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Design and top-down fabrication of metallic L-shape gap nanoantennas supporting plasmon-polariton modes

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ABSTRACT

In this work the design, fabrication and optical characterization of a polarization-sensitive L-shape nanoantenna device are reported. Such configuration supports plasmon-polariton modes that are combinations of in-phase and out-of-phase single antenna long-axis surface plasma oscillations. In the former case charges distributions induce in the gap region an intense hot spot while in the latter one a "zero-field spot" occurs in a plasmonic mode which can be referred to a non-zero dipolar momentum.

1. Introduction

Plasmonic nanoantennas have led to huge innovations both for the capability to efficiently interact with free propagating radiation and their property to confine electromagnetic energy inside of subwavelength regions called hot-spots [1–5]. The ability of antenna to enhance the electromagnetic field beyond the diffraction limit leads to several implications and advantages that can find applications in many branches of technology like photoconvertion [6,7], metamaterial engineering [8–10], non-linear optics [11,12], bio-sensing [13–15] and the really challenging single-molecule spectroscopy [16,17]. In particular, antenna dimers [18,19] are optimal systems for the fabrication of plasmon-assisted Raman sensors. Tailoring the antenna morphological parameters it is possible to finely tune the dipolar surface plasmonic resonance (SPR) wavelength around the spectral region of interest employed for enhanced Raman spectroscopy. Moreover the interspacing volume or gap between the apexes of the two antenna arms, under resonance conditions, can experience both strong field amplification and extreme energy localization. If the molecules of interest are placed inside the gap, the plasmonic enhancement effect can make the Raman signal easily detectable, thus showing the spectral fingerprints of the deposited molecules [20,21].

In this work the fabrication, by means of advanced lithographic techniques, and the characterization of L-shaped plasmonic antenna arrays are reported and explained in details. L-shape antenna dimer is a system which exploits the combination of single arm long axis plasmon-polariton modes. Single antenna nanostructures show dichroic behavior in the far-field spectrum, according to the polarization of the light impinging on them. In fact, because of the size-dependency of SPR [22–24], the antenna far-field spectrum shows a blue-shift of the resonance peak when the light polarization is rotated from a configuration parallel to the structure long axis to a configuration aligned to the short axis. Differently from what happens to the single antenna case, the L-shape nanostructure presents far-field dichroism which can be ascribed to the in-phase and out-of-phase combination of long axis plasmonic modes induced by different light polarization states. Considering the direct implication of this phenomenon in the electric field distribution, by simply rotating light polarization, it is possible to move from an intense hot-spot configuration to an almost "zero-field spot" in the gap region. In the perspective of improving the Raman signal-to-noise ratio, these results are quite promising and suggest a very flexible SERS functionalized device.

2. Experimental procedure

The top-down fabrication technique adopted to produce L-shape gap nanoantennas was Electron Beam Lithography (EBL). Since the fabrication of strongly coupled nano-systems (i.e. with inter-particle distance in the 10 nm range) with large accuracy and homogeneity is an essential requirement for the production of a Raman-active biosensor, such technique appears as one of

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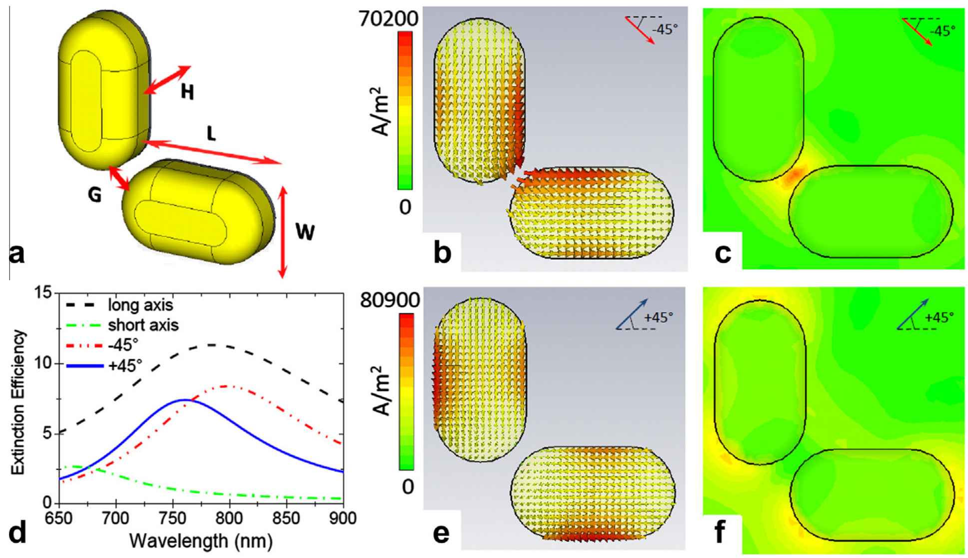

