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Fabrication of multiple large arrays of split ring resonators by X-ray lithographic process for sensing purposes

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ABSTRACT

In this paper we present the fabrication of multiple, large arrays of nano-metric split ring resonators, having variable aspect ratio, in order to obtain a sample suitable for prism-free plasmonic sensing applications. It has been shown that high aspect ratio structures present a richer longitudinal plasmonic resonant response, compared to thin geometries. In order to produce a platform suitable also for parallel measurements, the split ring resonators were arranged in ten square arrays, having an area of 1×1 mm, over a surface area of 12×18 mm. To obtain this result, we developed a fabrication process based on X-ray lithography. The choice of X-ray lithography as the main technique is justified by the possibility to obtain higher aspect ratio and to achieve large areas arrays of nano-structures in a single, fast exposure, compared to other techniques, such as Nanoimprint Lithography or Electron Beam Lithography. A new X-ray mask design was developed for achieving the ten large chips design. The fabricated split ring resonator arrays have been characterized by ellipsometric transmittance measurements in the visible and near-infrared range. The strong dependence of the split ring resonant response to the polarization of the impinging light, has been exploited to perform a test of the detection properties of the structure, functionalized with a mono-layer of self assembled dodecanethiols. The encouraging results of the detection test indicate the SRR geometry as a promising sensing structure.

1. Introduction

Surface plasmon resonance (SPR) has become, in the last decades, a powerful tool for detecting chemical and biological substances [1,2]. The SPR working principle derives from the electrons collective oscillations occurring at the interface between a metal and a dielectric. Those collective oscillations are known as surface plasmon polaritons (SPPs). Since the propagation of the SPPs varies as the dielectric medium properties change, the optical response of a SPR device, relying on the response of the SPPs, may vary when the dielectric changes, eventually resulting in a shift of the plasmonic resonance [3,4]. This mechanism is exploited for the detection of bio-chemical species deposited on the surface of the metallic medium [5].

The most common SPR devices are based on Kretschmann–Raether, or Prism Coupling, SPR configuration, and consist of a flat metal layer deposited on a prism. However, it is possible to bypass the use of the prism by nano-patterning the metal surface. Moreover, metal nano-structures allow to localize the plasmon mode within the structures themselves, and the resonant frequencies of the structure are tunable by tailoring the patterns' geometry [6].

In this work we present the fabrication of tall split ring resonators (SRR) in gold on transparent substrate (Fig. 1). Thin split ring geometries were originally studied for metamaterials applications and have been addressed in a wide literature [1,7–9]. The optical response of these structure presents a strong dependence on the polarization of the impinging light: in particular, when the electric field of the incident radiation is polarized parallel to the gap-bearing side of the SRR, an enhancement of the electromagnetic field occurs in the gap region [10].

The peculiarity of the structures proposed in the present work is the high aspect ratio, which may enrich the optical response of the SRR, because, as the height of the structure increases, several interesting Fabry–Perot resonances occur along the SRR vertical dimension [11]. These resulting spectral features can improve the ability of SRRs to serve as an effective sensing platform. The features may be observed in extinction measurements, i.e. the measurement of the fraction of the impinging radiation transmitted through the sample.

Bearing in mind the importance of the control of the geometrical parameters, we approached the structure fabrication using top-

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down lithographic techniques. We explored and developed, in particular, an X-ray lithography (XRL) based process for producing high volumes of tall, nano-metric split ring resonators.

XRL belongs to the class of parallel lithographic techniques [12]: this means that the pattern is replicated using an existing one. All constituent points of the pattern are addressed at the same time by the incident radiation, and the process is typically fast. As said, the pattern has to be first encoded into an object: the mask. The X-ray mask consists of an absorbing pattern supported by a frame, usually a membrane, transparent in the range of photon energies required for the exposures. The X-ray mask absorbing patter is generally produced by Electron Beam Lithography (EBL) and metal deposition.

In XRL process, the photoresist covered sample is exposed through the X-ray mask, which selectively filters the incoming radiation, creating in the photoresist a latent image corresponding to the mask absorber pattern.

The choice of X-ray lithography as the main technique is justified by the possibility to obtain higher aspect ratios and to achieve larger areas array of split ring resonators in a single, fast exposure, compared to other techniques, such as Nanoimprint Lithography (NIL) or Electron Beam Lithography [13].

The aim of this work is the fabrication of multiple, large area arrays of SRRs on a transparent substrate, to obtain a sample suitable for sensing purposes and parallel measurements in transmission.

The prepared samples were analyzed by means of transmittance measurement in order to verify the presence of the resonances. As a proof of concept, a thin layer of dodecanethiol was deposited on the nano-structures and the resonance shift due to the refractive index variation of the dielectric was shown.

