laser fluence, showing up as black in the reflectivity image and yellow in the transmission image, we interpret this optical response as bleaching within this spectral region. The strong change in the optical response highlights the potential of this technique for optical encoding [16] and multidimensional data storage [17] applications.

Figure 2(c) shows the spectra recorded with the in situ white light point probe setup. The spectra for both polarizations of the region before irradiation are practically identical, which confirms that the NPs have no preferred orientation as shown by the TEM image in figure 1. Moreover, the spectra are consistent with the colors of the unexposed region in the microscopy images shown in figures 2(a) and (b), since orange and red will be reflected and green and blue transmitted. The weak appearance of blue color in the images is due to the fact that the spectral intensity of the blue region of the white light source is low and the sensitivity of the digital camera in this spectral region is reduced. The spectra after...
irradiation are very different, which confirms that the laser pulses have reshaped the NPs, resulting in a large shift of the SPR from the red to the blue spectral region. The strong decrease in transmission in the blue–green spectral range is consistent with the color change in the laser-exposed regions in the microscopy images in figures 2(a) and (b). Besides, the polarization dependence of the spectra after irradiation indicates the formation of non-spherical NP with a preferred orientation. The SPR peak for $T_x$ lies at 440 nm compared to the peak of $T_y$ located at 500 nm, resulting in a peak shift of $\Delta \lambda_{\text{anisotropy}} = 60$ nm. These results indicate that the long axis of the ellipsoids formed is aligned along the orientation of the polarization of the laser light (y-axis). NP deformation into prolate spheroids along the axis of the laser polarization upon resonant excitation with multiple fs laser pulses has been reported [14] for spherical NPs prepared by a different method. The shaping mechanism proposed by the authors involves field-driven electron emission, preferably from the poles of the metal particles along the polarization axis, which will be trapped in the matrix, accompanied by emission of Ag ions, which eventually recombine at the poles [18]. We recall at this point that our experimental conditions correspond to off-resonance excitation of NPs, which might induce different mechanisms. We have confirmed, though, that NP reshaping accompanied by a blue-shift of the SPR is also possible with 800 nm excitation, although clear differences w.r.t. excitation at 400 nm are observed. A comparative study to investigate the role of non-resonant excitation in NP shaping is currently underway.

In order to investigate the shape and size changes of the NPs we have performed laser irradiations on the NP sample grown on carbon-coated mica in order to facilitate TEM studies of the laser-irradiated regions. We have ensured that the transmission spectra of the non-irradiated regions of the samples on mica and on glass are the same, in order to ensure a similar initial NP distribution. Figure 3(a) shows a TEM image of the film before irradiation, together with the corresponding fast Fourier transform (FFT) of the image, featuring a broad, circular distribution of spatial frequencies corresponding to an NP distribution with a broad size range and no preferential alignment.

The TEM image of the film after irradiation (cf figure 3(b)) is very different, as it displays a much lower number of NPs with a higher particle separation and an almost circular appearance. The corresponding FFT of the image reveals an elliptic distribution of spatial frequencies, with its short axis being aligned along the laser polarization direction. This axis corresponds to the long axis of the NPs in real space, which confirms unambiguously that the NPs have been reshaped into prolate spheroids. The average NP size of the sample can be extracted from the FFT images and yields values of $d = 11.3$ nm before irradiation and $d = 17.2$ nm for the short axis and $d = 20$ nm for the long axis after irradiation. The resulting aspect ratio of the prolate spheroids formed by laser irradiation is thus $d_s/d_l = 0.86 \pm 0.04$. It is worth noting that even such small shape anisotropy is capable of generating a pronounced anisotropy in the optical response, as shown in figure 2(c). We have measured the optical response of the irradiated region in this particular sample on carbon-coated mica and found the difference of the SPR peaks to be $\Delta \lambda_{\text{anisotropy}} = 33$ nm. The considerably smaller value compared to the one achieved on fused silica substrate is caused by the fact that irradiations performed in the film on carbon-coated mica had to be done at lower fluence (52 mJ cm$^{-2}$) in order to avoid sample damage, likely due to the lower thermal conductivity of the substrate. This implies that the aspect ratio of the spheroids achievable in the film on fused silica is higher.

