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Mid-infrared nanoantenna arrays on silicon and CaF_2 substrates for sensing applications

L. Businaro [a,*], O. Limaj [b], V. Giliberti [b], M. Ortolani [a], A. Di Gaspare [a], G. Grenci [c], G. Ciasca [a], A. Gerardino [a], A. de Ninno [a], S. Lupi [b]

[a] CNR – Institute for Photonics and Nanotechnology, Via Cineto Romano 42, 00156 Rome, Italy
[b] Università of Rome "La Sapienza", Piazz.le Aldo Moro 5, 00185 Rome, Italy
[c] CNR – Instituto Officina dei Materiali, S.S. 14, Km 163.500, 34149 Trieste, Italy

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ABSTRACT

We report on the fabrication and systematic characterization of nanoantenna arrays with several different geometries realized both on standard silicon (Si) substrates and Calcium Fluoride (CaF_2) substrates aimed at the realization of a mid-Infrared protein detector. In particular, we present a novel nanofabrication procedure which allows the adoption of CaF_2 in a standard lithographic process with results comparable to the ones obtained on silicon wafers. The transmittance and reflectance spectra of the nanoantennas, were acquired by means of an Infrared microscope coupled to a Michelson Interferometer. In all the nanoantenna devices, the plasmonic resonance follows a linear scaling relation: a lattice parameter change of a ±(5–10)%, indeed, results in a shift of the Si (1,0) plasmonic resonance frequency which is proportional to $1/a$. This scaling behavior offers a useful tool for device frequency tuning, which can be used to obtain a fine spectral overlap with the protein amide-I and amide-II bands. A Lorentzian analysis of the resonance peaks reveals that our nanostructures have an high Q factor ($Q = \nu_0/\Delta\nu$), demonstrating the effectiveness of our fabrication procedures.

1. Introduction

Optical mass sensors based on Surface Plasmons Resonances (SPR) in thin metal films are widely used in biomedical applications for detecting the formation of molecular layers at the film surface and for studying membranes and cell culture [1]. Although most SPR applications focus on the visible (VIS) and near Infrared (NIR) range, nevertheless some SPR techniques operating in the mid infrared (MIR) range have recently been developed [2–4]. The combined use of MIR spectroscopy and SPR provides several advantages over the standard SPR technique, being label-free, very sensitive and non-damaging for bio-molecules, whose fingerprints lay in the 2.5–10 μm wavelength range. In this context, the use of MIR plasmonic nanoantennas fabricated on Si substrate has recently been demonstrated by Adato and co-workers [2], providing a direct identification of the amide I and II absorption bands of a silk fibroin monolayer. Furthermore, the Surface Plasmon (SP) in the MIR range would be particularly useful in living cell studies, thanks to its large penetration depth which is comparable with the cell height and, thus, allows to probe the occurrence of intracellular process [5].

As a matter of facts, most MIR applications are based on the use of CaF_2 or BaF_2 UV/VIS/IR transparent windows, but these materials bring with them some characteristics, such as very poor adhesion for resists and metals and a high detrimental water solubility (mainly for BaF_2), that make them difficult to approach for the standard silicon technology and potentially incompatible with cell culturing.

In this work we have fabricated and characterized the behavior of different plasmonic nanoantenna arrays on silicon substrate by means of FTIR (Fourier Transform – InfraRed) spectroscopy, with the aim of realizing a mid-infrared protein detector. Nanoantennas arrays are 2D lattices of metallic nanostructures where the primary cell is repeated periodically along the two directions. We have investigated three different structures, namely rod-shaped, cross-shaped and square-shaped structures, each one of them realized in positive and negative tones (more details have been reported in materials and methods). The possibility to obtain a fine "lithographic tuning" of the plasmonic resonance has been demonstrated by applying a scaling factor to both the array lattice constant and the primary cell of 90%, 95%, 105%, and 110%. Furthermore, we present an innovative procedure which allows the adoption of CaF_2 substrates for the realization of plasmonic nanostructures. This procedure opens the way to the fabrication of lab-on-chip integrated plasmonic devices that could be used to study a biological

* Corresponding author.
E-mail address: luca.businaro@cnr.it (L. Businaro).

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sample with many different spectroscopic and imaging tools at the same time. We think, for example, at the detection of specific proteins nearby a live cell while it is observed by mid-IR spectroscopy [6,7].

2. Materials and methods

2.1. Devices fabrication

Following the recent paper by Adato and coworkers [2], we adopted, as a starting point for the primary cell of the plasmonic structures, a single $1100 \times 230 \times 100$ nm ($L \times W \times H$) metallic rod. Apart the single rod structure, we designed a simple cross, superimposing two 90° oriented rods, and a "square" obtained using four separated half 90° oriented rods. All these structures where realized on a silicon substrate, in both positive (i.e. metallic rods) and negative tones (i.e. empty rods in a continuous metallic film) and repeated periodically along the two directions using a lattice constant $a = 1500$ nm. The fabrication process of these nanostructures is based on electron beam lithography (Vistec EPBG-5HR 100 keV) using a 450 nm thick ZEP-520A resist film. The final metallic structures were then obtained by evaporation of thin adhesion layer (30 nm) followed by 70 nm thick Au film and lift-off (5′ in anisole at 50 °C in ultrasonic shaking bath). In order to perform a "lithographic tuning" of the plasmonic resonance frequencies, starting from the described six structures, we applied a scaling factor to both the lattice constant "a" and the primary cell of 90%, 95%, 105%, and 110%. Thus, we obtained a matrix of thirty 200×200 μm^2 patterned areas (five scaling factors for six different structures). The typical obtained results are shown in the SEM images placed as insets in Fig. 1 (frame 5×5 μm).

