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Localized surface plasmon resonance tuning via nanostructured gradient Ag surfaces

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ABSTRACT

Gradient surfaces, i.e. surfaces whose properties change gradually along the sample length, receive increasing attention as they facilitate optimization of surface properties for particular applications. In this study we present vacuum-based strategy for fabrication of irregular silver nanoparticle arrays with gradient optical properties. This approach is based on the magnetron sputtering of Ag performed at low pressure in argon atmosphere. The gradient character of deposited arrays is achieved by use of a movable mask that is introduced in the vicinity of the substrate. It is shown that this technique enables to tailor the course of the gradient of localized surface plasmon resonance (LPSR) either by the speed of the mask or by additional deposition of silver on the top of surface pre-seeded by the gradient nanoparticle arrays.

1. Introduction

Silver nanoparticles (NPs) with dimensions smaller than the wavelength of light received high attention in the last decades. The interest in Ag NPs is primarily due to their localized surface plasmon resonance (LSPR) that typically occurs in the visible part of spectra. This makes silver nanoparticles highly valuable for a wide range of applications such as for instance photovoltaics [1,2] or biosensing [3–6]. One of common strategies used for production of materials for these applications is deposition of Ag nanoparticles onto a supporting substrate by means of magnetron sputtering [7–9]. In this case isolated individual nanoparticles are formed in the early stage of the film growth. The size, shape and distance between created nanoparticles, i.e. the key parameters that influence LSPR [10–12], may be controlled either by the deposition conditions (pressure, magnetron current, distance between the substrate and sputtered target) or simply by the deposition time. This in turn makes it possible to produce surfaces with LSPR exactly matching the requirements for a particular application. However, in many cases the position of LSPR for optimal performance of Ag NPs arrays is unknown and thus has to be optimized. The optimization of the properties of produced 2D assemblies of silver NPs is still relatively laborious task as it commonly requires fabrication of large number of samples that have to be tested separately. Promising alternative strategy that is capable to replace this time and cost ineffective multi-sample approach is fabrication of gradient Ag nanoparticle coatings, i.e. coatings for which the properties of Ag nanoparticle film vary gradually and continuously along the substrate length. The performance of produced materials in certain parameter range can be thus evaluated on a single sample in dependence on the position on the sample. As compared to multi-sample approach this strategy enables sharpening of the window of optimal material performance. Taking into account the fact than in majority of plasmonic-based biosensing devices the spot from which the signal is collected is in order of tens of micrometers or higher, the required gradients should be produced on the scale significantly exceeding the spot size, i.e. in the millimeter/centimeter range. The main aim of this study is to demonstrate that this may be achieved by vacuum-based method that employs magnetron sputtering at low pressure, i.e. technique previously used for fabrication of nanocolumnar coatings [13,14].

2. Material and methods

The silver gradient coatings were deposited by magnetron sputtering using low-pressure, planar, water-cooled magnetron [15] equipped with silver target (purity 99.99%, 81 mm in diameter). The magnetic circuit that was designed with intensity of 0.2 T above the erosion track enabled to perform sputtering in the argon atmosphere at the pressure of 0.15 Pa, which assured directional flux of sputtered atoms onto a substrate as well as sufficient spatial homogeneity of deposited coatings (standard deviation of LPSR wavelength is less than 3%). The magnetron was powered by DC power supply and the current was 40 mA.

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Moveable mask was introduced in between the substrate and the low-pressure magnetron in order to enable fabrication of surface gradients of deposited silver coatings as schematically depicted in Fig. 1. The distance between the mask and the substrate was 3 mm. The gradient in the properties of the deposited silver arrays was then achieved by the gradual movement of the mask that resulted in different exposure times of different positions on the sample to the directional flux of incoming Ag atoms. The initial position of the mask was to shield the entire substrate from the flux of Ag atoms sputtered from the target. Simultaneously with the beginning of the silver deposition, the mask was moved in the direction along the sample length with the constant speed. The movement of the mask was realized by linear motion feedthrough (LewVac) equipped with a computer controlled stepper motor. This enabled to vary the speed of the mask above the samples that was in the range from 0.5 cm/min to 2.0 cm/min in this study. The total length of the movement was 3 cm.