In order to study the fluence dependence of the laser irradiation on NP reshaping, we have exploited both the high spatial resolution (<10 μm) of our in situ transmission probe configuration and the Gaussian spatial intensity distribution of the laser beam at the surface. The latter allows assignment of a well defined local fluence value to each spatial position of the irradiated area [19]. An alternative strategy for recording fluence-resolved spectra has been implemented by Stalmashonak et al, who projected the image of the irradiated area on the entrance slit of an imaging spectrometer [18]. Figure 4(a) shows the transmission image of the laser-irradiated region, in which the marked spatial positions, separated by 10 μm, have been measured individually. The corresponding $T_x$ and $T_y$ spectra (shown in figures 4(b)–(f))

![Figure 3](image-url)
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Figure 4. (a) Optical transmission microscopy image of the laser-irradiated region shown in figure 2(b). (b)–(f) Optical transmission spectra with polarized white light measured at the positions marked by the different symbols in (a). Each local position corresponds to a specific local fluence, quoted in each plot. The solid curves correspond to polarization along the $x$-axis, the dashed ones along the $y$-axis, with $y$ being the orientation of the laser polarization. The symbol size in (a) corresponds approximately to the size of the probe beam (<10 µm).

clearly show the continuous evolution of the NP shape with increasing (local) fluence.

At the border of the laser-modified region (figure 4(b), 18 mJ cm$^{-2}$) a weak shift of the SPR at $\lambda_{SPR} = 580$ nm (w.r.t. that one of the as-grown film, $\lambda_{SPR} = 650$ nm) is observed. Moving by 10 µm towards the spot center (cf figure 4(c), 31 mJ cm$^{-2}$), the measured spectra have changed completely, featuring a strong increase in transmission for $\lambda > 500$ nm and the formation of a strongly shifted SPR at $\lambda_{SPR} = 460$ nm. While up to this local fluence the $T_x$ and $T_y$ spectra showed no polarization anisotropy, a further increase in local fluence (figure 4(d), 47 mJ cm$^{-2}$) causes a splitting of the spectra, which further increases upon approaching the spot center (figures 4(e) and (f), 61 and 66 mJ cm$^{-2}$). In parallel with the splitting, the amplitude of the SPR increases significantly.

The observed evolution of the spectra as a function of local fluence provides a hint at the underlying mechanisms of self-organization and shaping in the present situation of near-coalescence NPs. In particular, the evolution of the spectra from figures 4(b) to (c) is consistent with bleaching of the broad absorption band in the red spectral region. Although the spatial position of this measurement did not fall entirely into the region of the yellow ring in figure 4(a), which we identified earlier as the region in which bleaching has occurred (cf figures 2(a) and (b)), a marked recovery of the transmission for $\lambda > 500$ nm and the formation of a strongly shifted SPR at $\lambda_{SPR} = 460$ nm. While up to this local fluence the $T_x$ and $T_y$ spectra showed no polarization anisotropy, a further increase in local fluence (figure 4(d), 47 mJ cm$^{-2}$) causes a splitting of the spectra, which further increases upon approaching the spot center (figures 4(e) and (f), 61 and 66 mJ cm$^{-2}$). In parallel with the splitting, the amplitude of the SPR increases significantly.

