

Fabrication and laser-assisted modification of the Ag particles ensembles supporting quadrupole plasmon oscillations

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Abstract A combination of physical vapour deposition, thermal annealing and laser irradiation was used to tailoring of the silver nanoparticles array on a quartz substrate. This method for control of optical properties is exploit 355-nm pulsed laser irradiation. Experimental separation of three main overlapped plasmonic modes, dipoles that correspond to parallel and perpendicular oscillations and quadrupole with maximum wavelength at 355 nm, in extinction spectrum of Ag nanoparticles ensembles was demonstrated. It was shown that the laser post-processing of the nanoparticles array in spectral vicinity of the quadrupole band leads to selective ablation of nanometer particles. This process resulted to close-packing of the nanoparticles ensemble on top of the substrate causing, in turn, formation of ‘hot-spots’ and absorptive bands in the near IR range. Using the laser post-processing as persistent spectral hole burning technique, a dephasing time of quadrupole plasmon resonances was experimentally defined for the first time.

Keywords Silver nanoparticles · Plasmon · Laser tailoring · Ablation · Quadrupole resonance · Dephasing time

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1 Introduction

Laser-induced fabrication and modification of metallic nanoparticles has been considerably developed during the last years. It was shown that laser illumination can modify bulk materials leading to surface structuring (Paradisanos et al. 2014), ablation (Tsuji et al. 2008), and fabrication of hybrid nanostructures (Vasileiadis et al. 2013). Interaction of cw and pulsed, nanosecond and femtosecond, laser radiation with plasmonic nanoparticles is especially attractive because it may lead to the desired changes of optical properties of such particles by their re-shaping (Vartanyan and Leonov 2016; Stalmashonak et al. 2009). In particular, a multi-step laser tailoring process in order to narrow the size distribution of self-assembled supported metal nanoparticles from 27 to 14% in the sizes standard deviation was demonstrated (Blázquez Sánchez et al. 2007). Same results for plasmonic nanoparticles were observed by (Resta et al. 2006). There is a method for implantation of gold, silver and alloy plasmonic nanoparticles into the surface of glass substrate by laser irradiation (Henley et al. 2013). The method of sintering which lead to red-shifting of silver nanoparticles absorbance by millisecond laser radiation was demonstrated by Peng et al. (2012). Periodic layered nanostructures of silver nanoparticles in polymer matrix were fabricated by laser radiation in ref. (Bagratashvili et al. 2010). Selective modification of nanoparticle arrays by laser-induced self-assembly was recently demonstrated also (Kalfagiannis et al. 2016). At the same time, a laser illumination may be employed to study such intrinsic properties of noble metal nanoparticles as plasmon dephasing time, chemical interface damping etc. (Bosbach et al. 2002; Hendrich et al. 2003).

Optical properties of the noble metal nanoparticles are mainly defined by collective oscillations of the conductive electrons against the crystal lattice called localized surface plasmons. These oscillations provide an enhancement of electric fields in the vicinity of the noble metal nanoparticles. Enhanced local fields form the basis for observation of surface enhanced Raman scattering, fluorescence modification and other physical phenomena that are used for development of biosensors, single molecule detection, optical tweezers, slow-light devices and in many other applications (Maragò et al. 2013).

It is known that a frequency of plasmonic oscillations depends on the material of the nanoparticle, its size and shape, and the dielectric permittivity of surrounding media. In the tough arrays of the nanoparticles formation of dimers and more complicated structures lead to the spectral shifts of the plasmonic frequencies. If the distance between nanoparticles is comparable with their sizes, then near electric fields of nanoparticles can lead to the appearance of ‘hot spots’ (Kang et al. 2015). The amplitude of electric fields in ‘hot spots’ is larger than the field amplitude inside the particles. For application of this property the distance between the particles must be equal or even less to their sizes. To control the interparticle distance on the substrate a combination of the methods and multistep processes can be used. For example, reduction of the distance between gold nanoparticles can be performed by evaporation technique, thermal annealing and second evaporation as described by Kang et al. (2015). Unfortunately, such approach of modification involves the whole ensemble of particles on the substrate. More accurate tuning of the optical properties of plasmonic nanoparticles can be achieved with selective heating. It is known that laser irradiation leads to the changes of the particles shapes that are in resonance with the laser frequencies (Stietz 2001). One of the most compelling examples of this phenomenon is persistent spectral hole burning in inhomogeneously broadened extinction spectra of metal island films (Bosbach et al. 2002).

