Tailoring the optical response of an embedded silver nanoparticle layer using nano- and femtosecond laser pulses

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Abstract

Artificial nanostructures consisting of metal nanoparticles (NPs) embedded in dielectric materials present exciting linear and non-linear optical properties, such as a pronounced surface plasmon resonance (SPR) or intense third order nonlinear optical susceptibility. These properties make metal NPs very promising for the design of optical devices with a tailored spectral response, provided that a good control over the NP morphology (size, shape and separation of the NPs) is achieved. Unfortunately, many NP fabrication techniques suffer precisely from this problem. Moreover, an important limitation of implemented nanostructures is their static performance, unable to adapt to changes that advanced applications demand.

We have set out to tackle the shortcomings of embedded metal NPs, their static and often non-optimized properties, paving the way for new applications. Tailoring of embedded NPs is a true challenge since the processing technique needs to be capable to overcome the forces exerted by the surrounding medium. Femtosecond (fs) laser pulses, however, are capable of doing so. Stalmashonak et al. have used this approach to reshape spherical silver NPs embedded in bulk glass into oblate or prolate spheroids with different aspect ratio [1]. We have recently shown reshaping of non-spherical, near-coalescence Ag NPs embedded in an ultrathin dielectric film using irradiation with multiple off-resonant fs laser pulses [2].

In this contribution we use resonant and off-resonant nanosecond (ns) and fs laser irradiation to shape embedded NPs and tailor the optical response of the NP system. The sample consisted of an ultrathin layer of embedded random-shaped near-coalescence silver NPs (Fig. 1(a)) produced by pulsed laser deposition [3], featuring a broad SPR at 650 nm. Exposure to a single ns laser pulse leads to an extraordinary change of the optical properties, forming a sharp SPR at 450 nm (Fig. 1(c)). SEM studies reveal the underlying mechanism to be a transformation into a distribution of well-separated spherical particles (Fig. 1(b)). To the best of our knowledge shaping of embedded NPs has only been achieved with fs laser pulses.

Moreover, we have developed an in-situ microscopy system combined with transmission and reflection micro-spectroscopy using a white light probe spot size of 4 μm. This system allows a real-time control during and after irradiation of the SPR and allows the determination of the absorption spectra for a full characterization of the optical properties. Exploiting the Gaussian intensity distribution of the laser spot, spectral maps as a continuous function of local fluence can be readily produced from a single laser spot.

Fig. 2 shows such a map, obtained by recording individual spectra for each position of a horizontal scan across the laser-irradiated region shown in Fig. 1(d). Dark regions in the map correspond to low transmission values and are therefore a direct monitor of the spectral position, width and strength of the SPR. Starting from outside the laser-irradiated region (-70 μm) a gradual narrowing, shift and amplitude increase of the initially broad SPR is observed upon moving towards the dark orange outer ring of the laser-written spot (c.f. Fig. 1(d)). The transition into the “ring” region is spectrally continuous, indicating a gradual NP size/shape/separation change of thermal origin, rather than a sudden threshold-like process as the microscope image in Fig. 1(d) might suggest. Moving further from the ring into the central light orange disk region is accompanied by only small spectral changes. The amplitude and width of the SPR within the entire disk region is constant.

The laser-modified system can be further fine-tuned by post-processing with multiple fs laser pulses at two different wavelengths (resonant or off-resonant), generating polarization anisotropy in the optical response, as illustrated in Fig. 3. The degree of the anisotropy is found to depend strongly on the irradiation wavelength. We attribute the larger shift induced for off-resonance excitation to the field-enhancement in the particle vicinity and field-driven electron ejection. In contrast, for resonant excitation (400 nm) enhanced absorption leads to less anisotropy due to stronger thermal effects.

The results open excellent perspectives for dynamically tuning, changing, switching and structuring the optical response of NP systems, paving the way for novel applications, including optical encoding and fabrication of complex, polarization-sensitive spectral masks.
References


Figures

Fig. 1: (a) and (b) show plan view SEM images of an as-grown and ns laser-irradiated region of a single Ag NP layer embedded in a thin a-Al₂O₃ film, respectively, evidencing the shape/distribution change Ag NPs undergo after irradiation. (c) transmission spectra of laser-irradiated and as-grown regions of the sample. (d) Color optical micrograph obtained in transmission.

Fig. 2: Spectrum-fluence map of the transmission (false color scale in percentage) measured along the marked x-axis of the irradiation spot shown in Fig 1(d). The correspondence between spatial position (top axis) and local fluence (bottom axis) has been calculated. Dashed vertical lines indicate the three regimes visible in the micrograph in Fig. 1(d), the light brown outside region, the dark orange ring and the light orange central disk.

Fig. 3. Transmission spectra obtained with polarized white light of the sample exposed to a single ns laser pulse and subsequently to multiple fs laser pulses at (a) 400 nm and (b) 800 nm wavelength. Tₓ and Tᵧ correspond to polarization along the x and y axis, with y being the orientation of the irradiation laser polarization.