The study of radiation attenuation in disordered silver nanoparticles arrays formed by dry aerosol printing

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Abstract. The interaction processes of continuous laser radiation with wavelengths 527 and 980 nm with disordered arrays of spherical silver nanoparticles formed by dry aerosol printing are studied. The arrays were deposited on a glass substrates in the form of lines of various thickness and differed in the mean sizes of nanoparticles. It is shown that the radiation attenuation by arrays with disordered nanoparticle structure depends on the optical effects both on isolated spherical nanoparticles and on nanoparticle agglomerates.

1. Introduction
The interaction of laser radiation with disordered arrays of metal nanoparticles (NP) may be described by absorption and scattering processes on the array elements. Resonant effects that occur on isolated particles and their ensembles due to collective interaction may significantly impact on the radiation propagation in such systems [1]. Thus, the radiation extinction enhancement on a fixed wavelength in disordered arrays in the model of dipole-dipole interaction of isolated NPs is expected to appear depending both on NPs geometric properties and the studied material electronic properties. For example, there were studied in detail the processes of the absorption resonant peak displacement for metal NPs depending on their shape [1], and in particular for spherical NPs depending on their diameter [2]. However, in conditions when the arrays NPs contact and form agglomerates and chains, they cease behaving as separate dipoles [3]. In this case, the interaction of laser radiation with such structures may be described by the excitation of plasmon modes on isolated NPs [1], as well as by the excitation of radiative modes of nanoantennas on NPs agglomerates [4]. It is the arrays formed by dry aerosol printing that are interesting due to the complex structure of dendrite-like NPs agglomerates characterized by collective electrical conductivity [5-7] and may be a model structures for studying the radiation interaction with disordered arrays of NPs.

In this paper we studied the dimensionless radiation attenuation coefficients of disordered arrays of spherical silver NPs formed by dry aerosol printing on glass substrates. In the experiments we varied the arrays thickness and the average NPs diameter, which were controlled by optical profilometer and transmission electron microscope (TEM) respectively. The NPs agglomerates size distribution was also measured directly in the gas flow by the electrodiffusion method.

2. Experiment
Silver NPs arrays in the shape of lines with a cross section profile close to the normal distribution were formed on the glass substrates by the dry aerosol printing technology described in [6-9]. The setup for the microstructures formation from such NPs is schematically presented in Figure 1(a).
Figure 1. (a) The scheme of the setup for the formation of silver NPs arrays; (b) The optical scheme of the setup for attenuation coefficient measurements.

Two types of studied microstructures were differed in the parameters of thickness and average NPs size. The first type consisted of primary particles with an average size about 20 nm, forming agglomerates with an average size about 160 nm, and the second type consisted of optimized particles with average sizes about 80 nm, basically not forming agglomerates. The size of the NPs forming an array was controlled by passing an aerosol with primary NPs through a gas circuit section heated to 500 °C with a flow rate 6 cm/s and by varying the concentration of primary particles in the flow [10]. The shapes and sizes of the deposited NPs and their agglomerates were studied by transmission electron microscope (TEM) JEM-2100 (JEOL) (Figure 2 insertions). Additionally, the statistical size distribution of silver NPs and their agglomerates in the aerosol stream after the focusing nozzle was measured by electrodiffusion method in the aerosol NPs analyzer SMPS 3936 (TSI Inc.) (Figure 2).

Figure 2. The statistical size distribution for (a) primary particle agglomerates and (b) particles with an average size about 80 nm. The insets show NPs TEM images.

The transmission spectra of the microstructures were studied in an optical setup, schematically presented in Figure 1(b). The dimensionless attenuation coefficient dependences for NPs arrays from their thickness were obtained from the measurements of the intensity of incident and transmitted coherent linearly polarized continuous (CW) laser radiation with wavelengths 527 and 980 nm in a stable
lasers operation regimes. The experiments were held by the radiation with a beam diameter 100 μm and a power 200 μW cut by a circular diaphragm from the central part of the laser beam normal distribution. The studied samples were scanned with laser radiation perpendicularly to their orientation with a substrate speed moving 150 μm/s. Due to the FWHM parameter of the arrays cross section about 300 μm the selected diameter of the scanning laser beam made it possible to obtain the radiation attenuation coefficients of microstructures averaged over a large number of NPs. In this case, a uniform section 100 μm wide without large height differences was selected on the cross-sectional profile of the studied array, which was associated with the corresponding values of dimensionless attenuation coefficients for each wavelength (Figure 3). The obtained dependences of the dimensionless radiation attenuation coefficient by the NPs layer from its thickness were interpolated by an exponential function with the $k_\lambda$ parameter representing the dimensional radiation attenuation coefficient for the array consisting of spherical silver NPs and NPs agglomerates with a given average diameter and size distribution respectively.

Figure 3. (a) The optical microscope image of a NPs array surface and (b) the array cross-sectional profile with the transmittance dependencies of this array measured by laser radiation with wavelengths 527 and 980 nm from the coordinate.

3. Results and discussion
Figure 4 presents the dimensionless attenuation coefficients dependences for NPs arrays from their thickness, interpolated by an exponential function, and dimensional attenuation coefficients for each wavelength and for each type of particles.
Figure 4. The dependencies of the dimensionless radiation attenuation coefficients for arrays of silver NPs with average diameters (a) 20 nm, forming agglomerates with an average size of 160 nm, and (b) 80 nm, not forming agglomerates, from the arrays thickness for laser wavelengths 527 and 980 nm.

According to the experimental results, all arrays of silver NPs better attenuate radiation with a wavelength 527 nm then with a wavelength 980 nm, which is explained by a higher absorption of spherical silver NPs due to the plasmon modes excitation at a short wavelength and correlates well with literary data, e.g. [2, 11]. Furthermore, the proximity of the dimensionless radiation attenuation coefficients for the two wavelengths in each arrays type (about 15%) may be a consequence of a wide size distribution for particles and agglomerates in arrays, which includes particle sizes with similar absorption efficiencies for each radiation type. However, arrays of NPs with an average size about 20 nm and an average agglomerates size about 160 nm more effectively attenuate incident radiation, compared with arrays of NPs with an average size about 80 nm that don’t form agglomerates. This occurs despite the fact that the radiation absorption efficiency for the given wavelengths increases simultaneously with an increase in the diameter of NPs [2]. This effect may be explained by the excitation of the longitudinal oscillation mode, resulting from the combining surface plasmons on NPs bounded to their nearest neighbors through dipole – dipole interaction [3, 12]. In this case the NPs in the agglomerates work as a whole, exhibiting the properties of extended dendrite-like plasmon nanoantennas [4].

4. Conclusion
The interaction of CW laser radiation with wavelengths 527 and 980 nm with the disordered arrays of spherical silver NPs, formed by dry aerosol printing, is determined by the radiation absorption and scattering processes both on individual NPs and on their agglomerates. This interaction results in a stronger attenuation of radiation with a wavelength 527 nm compared with 980 nm, which corresponds to literary data. The dimensionless radiation attenuation coefficients for arrays of NPs and their agglomerates with an average size about 20 and 160 nm respectively are one magnitude order higher than for arrays of NPs with an average size about 80 nm, not forming agglomerates. This peculiarity contradicts the well-established theory of increasing the NPs radiation absorption efficiency with increasing the composing NPs diameter, if not taking into account their agglomeration. This may be explained by the excitation of a longitudinal oscillation mode on NPs agglomerates, which arises as a result of combining surface plasmons on NPs bounded to their nearest neighbors through dipole – dipole interaction. In this case the NPs agglomerates in these arrays exhibit the properties of extended dendrite-like plasmon nanoantennas.
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