Note that experiments with spectral holes burning technique were mainly performed with nanoparticles that possessed a dipole resonant mode. In particular, this method allowed for determining of the dephasing times of the metallic nanoparticles. In this contribution, we propose to extend this technique for examination of larger nanoparticles with average diameter more than 100 nm. Such nanoparticles besides the well-known dipole mode possess the quadrupole resonance as well (Kelly et al. 2003). In what follows, we demonstrate that under laser irradiation at comparatively low energy fluence these particles may be transformed into close-packed ensembles of smaller nanoparticles with a number of potential ‘hot spots’ between them.

2 Experimental setup

Silver nanoparticles were prepared via physical vapor deposition in ultra-high vacuum. Samples were obtained as island films on the quartz surface at room temperature. Amount of deposited silver and the growth rate were controlled with the quartz crystal oscillator. As deposited silver films with the equivalent thicknesses of 10, 15, and 20 nm had continuous morphology. In this case we define the equivalent thickness as thickness of the bulk silver layer which volume is equivalent to volume of all nanoparticles in the island silver layer. It was controlled by quartz microbalances. After annealing at 250 °C for 1 h the dewetting process takes place and the films acquire a clear discontinuous morphology.

All samples were studied using atomic-force microscopy (AFM). Microscopic studies were carried out in the tapping mode with the probe resonance frequency of 283 kHz. The probe radius was about 10 nm.

After spectral measurements and morphology investigations, all samples were irradiated by the third harmonic of Nd:YAG-laser (355 nm wavelength, 10 ns pulse duration). The fluences were varied from 15 to 160 mJ/cm². The irradiation wavelength coincided with quadrupole band for all investigated samples. All spectral changes were analyzed in terms of the difference between the extinction spectra obtained before and after laser irradiation.

In a separate experiment the angular dependence of the optical density of a sample was investigated. In particular, transmission of the p-polarized light at normal incidence, as well as at 15°, 30°, 38°, and 45° grazing incidence were recorded.

3 Experimental results

At the chosen equivalent thicknesses, conditions of evaporation, and thermal treatment, island films with the average sizes of granules in excess of 100 nm were formed. The extinction spectra of all samples are inhomogeneously broadened due to the presence of islands of different shapes and sizes. (Fig. 1). These films possess both well-known dipole resonance mode in the visible range of spectrum and blue-shifted quadrupole mode. An increase of the equivalent thickness results in the red shift of both dipole and quadrupole resonances. This shift is due to the dependence of the resonance frequencies of both plasmon modes on the particle size. The observed decrease of the optical density of the thicker layers in the spectral vicinity of the dipole mode is due to the relatively small extinction cross-section of nanoparticles in this range (Hlaing et al. 2016).

Laser irradiation leads to a significant change in the films morphology as well as in their optical properties. These changes depend on both the film and the laser parameters. In the

