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Preparation of Au Nanostructure Arrays for Fluorometry and Biosensors Applications

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The paper describes the fabrication of random and ordered gold nanostructure arrays (NSA) of different morphology using island film thermal annealing and nanoimprint lithography techniques. Structural parameters of obtained NSA were investigated using atomic force microscopy method. Spectral characteristics of obtained NSA were studied in air atmosphere, and NSA light extinction spectra exhibited an expressed plasmon peak. Spectral position of localized surface plasmon resonance can be tuned depending on geometrical parameters of nanostructures, which is an important factor for resonant investigation methods of various types of molecular structures. Proposed technological approaches can be used to implement the resonance fluorometry in electromagnetic field of nanostructures (surface-enhanced fluorescence) method and in chemical and biosensors based on localized surface plasmon resonance.

Keywords: Localized Surface Plasmon Resonance, Nanostructures, Fluorometry, Biosensor.

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1. INTRODUCTION

Fluorescence phenomenon is widely used in optical devices, imaging microscopy, biology, medical studies and diagnostics. Improvement of fluorescence methods sensitivity, even down to single molecule detection limits, is needed in many applications, and this problem demands a solution at the present moment. One of the possible ways to enhance sensitivity is a method called resonance fluorometry in electromagnetic field of nanostructures (surface-enhanced fluorescence (SEF)), which is based on an arrangement of highly conductive surfaces near the source of photon emission. SEF provides general increase in fluorescence detection efficiency by changing and controlling the photon emitter electromagnetic environment. Near-field interaction between the emitter and surface modes of electromagnetic field is crucial in SEF. In particular, highly conductive surface capable of generating localized and polariton surface plasmons are efficient tools for SEF technique. Recent progress in nanoscale structured surface development extends application field of mentioned method significantly.

2. FABRICATION OF NANOSTRUCTURES FOR FLUOROMETRIC INVESTIGATIONS

2.1 State of the art

Fabrication of nanostructures for fluorometric investigations is a promising interdisciplinary study in the fields of biology, chemistry, physics and medicine [1, 2]. Development and exploitation of novel functional nanomaterials with well-defined structure and properties are of absolute importance for biochemical investigations [3-5]. During the last decade, a great number of nanomaterials and nanotechniques have been developed, opening up the new possibilities in biological and biochemical studies [1, 2, 6, 7]. Up to now, a number of novel nanomaterials, such as carbon and polymeric nanotubes [5], quantum dots [3] and magnetic nanoparticles [4] have been studied and utilized in biotechnology applications. Their unique physicochemical properties provide new basis for researching complicated biological processes that are difficult to study using conventional methods [3-7]. Nevertheless, most of widely applied methods in the nano-manufacturing of SEF chips at present time are based on utilization of materials with well-known properties, such as gold, silver, carbon and silicon.

Commonly used high-conductive surfaces with developed roughness are effective fluorescence amplifiers; however, they do not yield predictable results, and, consequently, the enhancement process can not be controlled, as well as in case of nanoparticles from colloidal solutions. This is explained by a strong dependence of fluorescence detection on nanoparticles size, shape and interparticle distance. Only uniform surface-bound nanostructure arrays with known surface 3D-geometry can provide a real possibility to perform preliminary estimation of final parameters when using SEF technique and ensure their stability and reproducibility.

In present work, two different approaches for nanostructures fabrication were used – a method based on gold island films preparation with subsequent thermal annealing and recently developed nanoimprint lithography (NIL) technique for creation of uniformly oriented and homogeneous NSA with controlled nanoparticle size, shape and spacing, which can be a basis for SEF chips development. The most evident advantage of the latter method is an exploitation of matrix templates for nanostructure preparation that makes NIL a high-throughput and cost-efficient process, which allows creating templates with relatively large linear dimensions and sub-10 nm resolution [8, 9].

