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Methodology for quantitative analysis of interparticle spacings in arrays of nanoparticles on solid-state substrates

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Abstract. A methodological approach is presented for quantitative analysis of geometric parameters of nanoparticle arrays, in particular the measurement of interparticle spacings, using a Delaunay triangulation algorithm. The development is motivated by the critical role of interparticle spacings in the formation of “hot spots” in surface-enhanced Raman scattering (SERS). The algorithm for automatic identification of nanoparticle centers in microscopy images and calculation of distances between nearest neighboring particles via Delaunay triangulation is described, along with data filtering criteria and the accounting of boundary effects to improve statistical reliability. The methodology is demonstrated on self-assembled arrays of nanoparticles obtained by thermal annealing of thin Ag films. The advantages of the proposed method and its limitations are discussed. The originality of the approach and its applicability to nanometrology and morphological analysis of nanostructured surfaces are emphasized.

Keywords: nanoparticles, interparticle spacings, Delaunay triangulation, SERS, hot spots, nanometrology, surface morphology

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Материалы конференции

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Методика количественного анализа межчастичных расстояний в массивах наночастиц на твердотельных подложках

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Аннотация. В работе представлена методика количественного анализа геометрических параметров массивов наночастиц, в частности межчастичных расстояний,

с использованием алгоритма триангуляции Делоне. Актуальность такого подхода обусловлена ключевой ролью межчастичных зазоров в формировании «горячих точек» в спектроскопии гигантского комбинационного рассеяния (ГКР). В работе описан подход к автоматическому определению центров наночастиц на микроскопических изображениях и вычислению расстояний между ближайшими соседними наночастицами, включая фильтрацию данных и учет краевых эффектов для повышения статистической надежности. Методика продемонстрирована на примере самоорганизованных массивов наночастиц, сформированных при термическом отжиге тонких пленок Ag. Обсуждаются преимущества предложенного подхода и его ограничения, а также его применимость в нанометрологии и морфологическом анализе наноструктурированных поверхностей.

Ключевые слова: наночастицы, межчастичные расстояния, триангуляция Делоне, SERS, горячие точки, нанометрология, морфология поверхности

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Introduction

Formation of arrays of plasmonic nanoparticles on solid surfaces is actively used to create substrates exhibiting the surface-enhanced Raman scattering (SERS) effect [1]. One of the most technologically straightforward methods for forming such arrays is the self-assembly of nanoparticles by thermal annealing of thin metal films [2]. At the same time, they do not possess the strict regularity achieved by lithographic methods, but significantly surpass structures obtained in liquid-phase processes in terms of the uniformity of spatial distribution [3]. Nevertheless, the morphology of such arrays remains sensitive to the formation conditions, which requires its quantitative control [4].

The efficiency of SERS signal enhancement in such arrays is largely determined by their morphology: particle size, array density, and, in particular, interparticle spacing. Narrow gaps between nanoparticles lead to the formation of so-called “hot spots” [5], providing maximal enhancement. As we showed previously [6], for arrays of silver nanoparticles the optimal gap is on the order of 20 nm, whereas an increase beyond ~40 nm leads to a sharp decrease in the probability of hot-spot formation.

For optimal tuning, a quantitative morphological analysis is required, including the evaluation of the distribution of interparticle spacings. While existing approaches to evaluate the mean nanoparticle size [7], particle sphericity [8], and array density are satisfactory, traditional approaches to estimate the mean interparticle spacing (e.g. manual measurements or indirect, density-based estimates) are subjective or labor-intensive. In this work, we present a methodological approach for automated evaluation of interparticle spacings in arrays of plasmonic nanoparticles based on Delaunay triangulation. The approach is demonstrated on arrays of nanoparticles formed by annealing a thin Ag film.

Materials and Methods

Ag nanoparticle arrays were formed on Si (100) substrates with a thermally grown SiO₂ layer 300 nm thick. Thin Ag films with equivalent thicknesses of 2–12 nm were deposited by magnetron sputtering (Q300TD Plus, Quorum, UK) using a 99.995% Ag target. The base pressure was

$\sim 1 \times 10^{-5}$ mbar and the argon working pressure was $\sim 1 \times 10^{-2}$ mbar. Thermal annealing was carried out at 80–300 °C in N_2 for 10 min. The sample morphology was examined by scanning electron microscopy (Helios G4 CX, Thermo Fisher Scientific, USA), and the images were used as input data for subsequent quantitative analysis of interparticle spacings.

Results and Discussion

To quantitatively evaluate interparticle spacings in arrays of plasmonic nanoparticles, we employed an algorithm based on Delaunay triangulation [9]. This approach objectively identifies pairs of nearest neighbors and computes the distribution of distances across the entire array. The main steps of the method are outlined below.

