Formation of planar plasmon microstructures by dry aerosol printing

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Abstract. Optical properties and microstructure of samples formed by dry aerosol printing are studied. Silver nanoparticles flat layers of two types were formed on substrates surfaces and were investigated by a spectrophotometer, a scanning electron microscope, and a transmission electron microscope. It is shown that all microstructures support plasmon resonance on individual nanoparticles with the Q factor depending both on the width of the nanoparticles size distribution in the aerosol and on their tendency to agglomeration and aggregation.

1. Introduction
The optical properties of planar arrays of nanoparticles (NPs) significantly depend on their material, morphology, and degree of ordering in the sample. For example, with the rise of the isolated NP size the wavelength of the radiation scattered by that NP increases. Moreover, the specific geometric shapes of NPs exhibit a certain spectral response, which was studied on colloidal NPs in [1]. The spherical shape of NPs is the most common and allows us to analytically predict the position of spectral features for both individual NPs [2] and periodic lattices with individual spherical NPs located in lattice points [3]. Thus, it was shown in [3] that square lattices of gold spherical NPs may simultaneously support several resonant features in the visible wavelength range associated with the excitation of plasmon oscillations. Other authors [4] studied same features of the extinction spectra depending on the geometry of the periodic silver NPs lattice. The study of such structures makes them indispensable in many areas of biology and medicine for targeted delivery of drugs [5,6], biomarkers and contrast agents based on individual NPs [7–9] and for the manufacturing of biosensors [10,11] and of neurocomputer interfaces [12].

At present, the task of manufacturing such structures is massively solved by the lithography and vacuum deposition methods [13]. At the same time, dry aerosol printing allows to synthesize by the spark discharge method [14] and to deposit chemically pure NPs in real time for similar tasks of manufacturing planar microstructures [15] with resonant features in optical spectra. However, in the transport process of aerosol to the substrate, individual NPs form dendrite-like agglomerates and aggregates that destroy the order and distort the optical spectra of the formed structures. Nevertheless, disordered NPs arrays are still able to support plasmon resonance, and therefore the formation of such structures by dry aerosol printing also looks promising for the applications described above.

In this work, disordered arrays consisting of spherical silver NPs, their agglomerates and aggregates were produced by dry aerosol printing on the surface of glass and silicon substrates. Optical transmission spectra in the range from 320 to 800 nm were studied for the obtained samples. It is shown that all microstructures support plasmon oscillations on individual NPs with the Q factor depending both on the width of the NP size distribution in the aerosol and on their tendency to agglomeration and aggregation.
2. Experiment
The studied silver NP structures were made by dry aerosol printing in the form of 3x3 mm\(^2\) flat square layers on substrates surfaces. Thus, glass and polished silicon substrates were used in the study of optical spectra and in the microscopic study of samples, respectively. Aerosol NPs were depositing through a coaxial nozzle with an outlet hole of 300 µm located at 1 mm from the substrate surface, according to the printing pattern shown in Figure 1 (b) by the red line. The line width was controlled by adjusting the flow rate of the additional shielding gas flow entering the nozzle in accordance with the works [16,17]. In the work the width of the printed line W was set to 150 µm. The printing step between the lines S was chosen experimentally such as, firstly, to minimize the surface waviness (Figure 1 (a)), and secondly, to create a sufficient thickness of the layer H, as the aerosol flow falling on the substrate surface could destroy the already formed lines.

![Figure 1](image)

**Figure 1.** (a) Scheme of the setup for the formation of silver NPs arrays; (a,b) Model image of the printing structure – the side view and the top view with the given template for deposition of NPs on a substrate (red line).

The morphology of NPs was studied by the transmission electron microscope (TEM) JEM-2100 (JEOL), for which they were depositing on copper TEM grids right after the structure was printed. Additionally, the sizes of agglomerates and aggregates of NPs were studied directly in the aerosol stream by the electrodiffusion method based on their differential electrical mobility via the aerosol NPs analyzer SMPS 3936 (TSI Inc.). The microstructure of the sample surface, including the features of NPs stacking, was studied by the scanning electron microscope (SEM) JSM 7001F (JEOL) on samples formed on the surface of polished silicon substrates. The sample thickness measurements were done in the cut of the central part of arrays by the optical profilometer S neox (SENSOFAR) with a 50x confocal lens. For that purpose we used a blade to perform a longitudinal cut of the structure, followed by a transverse shift for the removing of NPs. The optical spectra of samples made on glass substrates were studied by the spectrophotometer V-770 UV-Visible/NIR (JASCO) in the wavelength range from 320 to 800 nm with the radiation beam completely located inside the NPs array.