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2.2 Fabrication of random gold nanostructure array samples

Developed SEF chips fabrication technique based on gold island films with subsequent thermal annealing is a most affordable method yielding satisfactory results. Gold island films of varying thickness (from 10 to 60 nm) were obtained by thermal evaporation in vacuum on glass substrates. After island film deposition, samples were annealed at 550 °C for 6 hours in air atmosphere. As a result of annealing, gold film color changed from blue of different intensity to blue, violet and pink (depending on the film thickness) that confirms the formation of separated gold nanoparticles having different size on the glass substrate surface at specific initial film thickness values (e.g. see Fig. 1).

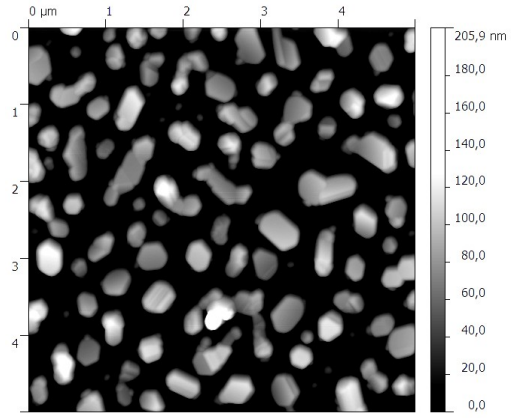

Fig. 1 – AFM image of SEF chip based on thermally annealed gold island film (sample №7)

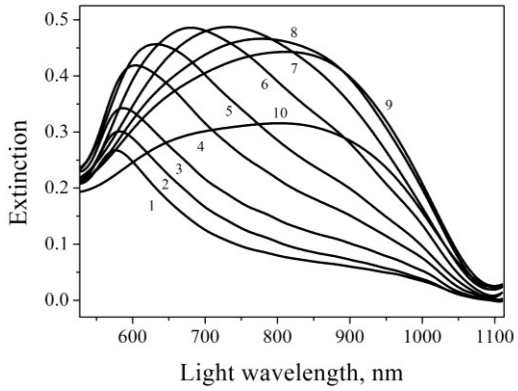

Fig. 2 – Measured extinction spectra of SEF chips based on thermally annealed gold island films with different initial gold island film thickness. Extinction spectra (which are numbered with reference to samples) exhibit peaks located in the wavelength range from 576 nm to 809 nm

2.3 Structural and spectral characteristics of thermally treated gold nanostructure arrays

As a result of microspectrophotometric measurements, light extinction spectra of the samples were obtained. It was found out that the peak position in the light extinction spectrum, which corresponds to the rise of localized surface plasmon resonance (LSPR) on individual gold nanoparticles, shifts towards longer wavelengths with increase in the initial gold island film thickness (see Fig. 2). Atomic force microscopy (AFM) results (see Table 1) revealed the direct relation between lateral dimensions and height of nanostructures produced after annealing and the initial gold island film thickness. Thus, it was shown that it is possible to tune the LSPR spectral position (see Fig. 2), and, therefore, the spectral profile of fluorescence surface enhancement, by changing the initial gold island film thickness. Developed SEF chips fabrication technology based on gold island films with subsequent thermal annealing can be exploited taking into account inherent technological limitations, which hinder the preparation of geometrically ordered nanoparticle arrays.

Table 1 – Spectral and structural characteristics of SEF chips based on thermally annealed gold island films with different initial gold island film thickness (sample numbers follow the initial gold island film thickness increase)

Sample number	Peak position in extinction spectrum, nm	Average equivalent diameter, nm	Average height, nm
1	576	56	27
2	582	56	28
3	585	85	35
4	604	143	35
5	633	152	47
6	680	235	53
7	733	330	61
8	776	470	91
9	809	524	114
10	804	N/A	N/A

3. FABRICATION OF ORDERED NANOPARTICLE ARRAY SAMPLES

3.1 NSA fabrication using nanoimprint lithography technique

Gold nanoparticle arrays were produced according to the following protocol. Glass substrates were cleaned in a 1:1 piranha solution (30 % H_2O_2:29 % NH_4OH), rinsed with a copious amount of DI:H_2O and dried using N_2. The resist was spincoated to the appropriate thickness on the substrates, baked for solvent removal and imprinted using the template. After nanoimprinting and sample separation, the residual polymer layer was removed using O_2 plasma reactive-ion etching. Metallization was accomplished using an electron beam evaporator by first depositing a 3 nm Ti adhesion layer followed by Au layer. Lift-off was performed by soaking the samples in acetone and using an ultrasonic bath. After completion of lift-off, samples were rinsed with methanol and isopropanol and dried with N_2.

