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Sensitive metal layer-assisted guided-mode resonance SU8 nanopillar array for label-free optical biosensing

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ABSTRACT

A novel polymer nanopillar lattice architecture for label-free optical biosensing based on the metal layer assisted guided-mode resonance (MaGMR) effect is presented. The device consists of a 2D array of SU8 nanopillars fabricated by e-beam lithography (EBL) on an optically-thick aluminum layer. EBL proximity effect, that is, the influence of the electron irradiation in the regions adjacent to those exposed by the e-beam – which is usually considered an undesirable fabrication issue – is positively used to create a non-uniform thickness, crosslinked SU8 film among the SU8 nanopillars on the aluminum layer. The optical response of the resulting SU8 nanostructure array exhibits a MaGMR under normally incident light interrogation. Spectral reflectance monitoring of the MaGMR upon the adsorption of water, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) and bovine serum albumin (BSA) molecules is employed to evaluate the surface sensing characteristics of the resonant nanostructure. The figure of merit of the device, defined as the quotient of the surface sensitivity and the resonance spectral width, is increased by two orders of magnitude (0.127 nm^{-1} versus 0.009 nm^{-1}) as compared with previous SU8 nanopillar array surface sensing architectures because of the high sensitivity and narrow spectral width of the MaGMR feature.

1. Introduction

Optical transducers based on submicro- or nano-structured materials for biosensing may lead to significant improvements in terms of sensitivity, selectivity, mass transfer and binding kinetics as compared to those based on macro- or non-structured materials [1]. This is due to their unique optical properties at the nanoscale and large surface-to-volume ratio. Additional advantages arise if nanostructured optical transducers are made of Si-based materials and polymers. These benefits include low cost, remarkable engineering possibilities and well-known surface functionalization chemistry.

Concerning nanostructured surfaces for optical biosensing, a wide variety of geometries can be found in the literature (e.g., stripes [2], beads [3], holes [4], columns [5–7]). Amongst these, optical sensing platform architectures based on nanoscaled columns or nanopillars (NPs) have received significant attention over the last years. This is because of: (i) NPs are relatively easy to fabricate by means of conventional micro and nanoprocessing techniques using a broad range of materials: semiconductors (e.g. Si [5], III-V [8]), metals (e.g. Au [9]) and insulators (SiO_2 [10], Si_3N_4 [4], polymers [11]), and (ii) NP based configurations can exhibit relevant optical effects (resonances, field confinement, etc) particularly useful for biodetection purposes.

SU8 epoxy based polymer has been shown to be a suitable material for implementing NPs for optical biosensing applications. This negative, chemically amplified resist can be micro- and nanostructured directly using standard irradiation-based (UV light, electrons or X-rays) patterning techniques [12–14]. It is specifically well-suited for creating high aspect-ratio structures and requires

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low exposure doses. In addition, SU8 has remarkable structural (mechanical robustness) and chemical properties (resistance to acids and bases and biofunctionalization feasibility) [15–18] that make it ideal for fabricating biosensors.

A relevant example of the latter is the demonstration of periodic arrays of SU8 NPs fabricated by electron-beam lithography (EBL) on SiO_2/Si [19] and ITO (indium tin oxide)/SiO_2 [20] substrates for label-free optical biosensing based on thin-film reflectance interference spectroscopy (TF-RIS) interrogation. This sensing platform allowed the determination of limits of detection of ~10 ng/mL for antiBSA (bovine serum albumin) [19] and antigestrinone antibodies [20] by monitoring spectral shifts of the structure interference pattern. However, in order to extend the range of applications to those requiring lower detection limits (such as single or small molecule detection) and/or allow the use of cost-effective read-out spectrometers that usually exhibit modest wavelength resolutions, further improvements in surface sensitivity and optical resonance quality are mandatory.

In this paper, we propose a new SU8 NP array-based optical sensor for biochemical sensing that exhibits superior performance than those of the aforementioned reported SU8 NP-based sensing architectures while adding no fabrication complexity and cost. The performance improvement arises from the device capability for exhibiting a metal-assisted guided mode resonance (MaGMR) [21], which is known to be advantageous as compared with those sensors based on TF-RIS in terms of resonance quality (better measurement resolution) and light-matter interaction at the sensor surface (increased surface sensitivity). Device fabrication and simulation details are described in Sections 2 and 3, respectively. Morphological analysis and optical and surface sensitivity performances are presented in Section 4. Finally, conclusions are collected in Section 5.