3. Results and discussion
In this paper we analyzed two types of samples differing in the average diameter of spherical NPs. The first type of microstructures consisted of primary synthesized NPs with an average size of 5 nm, tending to agglomerate in the gas flow into dendride-like structures and forming strong aggregates...
with an average size of 160 nm (Figure 2 (a,c)). Morphologically such resulting particles are characterized by a low degree of ordering. The second type structures were formed by NPs obtained by modifying aggregates of primary NPs in a section of the gas path heated to 750 °C. The composition of these NPs was characterized by the bimodality of their size distribution with maxima of 40 and 140 nm. The level of their agglomeration in the gas flow was insignificant and aggregation was not observed (Figure 2 (b,d)).

Figure 2. (a,b) TEM images and (c,d) size distributions of NPs forming structures and (e,f) SEM images of arrays surfaces for the first and second type structures.
Scanning electron microscopy of the sample surface allowed us to determine the features of NPs stacking (Figure 2 (e,f)). The surface of the first type structure, consisting of aggregates of primary NPs, turned out to be loose, while NPs in the second type structure were packed more compactly.

![Graph showing optical spectra](image)

**Figure 3.** Optical spectra of the first (a) and second type (b) microstructures without substrate.

The optical spectra of the microstructures under the study, with the pre-subtracted spectrum of the glass substrate, demonstrate resonant features in the range of 390-420 nm and are shown in Figure 3. In the transmission spectra for the first type structure only one resonant contour was observed, while for the second type structure this resonant contour split in two. We also noted that the transmission spectrum of the first type structure was higher compared to the transmission spectrum of the second type structure, i.e. the first type structure was more transparent, which corresponds to the thicknesses of the studied samples of 160 and 320 nm, respectively (Figure 4).

![Images of microstructures](image)

**Figure 4.** Surface images of the first (a) and second type (b) microstructures in an optical microscope with averaged cross-section profiles corresponding to this region.

The observed resonant features in the optical spectra of the samples are obviously related to plasmon oscillations on NPs and their agglomerates and aggregates in the samples. According to the SEM images, the structures under the study are disordered arrays of point-contacting NPs (for the second type structures) and NPs aggregates (for the first type structures). In the structures of the first
type, the degree of ordering is obviously much lower due to the fact that the structure is formed from disordered NPs aggregates of random shape. This explains the difference in the spectra and the lower Q factor of the resonance for the structure of the first type.

The discussed wide absorption resonance in the range of 390–420 nm logically corresponds to the Mie resonance on individual silver particles [2]. Thus, the splitting of the resonance for the second type structure is in good agreement with the positions of the Mie resonance on individual NPs of two particular sizes with diameters of 40 and 140 nm (Figure 2 (d)) at wavelengths of 393 and 414 nm, respectively [18]. However, the position of the resonance for the first type structure at a wavelength of 397 nm is extremely unusual for the position of the resonance on individual silver NPs with a diameter of 5 nm. However, considering this microstructure in the model of aggregated particles with a size of about 160 nm, it can be argued that the NPs in the aggregates work as a whole, showing the properties of extended dendride-like plasmon nanoantennas [19]. In this case, with an increase in the size of the aggregates the resonance redshifts. This is observed in the optical spectra for the first type structure. At the same time, a higher Q factor of the observed resonances can be achieved by reducing the width of the NP size distribution and preventing their agglomeration and aggregation [14].

4. Conclusion

Spherical silver NPs arrays formed by dry aerosol printing support plasmon oscillations, appearing in the optical spectra in the form of wide wavelength areas of radiation absorption. The Q factor of these resonances is small both for arrays of NPs with an average diameter of 5 nm, tending to agglomerate in the gas flow into dendride-like structures and forming strong aggregates with an average size of 160 nm, and for arrays of NPs with an average diameter of 140 nm, mostly not forming agglomerates. This peculiarity of the two types of arrays under the study may be a consequence of a wide range of NP size distribution and may also be associated with their random agglomeration and aggregation. In all cases, the observed resonant features are logically associated with the excitation of Mie oscillations on individual NPs. However, in the case of a structure consisting of primary NPs with a diameter of 5 nm, the resonance redshifts due to their aggregation, when considering the aggregates as extended dendride-like plasmon nanoantennas. The observed resonance splitting for the structure of the second type is explained by the bimodal size distribution of NPs with maxima of 40 and 140 nm. Thus, various sensors can be created on the basis of the manufactured structures, provided that the Q factor of the resonances under consideration increases by reducing the width of the NPs size distribution and their tendency to agglomeration and aggregation.

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