Fig. 1. (a) 3-D sketch of L-shape antennas showing the geometrical parameters representative of the morphology. (b and c), respectively current density and electric field intensity 2-D plots for normal-incidence light polarized at −45° valued at λ = 810 nm. (d) Theoretical extinction efficiency spectra of L-shape antennas (L = 190 nm, W = 110 nm, H = 60 nm and G = 20 nm) and of their single antenna arm; in black dashed line the long axis reference extinction spectrum of single antenna, in green dotted/dashed line the short axis reference extinction spectrum of single antenna, in red double-dotted/dashed line the L-shape antenna extinction spectrum for −45° polarization and in blue continuous line the L-shape antenna extinction spectrum for +45° polarization. (e and f), respectively current density and electric field intensity 2-D plots for normal-incidence light polarized at +45° valued at λ = 760 nm. (For interpretation of color in this figure, the reader is referred to the web version of this article).

the optimal choices both for the level of structure shape accuracy and of inter-particle separation that it guarantees.

The first step in the fabrication process consists in the nanostructure design. Dimer configuration, whose schematic is shown in Fig. 1(a), is defined by the geometrical parameters length L, width W, height H and inter-particle gap G. Since dimers are fabricated in arrays, another significant parameter to be defined consists in the inter-structure spacing S. Different matrices of L-shape antennas have been produced changing the inter-particle distance G. The substrate on which the nanostructures have been fabricated is CaF_2 (100), particularly addressed in literature for its high optical transparency in the visible and near-infrared (NIR) regions.

The EBL nanopatterning procedure involved several steps; substrate-cleaning in an ultrasonic bath of acetone and oxygen plasma exposure have been firstly carried out. Hence PolyMethylMethacrylate (PMMA) electronic resist has been spin-coated on the substrate. After the spin-coat, annealing has been done at 180 °C for 7 min in order to obtain a uniform film. To prevent surface charging effects during the electron exposure, 10 nm Al layer has been thermally deposited on the PMMA surface. Therefore EBL machine (electron energy 20 keV and beam current 45 pA), equipped with a pattern generator (Raith 150-two), has been used for the nanostructure patterning. After the Al removal in a KOH solution, the exposed resist was developed in a conventional solution of MIBK/isopropanol (IPA) (1:3) for 30 s. Physical Vapour Deposition (evaporation rate 0.3 Å/s), respectively of 5 nm Ti as adhesion layer and 55 nm Au has been performed on the sample. Finally, the unexposed resist was removed with acetone and rinsed out in IPA. O_2 plasma ashing at 200 W for 60 s was used to remove residual photoresist and organic contaminants for an improved lift-off. An annealing cycle at 200 °C with a duration of 15 min has been performed on the sample in order to investigate the effect of grain boundaries on the electron relaxation rate [25] and therefore on the optical behavior of L-shape nanoantennas. There is evidence in literature according to which Au deposited on a substrate at room temperature tends to aggregate in grains at a metastable energetic level. By increasing the temperature the internal dynamic of the system can be sped up, thus promoting a polycrystalline grain growth and grain boundary migration [26]. This process has been demonstrated to clearly affect the electron scattering rate which in turns will induce a blue shift of the plasmon resonance [25].

During the optical characterization, the sample has been illuminated at normal incidence with a linearly polarized visible-NIR (DH-2000-BAL, Ocean Optics) light spot of 30 μm diameter performing far-field transmission spectroscopy (HR4000, Ocean Optics) for different light polarizations.

The morphological characterization has been carried out by means of a Dual Beam (SEM-FIB) – FEI Helios NanoLab working at 10 keV beam energy and 0.14 nA electron current. Images have been acquired at normal and 30° to normal tilt angle.

3. Calculations

The optical and morphological characterizations have been supported by simulative tools, in order to understand the charge distributions and the modes excited inside of the structures responsible for the observed far-field resonances. Simulations at finite elements have been performed by means of commercial software (CST Studio Suite 2010) which solves Maxwell's equations in the discrete frequency domain.

In order to take under consideration the inter-band transitions of the metals in the visible region, dispersion relations of Au and Ti were loaded in the software in accordance to the model of Lorentz–Drude [27]. The L-shaped nanostructures were assumed to be embedded completely in an effective medium with dielectric constant $\varepsilon_{eff} = (1 + n^2)/2$, where n = 1.43 is the refractive index of the CaF_2 substrate [28,29]. Periodic boundary conditions are used to simulate the response of an array of nanoantennas with a spacing of 100 nm in both directions on the plane. From the simulation it has been possible to extract the extinction efficiency Q_{ext} defined as the ratio of the extinction cross section σ_{ext} of the structure to its geometric cross section σ_{geo} and related to the relative transmission measured by:

$$Q_{ext} = \frac{\sigma_{ext}}{\sigma_{geo}} = \frac{A(1 - T_{rel})}{Na} \quad (1)$$