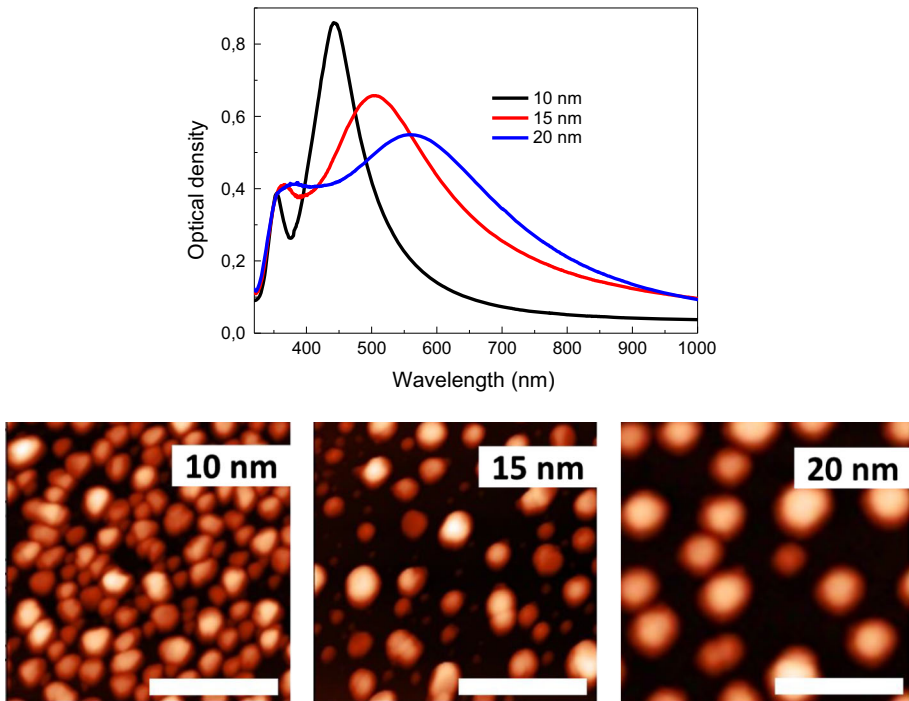


Fig. 1 Optical density spectra and AFM-images of silver island films with different equivalent thicknesses. White bars correspond to 1 μm

Fig. 2a the optical density spectra evolution is presented for the silver films of 10 nm equivalent thickness. At the laser fluences $<40 \text{ mJ/cm}^2$ no noticeable changes of the film morphology and optical properties were observed. On the other hand, at larger fluences the red shift of the quadrupole band and the diminishing of its amplitude was observed (see ‘Value of changes’ panels in Fig. 2).

These spectral changes are accompanied by drastic morphology modifications. AFM images (Fig. 2b) show that the surface number density of the silver nanoislands was changed. Simultaneously, maximum of the size distribution shifts from $135 \pm 35 \text{ nm}$ before irradiation to $80 \pm 30 \text{ nm}$ after laser irradiation by 10 laser pulses with the fluence of 160 mJ/cm^2 per each pulse.

Analogous fragmentation for nanoparticles was observed by authors (Nichols et al. 2002). Of particular importance is a more efficient vaporization of nanoparticles by the laser energy, due to the finite extent of the material in the laser field, which increases the relative importance of the breakdown-induced shock wave in smaller nanoparticle formation. Due to this fact the ablation threshold can be decreased, but in addition, at resonant coupling of quadrupole mode of nanoparticles with laser pulse, the electric field enhancement and its localization around particle contribute to ablation threshold decreasing. While typical values of energy fluence for ablation varied from $\sim 100 \text{ mJ/cm}^2$ (Kalfagiannis et al. 2016; Nichols et al. 2002) we demonstrate the plasmon assisted-modification at 40 mJ/cm^2 . Thus, through the adjustment of processing and ensembles parameters, it should be possible to enhance and control the distributions of nanoparticle sizes by laser post-processing.