This technique can be used to create a variety of structures by simply using different one-dimensional gratings (i.e. with various duty cycles or periods) and relative angular orientation of the gratings for successive imprints.

3.2 Characteristics of produced ordered NSA samples

Structural characteristics of ordered NSA were investigated using atomic force microscopy method. NIL-fabricated NSA samples of different geometry were studied. These samples were comprised of parallelepiped-

shaped nanoparticles, located in an ordered array with square or rectangular lattice. Typical AFM image of nanostructure array fabricated using mentioned technique is shown in the Fig. 3.

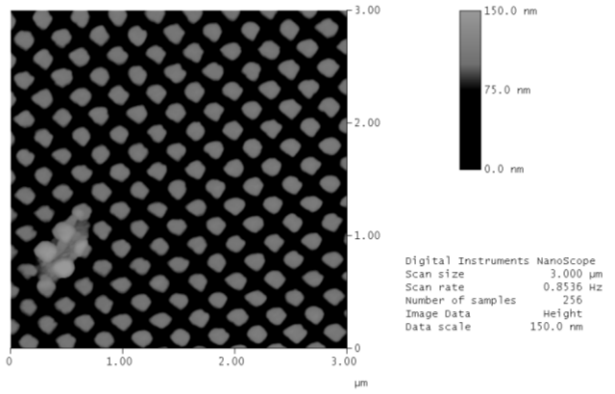

Fig. 3 – AFM image of NSA sample №2 produced using NIL

Spectral characteristics of produced ordered NSA were investigated in air atmosphere (see Fig. 4) and yielded the following results. Unpolarized light extinction spectra for each of samples exhibited bands with an expressed peak, which is characteristic for excitation of plasmonic oscillations in metal nanostructures. Extinction peaks spectral positions of investigated samples differ and depend on the geometrical parameters of nanostructures. Extinction peak parameters estimated by fitting measured NSA light extinction spectra with a lorentzian function are presented in Table 2.

The presence of expressed extinction peak allows exploiting ordered NSA as localized surface plasmon resonance sensor elements and SEF chips. It is evident from Fig. 4 that application of nanoimprint lithography technique allows producing NSA, which exhibit extinction peaks in different spectral regions, and, therefore, are able to operate at different incident light wavelengths.

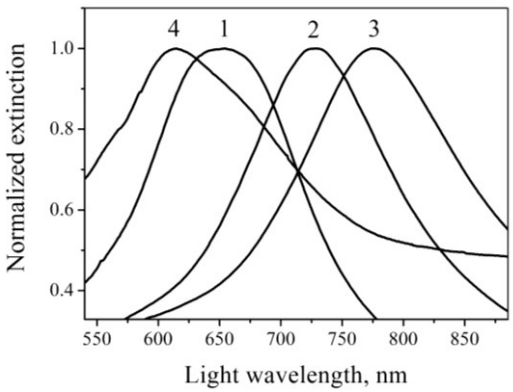

Fig. 4 – Normalized measured unpolarized light extinction spectra of ordered NSA samples №1-4

Table 2 – Spectral characteristics of ordered NSA samples produced using NIL

NSA sample number	Peak position in extinction spectrum, nm	Peak FWHM, nm	Extinction at peak maximum
1	652	160	0.35
2	731	154	0.82
3	783	171	0.64
4	606	173	0.28

4. CONCLUSION

Samples of random and ordered gold nanoparticle arrays with different morphology were fabricated using thermal annealing of vacuum-evaporated island films and nanoimprint lithography methods. Physical characteristics of produced structures were studied using atomic force microscopy method. Investigation of spectral characteristics of obtained NSA revealed the presence of expressed plasmonic peak in the NSA light extinction spectra. Developed technologies allow implementing the fluorescence signal enhancement technique using the localized surface plasmon resonance in highly conductive nanostructures.

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