Morphology of produced silver coatings was determined by means of scanning electron microscopy (SEM). SEM analysis was performed using Mira3 (Tescan) scanning electron microscope operated with accelerating voltage 15 kV in secondary electron mode. Cleaned, on-side polished Si wafers (ON semiconductors) were used as substrate material. The size distribution as well as mean inter-particle distance was determined from acquired SEM

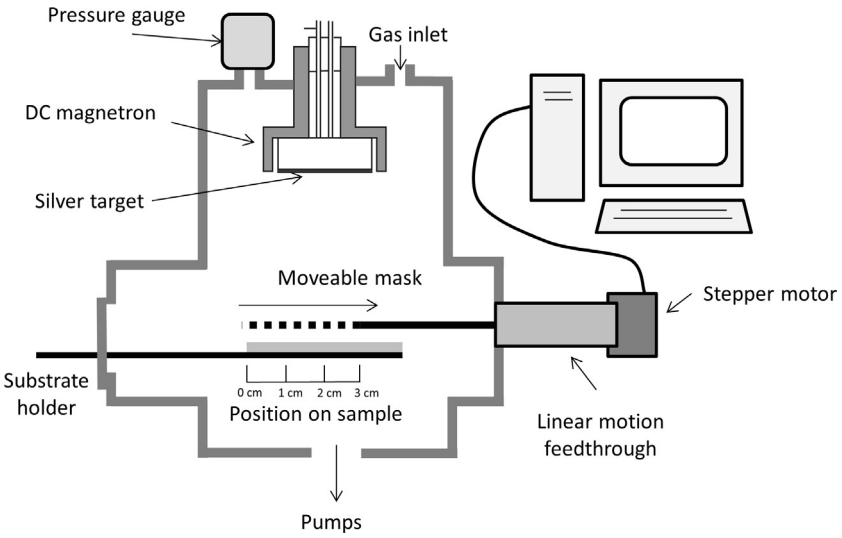

Fig. 1. Schematic illustration of the deposition system.

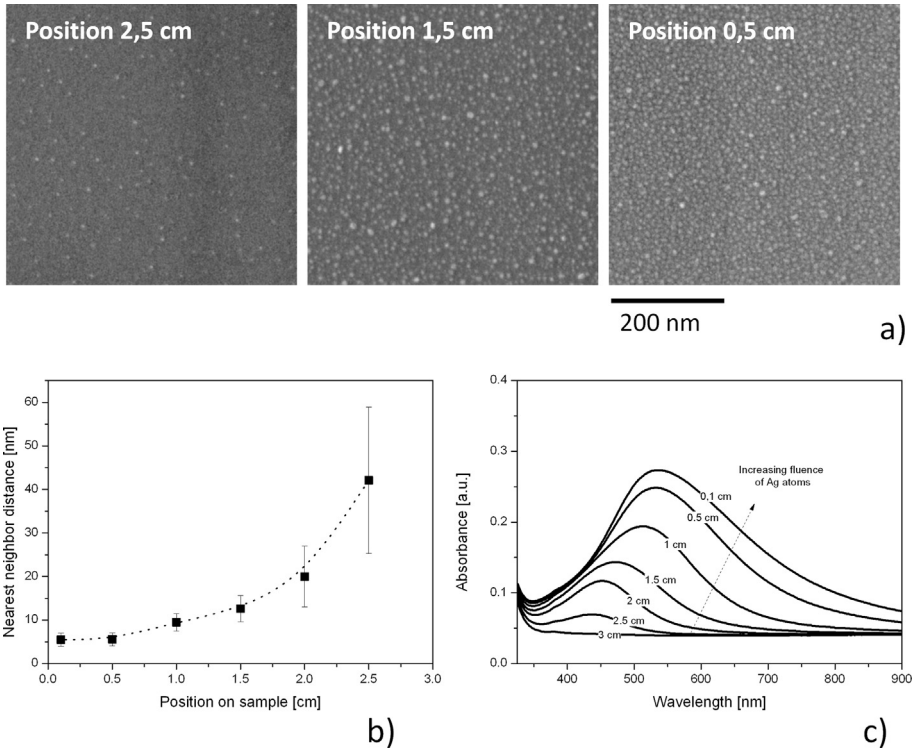

Fig. 2. a) SEM images acquired at different positions on sample b) inter-particle distance and c) UV–Vis spectra measured along the sample length. Speed of the movable mask 1 cm/min.