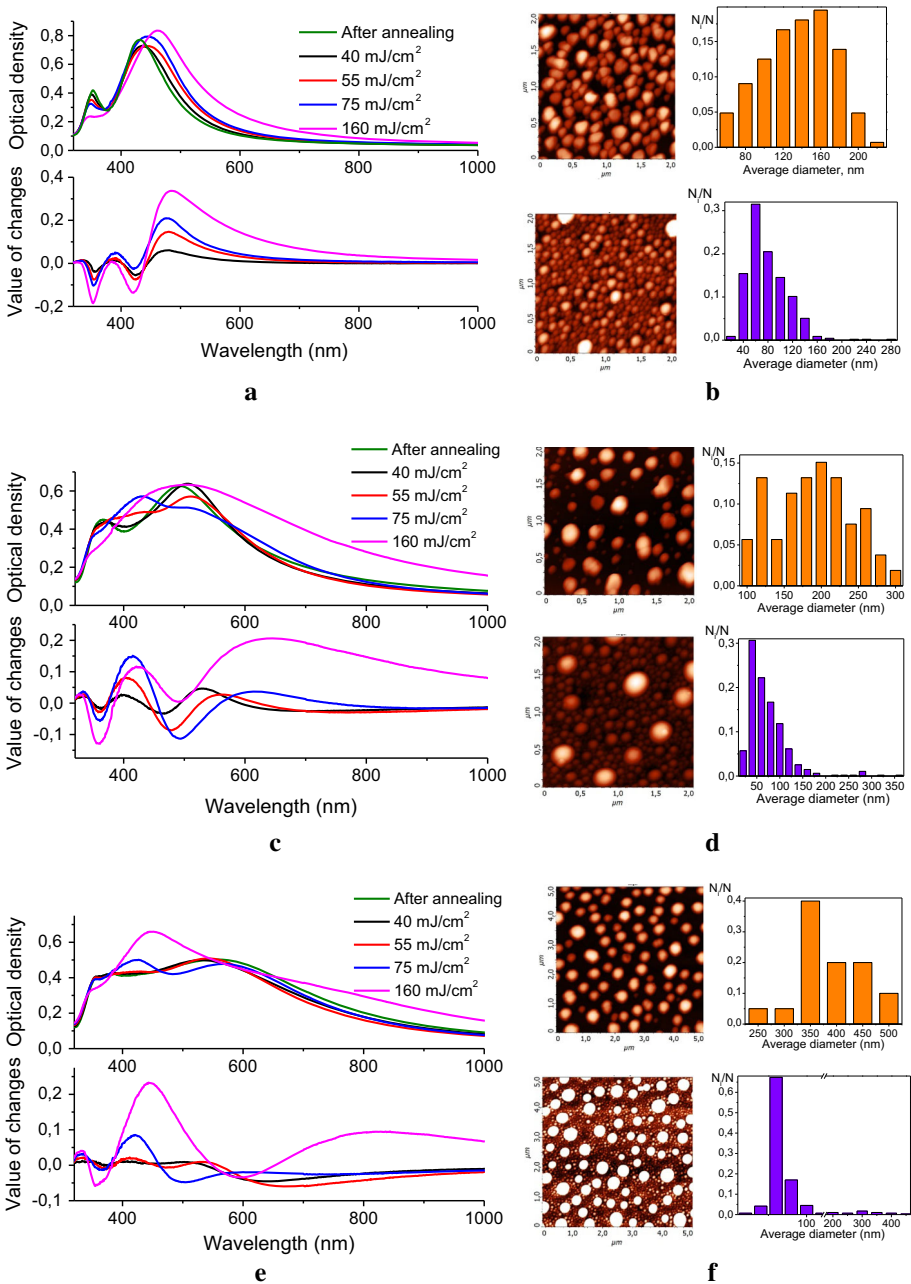


Fig. 2 Optical density spectra and their changes of **a** 10-, **c** 15-, and **e** 20-nm silver island films after laser irradiation. **b**, **d**, **f**—AFM images and size distribution histograms before (*upper panels*) and after irradiation (*lower panels*). Each sequence of irradiations includes 10 monopulses

Besides degradation of the quadrupole band that was in resonance with the laser radiation, considerable changes in other spectral ranges take place as well. In the samples with equivalent thicknesses of 15 nm and 20 nm reduction of the optical density in the

spectral range of 500–600 nm after 75 mJ/cm^2 pulse irradiation was accompanied by the growth of the optical density in the spectral range of 400–500 nm. The most intense pulses with the fluence of 160 mJ/cm^2 led to the optical density increase in the long wavelength spectral range starting from 600 nm.

The observed reduction of the dipole resonance mode (red-shifted relative to quadrupole modes) is correctly explained by fragmentation of the huge nanoparticles clearly seen in AFM images. After irradiation of these samples by laser pulses with the fluence of 45 mJ/cm^2 two maxima appear in the optical density spectra. These maxima correspond to the dipole plasmon oscillations of the huge particles and their fragments formed after irradiation. The average size of nanoparticles in the film with equivalent thickness of 15 nm before irradiation was of $190 \pm 55 \text{ nm}$. Laser irradiation led to formation of two groups of the particles that differ from each other by the average sizes. The first group consists of the parts of huge nanoparticles with the size of $280 \pm 35 \text{ nm}$ formed at the preparation stage. The second group of nanoparticles consists of the fragments of huge nanoparticles with the average size of $65 \pm 30 \text{ nm}$.

Laser irradiation of the film with equivalent thickness of 20 nm (Fig. 2e, f) leads to the reduction of the average size of nanoparticles from the value of $390 \pm 60 \text{ nm}$ before irradiation to the value of $55 \pm 15 \text{ nm}$ after irradiation and to a minor population of huge islands of $310 \pm 70 \text{ nm}$ in size.

The complex nature of the high-frequency plasmon band was revealed by the measurements of transmission of the p-polarized light at oblique incidence (Fig. 3). The spectral position of the high-frequency peak at 373 nm observed at normal incidence is in a reasonable agreement with the position of the quadrupole resonance in oblate silver nanospheroids (Kelly et al. 2003). On the other hand, as the angle of incidence increases a new band with the maximum at 355 nm starts to grow. This behavior unambiguously connects this band with the dipole mode oriented perpendicular to the substrate surface. Thus, we can conclude that there are three different kinds of oscillations in an ensemble of the Ag nanoparticles: one quadrupole mode and two dipole modes. As the nanoparticles are assumed to be oblate, the long wavelength mode corresponds to the oscillations along the major axis that is parallel to the substrate, while the short wavelength mode corresponds to the oscillations along the minor axis that is perpendicular to the substrate.