At the first step, images of nanoparticle arrays are processed using a watershed segmentation algorithm based on the classical Vincent algorithm [10]. This approach makes it possible to correctly identify individual nanoparticles, including segmentation of closely spaced objects. After segmentation, the coordinates of their centers of mass (x_i, y_i) are determined and used for subsequent calculations.

At the second step, a Delaunay triangulation is constructed over the set of nanoparticle centroid coordinates – the plane is partitioned into triangles such that no other point lies inside the circumcircle of any triangle. Owing to this property, the edges of the triangulation connect nearest-neighbor pairs, which enables identification of nanoparticle pairs for the subsequent calculation of interparticle spacings.

At the third step, for each pair of neighboring nanoparticles (i, j), defined by the edges of the triangulation, the Euclidean distance between their centers is calculated (1):

$$d_{ij}^{\text{center}} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2}. \quad (1)$$

The resulting array d_{ij} describes the distribution of center-to-center distances across the entire nanoparticle array. From this dataset, statistical parameters can be calculated, such as the mean center-to-center distance.

In the fourth step, the center-to-center distances are, if necessary, converted into edge-to-edge (interparticle) distances (2):

$$d_{ij}^{\text{spacing}} = d_{ij}^{\text{center}} - (r_i + r_j), \quad (2)$$

where r_i и r_j are the radii of the corresponding nanoparticles.

Since real nanoparticles are not ideal spheres, the radius of an equivalent disk is used as a size metric (3):

$$r_{eq} = \sqrt{\frac{S}{\pi}}, \quad (3)$$

where S is the projected area of the particle in the image.

When analyzing the data, filtering criteria must be applied to exclude distorting factors and random artifacts. First, any incorrectly identified “particles” should be excluded – for example, small noise objects from segmentation or fused agglomerates that do not represent individual nanoparticles. To achieve this, constraints on the allowable range of object area/size are introduced at the segmentation stage (for instance, objects much smaller or larger than typical nanoparticles in the sample are excluded by default).

Secondly, after constructing the Delaunay triangulation, it may be necessary to filter out edges that do not correspond to true nearest neighbors. While the triangulation generally links actual nearest neighbors, in cases of non-uniform nanoparticle distribution some edges may be significantly longer than the average. Excessively large distances between points indicate that, although these particles are connected by a triangulation edge, they are in fact too far apart. In the context of plasmonic resonance interactions, such particles cannot be considered nearest neighbors. Therefore, an upper threshold d_{max} can be introduced for d_{ij} , with edges exceeding this value excluded from the statistics. The threshold is selected based on physical considerations; filtering by d_{max} allows one to focus specifically on local interparticle distances that are critical for the formation of “hot spots”.

When analyzing nanoparticle arrays, particular care must be taken with those located at the image boundaries. A nanoparticle situated near the edge of the image may not have all of its nearest neighbors within the field of view; as a result, the Delaunay triangulation for such a limited dataset connects it only with neighbors inside the frame, often yielding overestimated distances. Moreover, for a nanoparticle positioned at the image boundary (whose projected area is only partially captured), the equivalent disk radius will be strongly underestimated. To eliminate systematic error, the influence of boundary nanoparticles must be minimized. Therefore, in the analysis, only nanoparticles fully contained within the image area should be considered. An alternative or complementary approach involves introducing an artificial boundary: beyond the image, mirror reflections of edge nanoparticles are drawn, creating the effect of a periodic continuation of the structure. When the triangulation is constructed, this artificial periphery makes it possible to obtain more accurate connections for boundary nanoparticles.

To obtain reliable estimates of interparticle distances, a sufficiently large sample size is required – an analysis of hundreds of nanoparticles and thousands of neighbor pairs usually provides the necessary statistics. The assessment of stability includes not only the mean value but also measures of dispersion: the standard deviation (σ), the coefficient of variation ($C_{var} = \sigma/d_{avg}$). As the number of analyzed nanoparticles increases, the error of the mean decreases as (4):

$$\Delta d = \frac{\sigma}{\sqrt{M}}, \quad (4)$$

where M is the number of neighbor pairs.

In addition, the shape of the distance distribution is also taken into account. In real arrays, it may deviate from a purely random form due to correlations in particle arrangement: regular structures lead to a narrowing of the distribution, whereas aggregation results in a “tail” of large distances. Constructing histograms and evaluating their characteristics makes it possible to identify and describe these features in the arrays.