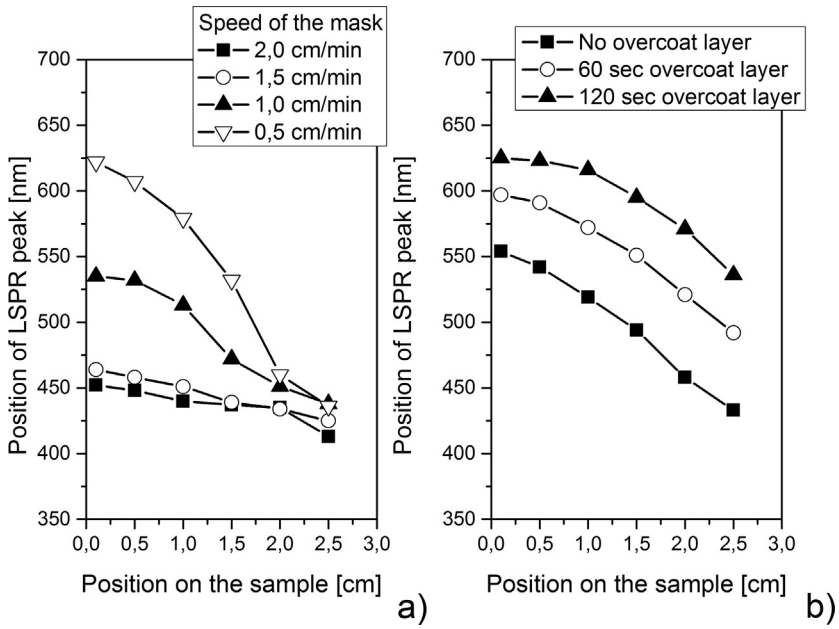

Fig. 3. Position of LSPR peak a) in dependence on the position on the samples for different speeds of movable mask and b) for samples with base layer of Ag NPs deposited at mask speed 1 cm/min and overcoated with Ag for 60 s and 120 s.

images using statistically relevant number of individual Ag NPs (typically 100–200). The mean distance between NPs is given as the average of the distances between the nearest neighbors.

Optical properties of silver films deposited onto a glass slides (soda lime glass, Marienfeld) were investigated by UV–Vis spectrophotometry. The UV–Vis spectra were acquired in the spectral range 325–900 nm by Hitachi U-2910 spectrophotometer.

3. Results and discussion

The first step of this study was evaluation of the morphology of produced coatings. The examples of typical SEM images acquired at three different positions on the gradient sample produced at mask speed 1 cm/min are depicted in Fig. 2a. These figures correspond to different exposure times of the substrate to the flux of atoms emitted from the magnetron target. Taking into account the speed of the moveable mask the position 0.5 cm corresponds to 150 s exposure time and position 2.5 cm was exposed to the beam of incoming particles for 30 s. As can be seen the nanoparticle arrays were in all cases composed of individual and separated Ag nanoparticles with approximately circular shape. The size of the individual NPs was found to be not significantly influenced by the exposure time and was in the range 4–6 nm. The only parameter that distinguished different positions on the sample was the amount of NPs and with it connected inter-particle distance that varied from 42 ± 17 nm observed for the position 2.5 cm (exposition time 30 s) to 5.5 ± 1.5 nm for the position 0.5 cm (exposition time 150 s) measured from center to center of individual NPs (Fig. 2b).

The differences in the gap between individual NPs naturally had strong impact on the plasmon coupling between NPs. As demonstrated in previous studies the decrease of inter-particle distance causes substantial red-shift of LSPR [16] and the plasmon shift normalized by the LPSR wavelength maximum of isolated particle scales with the ratio of inter-particle gap normalized by nanoparticle size [12,17,18]. The same behavior was observed also in our case, which is demonstrated in Fig. 2c: the LSPR shifted to higher wavelengths as the exposure time of particular position on the samples increased, i.e. as the inter-particle distance decreased. This in turn resulted in formation of surface with gradient of LSPR wavelength maximum.

From the point of possible applications it is important not only to produce gradient surfaces, but also to tailor the slope of the gradient. Two strategies were tested in this study. In the first one the speed of movable mask was varied. The slope of the gradient of LSPR peak in this case increased with decreasing speed of the mask as can be seen in Fig. 3a. In other words, lower speed of the mask caused bigger differences of amount of incoming Ag atoms and thus also bigger differences in inter-particle distances on different positions on the sample.

The second possibility how to control the course of LPSR is a two-step deposition procedure. The first step is pre-seeding of the substrate with gradient array of Ag NPs. In the second step additional deposition of silver on the top of pre-seeded substrate is performed without the mask above it. This additional deposition step led to the decrease of the inter-particle distances on the entire substrate which resulted in the LPSR shift to higher wavelengths as compared with the samples without the overcoat (see Fig. 3b).

4. Conclusions

Silver nanoparticle arrays with gradient of LSPR were prepared by means of magnetron sputtering at low pressure. It is shown that the gradient of LSPR may be achieved by gradual movement of a mask above the substrate. By this way it is possible to control the amount of incoming silver atoms and morphology of produced coatings and thus also their optical properties. This in turn results in gradient of LPSR along the sample length, whose course can be varied by the speed of the mask as well as by additional overcoating of pre-seeded NPs gradient array by silver. Such materials are highly valuable mainly with respect to fundamental studies focused on emerging plasmonic based biosensors and optimization of their performance.

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