The angular dependences of the extinction spectra for the as prepared (annealed) and the laser irradiated films appeared to be very different. In smaller particles that appeared after laser irradiation quadrupole oscillations are too weak to be observed in the extinction spectra. Hence, the blue band disappeared after illumination. At the same time, strong

Fig. 3 Optical density spectra of annealed 15-nm (marked 'A') Ag film before irradiation measured at different angles (given after the letters) and the same film after laser irradiation (marked 'I'). Arrows indicate evolution of the spectra when the angle of incidence is increased

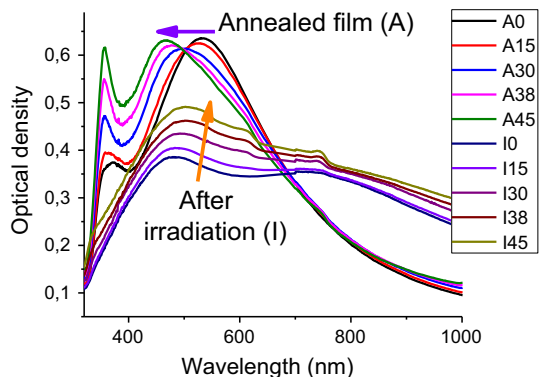
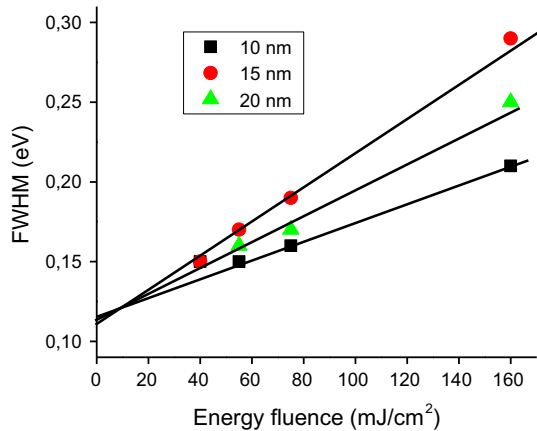


Fig. 4 Fluence dependence of the FWHM of the spectral holes burnt in the quadrupole band of the silver films of different thicknesses under the laser irradiation at the wavelength of 355 nm. Linear extrapolation to the zero fluence gives the estimate of the homogeneous width of the quadrupole plasmon mode



electrostatic interaction between small densely packed particles leads to the optical density enhancement in the spectral range of 700–1000 nm.

Finally, we utilized the technique of persistent spectral hole burning (Bosbach et al. 2002) to estimate the dephasing time of the quadrupole mode. Figure 4 plots the fluence dependence of the full width at half maximum (FWHM) of the spectral holes burnt in the quadrupole band. The homogeneous width obtained via extrapolation to the zero fluence is equal to 113 meV. Within the experimental error same values were obtained for all three films with different equivalent thicknesses. The dephasing time that corresponds to this homogeneous width is equal to 12 fs. This value is similar to the values obtained previously for dipole plasmons.

4 Conclusion

Let us summarize the most important findings of this work. First, we show that the combination of physical vapor deposition, thermal annealing and laser irradiation leads to the production of nanoparticle arrays with diverse but well controlled properties. In this process we experimentally demonstrated the possibility to enhance the laser-induced modification by relatively small quanta of 355-nm pulses.

Second, we experimentally separate two overlapping features in the extinction spectrum of supported silver nanoparticles arrays: quadrupole mode and the dipole mode that corresponds to the oscillations perpendicular to the substrate surface. It was checked that the last mode does not contribute to the extinction spectra of the s-polarized light.

Third, we showed that laser irradiation of Ag nanoparticles ensembles in the spectral vicinity of quadrupole band leads to the fragmentation of larger particles and broadening of the extinction spectra. Such laser action upon the granular silver film is in opposition to the previously known laser annealing process that was observed when the laser was tuned on the dipole band (Vartanyan and Leonov 2016). That process leads to the narrowing of the plasmon spectra. The observed fragmentation may be used for production of ensembles of the close-packed plasmonic nanoparticles much-in-demand for ‘hot spot’ applications.

Finally, we experimentally defined the dephasing time of quadrupole plasmon resonance of silver nanoparticles for the first time by persistent spectral hole burning technique.

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