2. Experimental methods

The SRRs were designed to show resonances in the visible and near-infrared range when illuminated at normal incidence. Electric field maps (not shown) indicate that, when the impinging light is polarized such as the electric field is aligned to the gap bearing side, an electromagnetic field enhancement is obtained in the gap region at resonances, whose fingerprint can be observed in the far-field extinction spectra as transmittance peaks. The geometrical features of the structure are the following: period p = 460 nm, side length l = 390 nm, gap d = 60 nm, line width w = 120 nm (Fig. 1, inset). We produced SRRs having different heights, varying from h = 200 nm to h = 400 nm.

In order to enable transmittance measurements, by a standard ellipsometric setup, a transparent substrate for the SRRs array is required. The chosen substrate is ITO covered soda lime, which is transparent in the visible and near-infrared wavelength range. To make the characterization easier, the total area of the SRRs arrays was designed to be 1 × 1 mm.

In order to obtain multiple, large chips of densely packed nano-SRRs on a single substrate, it is convenient to develop a fabrication strategy able to produce several patterned areas at the same time. We used X-ray lithography as the main technique, since on one hand it enables the realization of large-scale dense arrays of high aspect ratio structures, on the other it needs reduced lithographic times. In this work we took advantage of LILIT (Laboratory for Interdisciplinary Lithography) beamline, a lithographic beamline based on a bending magnet, working from soft (1.5 keV) to hard (10 keV) X-rays, and installed on the third generation synchrotron ELETTRA (Trieste, Italy). The relatively large width of the X-ray beam (50 mm) at the mask-sample assembly allows the exposition of large areas, up to few square centimeters.

The final sample design consisted of ten nano-patterned chips, having an area of 1 × 1 mm, on a transparent substrate, having a minimum area of 12 × 18 mm. To obtain this result, a novel design for X-ray mask was developed and produced: instead of a single, large membrane, a number of smaller membranes, corresponding to the final number of chips, has been produced on a single frame. This design improved the mask stability and reduces the damages due to handling.

The multiple membrane substrate (Fig. 2) was produced in silicon nitride (Si_3N_4) from a silicon wafer covered in silicon nitride on both sides. The silicon nitride wafers, produced by Plasma-enhanced Chemical Vapor Deposition (PECVD), were purchased by the University of Minnesota. The Si_3N_4 was selectively removed from one side of the wafer by a Reactive Ion Etching (RIE) process in a gas mixture of O_2/CF_4, protecting the areas not to be etched by a photoresist mask, previously obtained by UV Lithography. The UV mask design replicated the multiple membrane design. The membrane fabrication was completed by wet etching of Si in KOH at 65 °C for 12 h.

The side of the wafer which was not etched, i.e. the membranes, was metalized by e-beam evaporation of 10 nm of chromium and 20 nm of gold. This operation was essential to fabricate the subsequent X-ray mask gold absorber pattern by electrochemical growth.

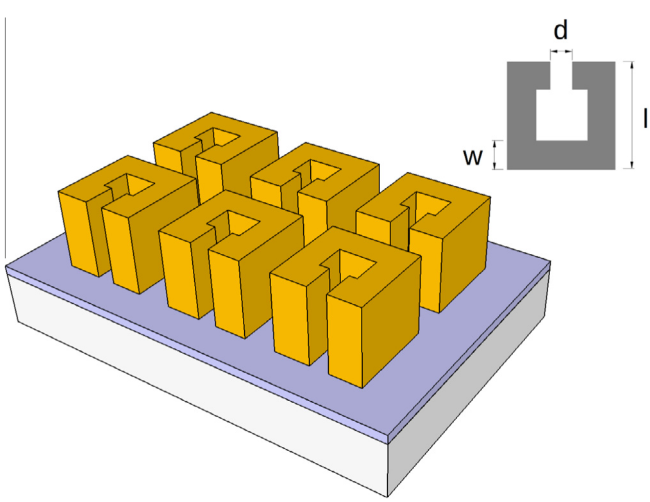

Fig. 1. Schematic of the SRR gold array on ITO covered glass. Inset: SRR scheme in top view.

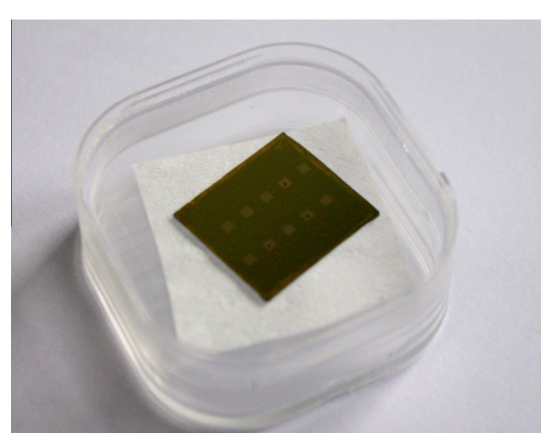

Fig. 2. Fabricated ten membranes X-ray mask. Silicon nitride membrane thickness: 500 nm. Silicon frame size: 12 × 18 mm. Membrane size 1.2 × 1.2 mm.