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A possible reason might be the use of off-resonance excitation in our case. Off-resonance fs laser excitation of NPs in water has been shown to benefit from strong near-field enhancement in the vicinity of the NP, leading to plasma formation in the surrounding water, together with reduced particle heating when compared to resonant excitation [20]. Applied to our case, off-resonance excitation is therefore likely to cause plasma formation in the dielectric matrix in contact with the NP, which in turn will contribute to the shrinking of the NPs by silver out-diffusion. After electron plasma relaxation and energy transfer in the form of heat to the lattice, the particle–matrix interface region is most likely in the liquid phase, which strongly favors diffusion of silver atoms into the matrix, leading to spectral bleaching. The disintegration of NPs forms the basis for the formation of NPs with different sizes and distributions, which can be observed when further increasing the local fluence (cf figure 4(d)). Given the spheroidal shape of the new NPs formed in this fluence regime (cf figure 3(b)), melting is involved, since the liquid phase is characterized by a high surface tension, aiming for surface minimization. The increase of the aspect ratio of the spheroids upon a further fluence increase is caused by the high transient electric field of the fs laser pulses, which induces strong oscillations of the electron distribution of the NPs along the polarization direction of the laser [18], effectively shaping the NPs into prolate spheroids.

We have considered the possibility of chemical reactions of silver with the Al$_2$O$_3$ matrix upon irradiation, which in principle could be triggered by near-field enhancement. This might lead to the formation of Al NPs and partial oxidation of Ag. Since Al NPs have their SPR in the UV [21], out of reach of our spectroscopic window, we cannot rule out the formation of Al NPs. However, the presence of a pronounced SPR at 440 nm indicates that the dominant process is the formation of shaped Ag NPs, and the possible formation of Al NPs or partial oxidation are, if present, of limited importance. Also, if oxidation were a major issue, a red-shift of the SPR together with a broadening of the absorption band would be expected [22].
Figure 5. TEM images of the embedded Ag nanoparticle layer (a) outside and (b)–(d) inside the irradiated region at different local positions. The corresponding local fluences are (a) 0 mJ cm$^{-2}$, (b) 31 mJ cm$^{-2}$, (c) 43 mJ cm$^{-2}$, (d) 52 mJ cm$^{-2}$.

In order to shed more light on the transformation pathway from near-coalescence NPs to shaped NPs, we have performed additional TEM studies on different local positions (and thus different local fluences) of the laser-irradiated regions. As can be seen in figure 5, the transition from as-grown NPs to NPs exposed to a moderate fluence of 31 mJ cm$^{-2}$ (figure 5(b)) features the appearance of white spots at the border of numerous NPs. This phenomenon is consistent with our interpretation of the spectral data in figure 4, that the use of non-resonant laser irradiation leads to a strong field enhancement at the NP border, triggering plasma formation and shrinking of the NPs by silver diffusion. At increasing local fluences (figures 5(c) and (d)), the number and spatial extension of the white spots increases along with a reduction of the number of remaining NPs. At the highest fluence, the number density has decreased markedly together with the already observed form change into spheroids. The white spots outline the original position and spatial extension of the as-grown NPs. It is worth noting that the local fluence regime of figures 5(b) and (c) corresponds to the regime of spectral bleaching, demonstrating that its origin is the near-field enhancement induced particle shrinking at the interface NP-matrix.

4. Conclusions

We have demonstrated that irradiation with multiple fs laser pulses is a suitable approach for controlled reshaping of very heterogeneous distributions of metal NPs. Ultrathin near-coalescence NP layers with a broad size distribution are found to reorganize and reshape into a narrow size distribution of aligned prolate spheroids. The corresponding change in the optical properties of the composite material is strong, leading to a shift of the SPR from the red to the green–blue spectral region. The aspect ratio of the spheroids can be controlled in straightforward fashion by adjusting the laser fluence. The use of in situ microscopy combined with point-probing transmission spectroscopy with sub-10 µm resolution allows control of the optical properties of the composite material and thus of the shape size distribution of the NPs during irradiation. This approach offers excellent perspectives for optical encoding [16] and fabrication of complex, polarization-sensitive spectral masks starting from thin films with near-coalescence distributions of NPs, while preventing physical and chemical degradation of the NPs by embedding them in a dielectric film. By using stacked NP multilayer systems we can potentially achieve five-dimensional optical recording [17], extending the current four dimensions achieved (two lateral, spectral and polarization) by depth resolution.

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