Example of application

The proposed methodology was applied to analyze the evolution of morphological parameters in arrays of silver nanoparticles formed by thermal annealing of discontinuous Ag films with equivalent thicknesses of 2–12 nm on Si/SiO₂ substrates [6]. Figure 1 shows typical SEM images for a series of samples: with increasing annealing temperature, the nanoparticles grow larger and the structure becomes less dense as a result of fragmentation, surface diffusion, Ostwald ripening, and coalescence.

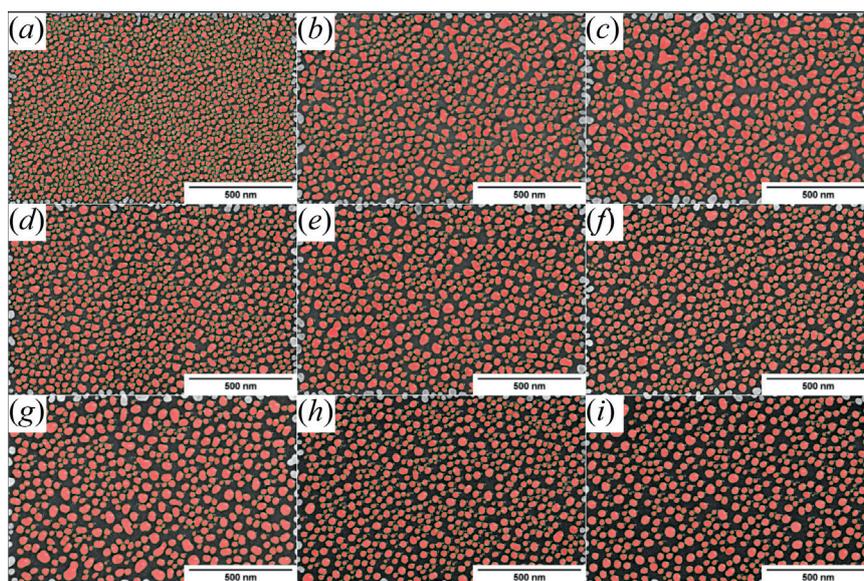


Fig. 1. Morphology of Ag nanoparticle arrays obtained by annealing a 6 nm thick film at different temperatures: (a) without annealing; (b) 80 °C; (c) 90 °C; (d) 100 °C, (e) 110 °C, (f) 120 °C, (g) 140 °C, (h) 160 °C, (i) 200 °C

Each image was analyzed using the Delaunay triangulation method, which made it possible to automatically determine the distribution of interparticle distances. Figure 2 shows the dependence of the mean distance on the annealing temperature for films of different initial thicknesses. For thinner initial films (≤ 6 nm), a monotonic increase in interparticle distance is observed, whereas for thicker films (≥ 8 nm), non-monotonic trends appear, associated with the competition between particle coalescence and growth.

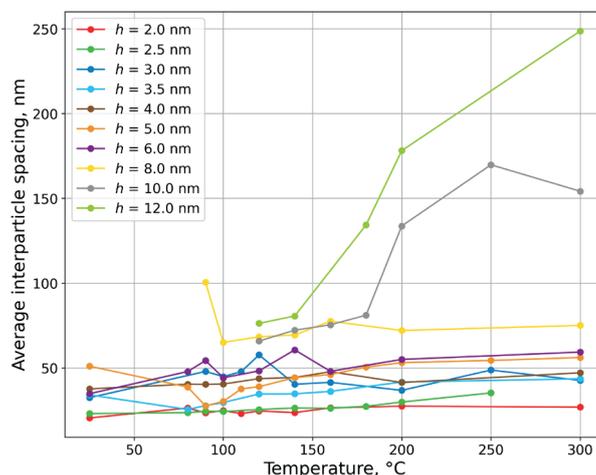


Fig. 2. Dependence of the mean interparticle spacing between Ag nanoparticles on annealing temperature for different initial film thicknesses [6]

Conclusion

A methodological approach has been proposed for the quantitative evaluation of interparticle distances in arrays of plasmonic nanoparticles based on Delaunay triangulation. The method makes it possible to automate the processing of microscopic images, objectively identify pairs of neighboring nanoparticles, and calculate distance distributions while accounting for filtering criteria and the exclusion of boundary particles. The methodology described in this work was implemented in a software developed in Python 3 [11].

The application of the methodology to arrays of silver nanoparticles formed by thermal annealing of thin films demonstrated its effectiveness for analyzing morphological evolution. The obtained dependencies of the mean interparticle distance on annealing temperature and initial film thickness reflect the competition between fragmentation, diffusion, and coalescence processes.

The described approach represents a convenient and reproducible tool for nanometrology, enabling the correlation of morphological characteristics with the functional properties of nanostructured substrates.

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