Arrays of Metal Nanostructures for Plasmon-enhanced Spectroscopy

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Abstract. We report on the study of localized surface plasmon resonances (LSPRs) arising in arrays of metal (Au) nanoclusters, dimers, and nanoantennas under the influence of external electromagnetic radiation. Using nanolithography, the plasmonic arrays with different morphologies including cylindrical nanoclusters and dimers, linear and H-type nanoantennas were fabricated. Their LSPR frequencies were determined from the analysis of optical reflection and IR spectra. LSPR frequency depends strongly on morphology of metal nanostructures and is varied from visible to terahertz spectral range with variation of the structures from cylindrical nanoclusters to the nanoantennas with a high aspect ratio. We established the interconnection between the structural parameters of the plasmonic arrays and their LSPR frequencies based on the results of 3D electrodynamic simulations.

1. Introduction

The fabrication of metal nanoclusters and characterization of their plasmonic properties is a subject of comprehensive reviews [1-3]. Arrays of metal nanoclusters of various size, shape, and areal density were fabricated using a variety of synthesis methods. Among those methods of nanolithography offer the unique opportunity to fabricate nanostructures arrays with precisely controlled structural parameters such as size, shape, period, and morphology.

These parameters allow the plasmonic nanostructure properties to be tuned in a wide spectral region. The tunable plasmonic properties secure a wide range of applications of the metal nanostructures including photocatalysis, energy harvesting, sensing, and plasmon-enhanced spectroscopies [4]. The latter refers to surface- and tip-enhanced Raman scattering (SERS and TERS), photoluminescence, and infrared (IR) spectroscopies. The first two operate in a visible spectral range and require utilizing the metal nanoclusters having appropriate LSPR energies, while metal nanoantennas reveal LSPR resonances located from near IR to terahertz spectral range which were applied for spectroscopic analysis of variety of materials by surface-enhance infrared absorption (SEIRA).
The most often used nanoantennas have a linear shape and represent metal rods (for example, Au, Al, Ag) with a width of about 100 nm, the characteristic length which can vary in the range from tens of nanometers to several micrometers. As a rule, nanoantenna arrays are fabricated on dielectric (SiO$_2$, CaF$_2$, Al$_2$O$_3$) or semiconductor (Si) substrates. Metal nanoantennas with more sophisticated morphologies (crosses, circles etc) were also fabricated by nanotechnology and their plasmonic properties were a subject of extensive research [5].

Both conventional Raman and IR spectroscopies have a relatively low sensitivity for detecting the vibrational modes in organic or inorganic molecules which is not sufficient for sensors applications. The idea of SERS is based on specially designed Au nanocluster arrays providing high electromagnetic field in the immediate vicinity of the plasmon nanoclusters under resonance excitation when the frequency of the incident electromagnetic radiation coincides with the eigenfrequency of the LSPR in the nanoclusters [6]. As a result, the local electromagnetic field near the nanoclusters is enhanced, which makes it possible to detect Raman signal from a small amount of substances placed in the local field [6]. In the case of SEIRA, Au nanoantennas with the LSPR frequencies matching those of the vibrational modes of the probed molecules are used to induce a local electromagnetic field in the vicinity of the nanoantenna edges and thus to enhance IR absorption by the molecules located near the edges [5].

In this paper, arrays of metal nanoclusters, dimers, and nanoantennas which possess LSPR with the energies located from visible to terahertz spectral range were fabricated by nanolithography and their plasmonic properties were investigated by optical and IR spectroscopies.

2. Experimental

The optimum structure parameters for nanostructure arrays were determined by the Finite Difference Time Domain (FDTD) method using the commercial package by Lumerical (Vancouver, Canada) and electrodynamic simulations using 3D full wave simulations in the software ANSYS Electromagnetics Suite 18 [7] to set up the plasmon resonance to a specific wavelength in the visible and mid infrared spectral range, respectively.

Homogeneous arrays of Au nanoclusters and dimers (10×10 μm$^2$ in size) as well as nanoantennas (3×3 mm$^2$) with structural parameters determined from the calculations were formed by focused ion beam on either on pure Si (001) substrates or those covered with SiO$_2$ layer of different thickness (8 and 77 nm). The width (height) was chosen to be 60 nm (50 nm), and the nanocluster size and antenna length was varied within 20–200 nm and 2–15 μm, respectively. Figs.1a,b and Figs.2a,b demonstrate a typical scanning electron microscopy (SEM) images of the nanostructure arrays using the same Raith-150 system at 10 kV acceleration voltage, 30 μm aperture, and 6 mm working distance.

IR transmission spectra of Au nanoantenna arrays were measured in the spectral range from 100 to 4000 cm$^{-1}$ using a Bruker Vertex 80v Fourier spectrometer. For further estimations, the ratio of the IR transmittance spectra corresponding to light polarization along the axis of the nanoantenna arrays and perpendicular to it was calculated and analyzed. The reflection spectra of Au nanocluster and dimer arrays were measured utilizing a Bruker Vertex 80v FT-IR spectrometer supplied with a Hyperion 2000 microscope in the range from 400–900 nm equipped with a 40x objective.

3. Results and discussions

The reflection spectra measured from nanocluster and dimer arrays (not shown here) indicate pronounced maxima attributed to the LSPR modes. Comparison with the calculations of reflection spectra, which will be described elsewhere, allows the exact determination of the LSPR position as a function of nanocluster size for both types of the arrays and is shown in Figs.1c,d. The information on the LSPR position can be used for performing the resonant SERS experiments.
Figure 1. Representative SEM images of Au nanocluster (a) and dimer (b) arrays. LSPR energy determined for nanoclusters (c) and dimers (d) fabricated on a Si substrate covered with SiO₂ layer (8 and 77 nm) and pitch size (130-250 nm) as a function of the cluster diameter.

The dependence of LSPR position as a function of nanoantenna length was already determined from IR experiments [8] and shows a linear behavior. This dependence can be easily used to match the LSPR position to the frequency of vibrational modes in analytes for further SEIRA experiments. However, for unambiguous identification of analyte, the information on the frequency position of several modes located in different spectral range is strongly needed. Here, we demonstrate nanoantenna array which consists of 4 areas with nanoantennas having different lengths as shown in Fig.2a. This array provides 4 dips in IR transmission spectrum corresponding to the LSPR originated from antennas of different lengths (Fig.2c).

Figure 2. Representative SEM image of linear (a) and H-type (b) Au nanoantenna arrays. IR spectra of Au linear (c) and H-type (d) nanoantenna arrays with pronounced minima corresponding to LSPR positions.
To make nanoantennas more effective in terahertz spectral range, the H-type nanoantennas with structural parameters optimized in the electrodynamic simulations were fabricated (Fig.2c). Their LSPR positions were determined from IR transmission spectra (Fig.2d). These nanoantennas arrays are well suited for investigation of the phonon modes from novel semiconductor nanostructures [8-10].

4. Conclusion
We report on the experimental determination of LSPR positions for different types of arrays of Au nanostructures of various nanocluster size and morphology which were fabricated using nanolithography on transparent and opaque substrates. The interconnection between the structural parameters of the plasmonic arrays with their LSPR position was established on the base of the comparison of optical reflection and IR spectra with the results of 3D electrodynamic simulations. The implementation of plasmonic arrays with well controlled LSPR positions and multiple LSPRs is essential for surface-enhanced Raman scattering and IR absorption.

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