2. Materials and methods

2.1. SU8 nanopillar fabrication

Silicon substrates were cleaned using piranha solution (H_2SO_4 96% + H_2O_2 30% 3:1 at 130 °C for 10 min), then washed in deionized water, rinsed in isopropanol and dried with nitrogen gun. Then, the Si substrates were coated with a 100-nm-thick aluminum film by electron-beam thermal evaporation (deposition rate = 1 nm/s). SU8 2000.5 EBL resist (MicroChem Corp.) was spun at 3000 rpm on the Al films and soft-baked at 110 °C for 1 min on a hot plate. Next, 600-nm-period 2D square lattices of circular solid dots were written in the resist film by EBL at 50 kV and 50 pA in a Crestec CABL-9000 C high-resolution EBL system. The EBL writing process was carried out by a multi-spot procedure, that is, by using unfocused ultra small nanocircle patterns, which allowed us to determine the diameter of the circular dots between 260 nm and 350 nm. Out-of-focus blur was carried out by counting full turns at the manual focus control of the EBL system at constant magnification.

After e-beam exposure, the samples were post-baked at 80 °C for 3 min to crosslink the SU8 irradiated regions. Next, the uncrosslinked resist was removed by rinsing the samples in MicroChem SU8 developer at −15 °C for 7 s, and gently dried with nitrogen flow. Finally, the resulting SU8 NP arrays were hard-baked at 250 °C for 10 min after a 12 min ramp starting at 80 °C to provide high structural robustness to the SU8 nanostructure.

2.2. Structural and optical characterization

A FEI Inspect F50 scanning electron microscope (SEM) was used to study and measure the SU8 NPs shape and dimensions. To study the SU8 NP array cross-section, some samples were chemically treated with a 10 g/L KOH aqueous solution to remove the underlying Al layer.

The devices were optically characterized using a low numerical aperture objective (4×, NA = 0.1) to shine and collect the reflected light to/from the nanostructure array. The aperture angle was 5.7°, which restricts light detection to the zero-order diffraction. A Fourier transform visible-infrared (FT-VIS-IR) spectrometer (Bruker Vertex 70 adapted to visible range), with a resolution of 20 cm^{-1}, 3000 scans (10,000 for the background) was used to record the reflectance spectrum.

2.3. Surface sensing experiments

Surface sensitivity of the SU8 NP arrays was characterized by measuring the spectral reflectance of the devices (Section 2.2) before and after the adsorption of three types of molecular adlayers: water (humidity test), 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) (small organic molecule) and BSA (protein). Previous to the adsorption experiments, the devices were treated with H_2SO_4 96% for 1 min to activate the SU8 surface through the opening of epoxy rings, which makes the SU8 surface hydrophilic [11]. Then, they were rinsed in water, dried with a compressed air gun and heated at 120 °C on a hot plate for 10 min to evaporate all water residues.

Humidity tests (water vapor adsorption) were performed by exposing a device to water vapor in a closed bath chamber at 36 °C during 2 min, without water condensation. Water desorption was carried out by heating the samples on a hot plate at 120 °C for 10 min.

BSA adsorption was achieved by, first, depositing a 50 μL drop of BSA (20 μg/mL in HEPES 10 mM, adjusted to pH 7.4) on a SU8 array for 30 min. Then, after washing and drying the sample with a compressed air gun, another 50 μL drop of BSA (50 μg/mL) was deposited on the array for 30 min to saturate the device surface with BSA [19]. The same protocol was carried out in another device with just HEPES solution in order to investigate the effect of HEPES adsorption.

3. Optical simulations

The reflection spectrum and field distributions of a modeled SU8 NP array were calculated by the finite-difference time-domain (FDTD) algorithm. Fig. 1 shows a 3D representation and a schematic cross-sectional view of the simulated structure. It consists of a 3 × 3 square lattice of SU8 pillars resting on a 100-nm-thick Al layer deposited on a semi-infinite Si substrate. The geometry of each SU8 pillar is defined by the superposition of a cylinder (diameter d_{pillar} = 300 nm and height t_p = 400 nm) and a truncated neiloid (height t_b = 350 nm, top diameter d_{pillar} = 300 nm and bottom diameter $d_{neiloid}$ = 1440 nm) sharing the same axis, on the Al layer. The truncated neiloid represents the crosslinked SU8 material around the cylinders produced by the EBL proximity effect (i.e. the influence of the electron irradiation in the regions adjacent to those exposed by the e-beam) [22]. The top cladding (superstrate) is assumed to be air. The dielectric constant of Al was modeled by the well-known Drude–Lorentz equation with the fitted parameters reported elsewhere [23]. The refractive indexes of SU8, Si and air were assumed to be frequency-independent and equal to 1.58, 3.15 and 1 respectively. Periodic boundary conditions were chosen along the device plane coordinates (x- and y-axis of the array) and perfectly matched layer (PML) boundary condition was used along the incident beam propagation direction (z-axis), normal to the device plane. Frequency analysis of the reflection was achieved by launching a pulsed excitation from the superstrate region and calculating the fast Fourier transform (FFT) of the time-domain field