The above described positive structures were also realized on CaF_2 substrates obtained from an IR-grade CaF_2 disk (Crystran Ltd., UK). In order to use CaF_2 substrates in a standard lithographic process with results comparable to the ones obtained on silicon wafers, the material surface was sputter-coated with a thin (~10 nm) silicon film (sputtering with Ar at 1.2×10^{-3} mbar, 600 W DC applied for a total time of 15 s). Further details on the CaF_2 (bulk)/Si (10 nm) bilayer have been published elsewhere [8]. The devices have than be realized using the same lithographic steps described above, apart for a small increase in the ZEP 520 A exposure dose.

2.2. FTIR measurements

The transmittance and reflectance of the plasmonic nanostructures were measured by means of an Infrared microscope coupled to a Michelson Interferometer (Bruker IFS 66v/S). For both measurements an aperture of 100 μm was used to focalize the IR beam into each device, whose size is 200×200 μm^2. The reflectivity has been extracted through the ratio $R = I^R_{\text{sample}}/I^R_{\text{gold}}$, where I^R_{sample} is the intensity of radiation reflected by the sample and I^R_{gold} is the intensity reflected by a 70-nm-thick Au film on a double polished Si wafer. The transmittance, defined as $T = I^T_{\text{sample}}/I^T_{\text{Si}}$, has been calculated considering as reference the intensity transmitted through a Si wafer. Polarization dependent measurements have been acquired by using a KRS-5 polarizer.

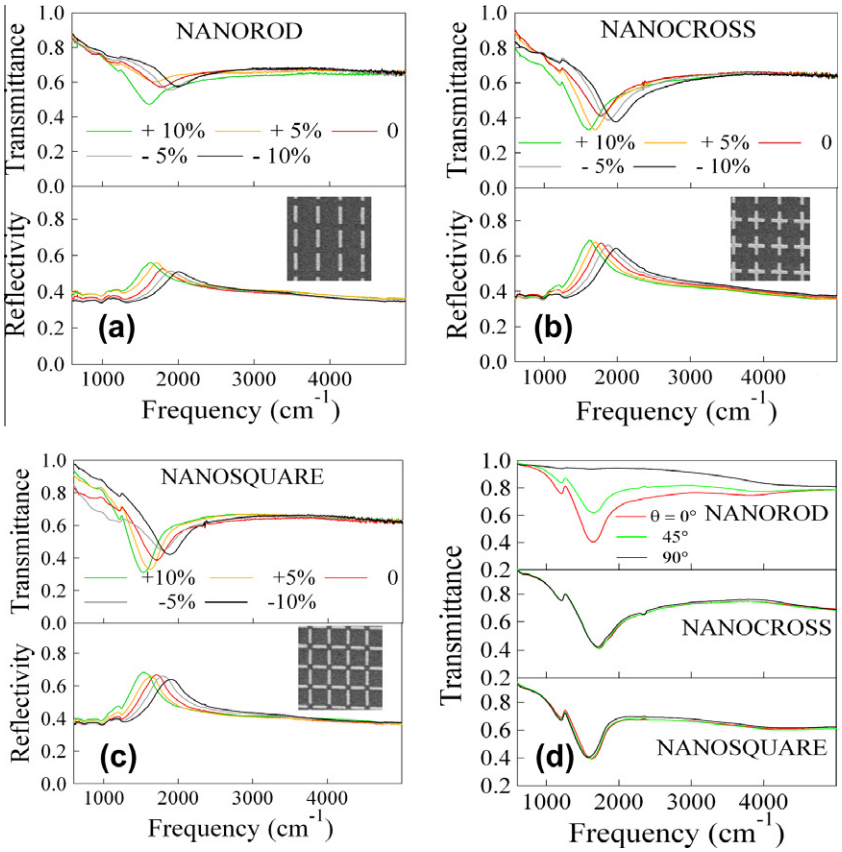

Fig. 1. Transmittance and reflectance spectra of positive nano-rod (panel a), nano-cross (panel b) and nano-square (panel c) devices as a function of the frequency for different values of the lattice constant. SEM images of the corresponding nanostructure are provided in the insets (frame 5×5 μm). Transmittance spectra of the direct devices at different polarizations (panel d). Angle θ indicates that the electrical field is directed along the long side ($\theta = 0°$) or the short side ($\theta = 90°$) of the rod pattern. A lattice constant $a = 1500$ nm has been chosen. Devices have been realized on Si-substrates.