Template-Stripping Fabricated Plasmonic Nanogratings for Chemical Sensing

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Abstract Template stripping has been applied to transfer one-dimensional nanograting structures fabricated by interference lithography (IL) onto planar supports (i.e., glass slides and plane-cut optical fiber tips). A thin adhesive layer of epoxy resin was used to facilitate the transfer. The UV-Vis spectroscopic response of the nanogratings supported on glass slides demonstrated a strong dependency on the polarization of the incident light. The bulk refractive index sensitivities of the nanogratings supported on glass were dependent on the type of metal (Ag or Au) and the thickness of the metal film. The described methodology provides an efficient low-cost fabrication alternative to produce metallic nanostructures for plasmonic chemical sensing applications.

Keywords Plasmonic · Nanogratings · Template stripping · Optical fiber · Interference lithography (IL)

Introduction

The fabrication of nanostructures has been a vibrant research area in the last few years. A main drive for the wide interest in the field is the potential for applications of nanostructures in chemical sensing and detection [1–3]. In the specific case of metallic nanostructures, the chemical sensing mechanism is based on the excitation of surface plasmon (SP) modes at the interface between the metal and the medium containing the analyte of interest. Several types of metallic nanostructures, such as nanoparticles [4, 5], nanoholes [6, 7], nanoslits [8], and nanogratings [9], are able to support SP modes when the resonance conditions are satisfied. The developments of these “plasmonic” sensors have been centered in the desire of generating structures that optimize analytical figure of merits, such as sensitivity, resolution, and limit of detection (LOD). Nonetheless, the possible commercial translation of those types of nanosensors also depends on the complexity of the fabrication process. In this regard, processing time, cost, and ease for mass production also become important evaluation parameters.

Plasmonic nanosensors have been fabricated by different techniques, ranging from chemical synthesis to nanolithography [10]. A variety of nanofabrication methods have been explored in the recent decades, mainly due to the emergence of advanced lithography facilities in various research centers around the world. Among them, electron beam lithography (EBL) and focused ion beam (FIB) milling are the two techniques that allow maximum control over the fabrication precision and resolution. Therefore, these techniques have been widely used to fabricate different types of nanostructures for prototypes and proof-of-concept experiments [11]. The limitations of these techniques, however, are related to their low throughput and their inability to quickly pattern larger areas. Interference lithography (IL) offers an alternative that provides large area patterning of periodic nanostructures with easy manipulation of the nanostructure geometric parameters, which is useful for sensor optimization [12]. This maskless lithography technique normally utilizes the optical interference between two laser beams to produce a uniform periodic pattern that impress a photoresist [13]. The technology is
relatively time and cost efficient and compatible with the common approaches currently used in microfabrication [14].

In this work, the IL technique was used to fabricate nanograting templates that were transferred to different glass surfaces. The template-stripping procedure has been reported [15] to yield metallic nanostructures capable of plasmonic-based chemical sensing. This strategy has not only leveraged the available nanofabrication methods but also greatly improved the fabrication throughput. Here, we demonstrated the implementation of IL template-stripping procedure to transfer the nanograting pattern to glass slides (1 in.²) and optical fiber tips (OFTs) with small contact surfaces (~50 μm of core diameter). Plasmonic nanograting structures (made of either Au or Ag) have been explored for chemical sensing [8, 16]. Typically, the transmission of white light through those one-dimensional nanostructures (with grooves and ridges) presents clear dips and peaks in the visible NIR range. Another aspect of the one-dimensional nanostructures presented here is their dependence on the incident light polarization. This property has been explored to eliminate non-polarization-dependent background interferences [17].

**Experimental Section**

**Template Preparation via IL**

Microscope glass slides (1 in²) and optical fiber tips (OFT—50-μm core diameter) were used as support for the plasmonic structures. The glass slides were first sonicated in a water bath and then cleaned with copious amounts of acetone, methanol, ethanol, and isopropanol, respectively. After oven-drying (T ~120 °C) and cooling to room temperature, the glass slides were ready to be spin-coated with 1:1 Microposit SC 1827 positive photoresist diluted with Microposit thinner type P at 2000 rpm for 30 s. The substrates were then pre-baked in an oven at 120 °C for 10 min to remove the solvent from the photoresist layer. Next, the glass substrate coated with the photoresist was then mounted on the interference lithography setup (Lloyd’s interferometer) [18] and exposed to a 458-nm laser (Coherent argon ion laser) once for 45 s (the energy density of the laser was 100 mJ/cm²). After the laser exposure, the photoresist film was developed in 1:3 Microposit 351 developer diluted with deionized water (produced through Barnstead Millipore system, resistivity of 18.2 MΩ·cm) for 45 s under gentle motion parallel to the grating axis to generate a uniform one-dimensional photoresist template. The photoresist templates were then evaporated with either gold or silver using electron beam and thermal evaporator (Angstrom Engineering Glove-box Evaporator, deposition rate of 1 Å/s). The film thicknesses were either 100 or 200 nm. Similar cleaning procedure was applied to a bare OFT (model AFS from Thorlabs, core diameter of 50 μm), which has been previously plane cleaved and polished.

**Template-Stripping Procedure**

The stripping procedure is summarized in Fig. 1. A silver (or gold) evaporated on the photoresist template was pressed against a glass slide coated with the epoxy adhesive (step a in Fig. 1). The sandwiched system was then exposed to light from a 100-W incandescent lamp. The sandwiched system was left in a benchtop area and illuminated overnight (~12 h). When the epoxy was cured, the patterned silver (or gold) was stripped from the original template (step b, in Fig. 1). The stripped substrate was subject to a final rinsing with ~5% NaOH to remove any remaining photoresist from the metal surface. The surface morphology of the substrates was then characterized.

**Surface Plasmon Resonance (SPR) Refractive Index Sensing with Template-Stripped (Large Area) Substrates**

The SPR measurements for the glass slides coated with metallic nanogratings were realized in transmission mode at normal incidence using an UV/Vis/NIR spectrometer (Perkin Elmer Lambda 1050). Small modifications were required on the sample and reference compartments to host a liquid cell with the patterned samples. The cell was fabricated from transparent polydimethylsiloxane (PDMS) which allow liquid to be flown to a 400-μL sealed pocket in contact to the surface (sensing area 2 × 2 cm²) of the metallic substrate. Glucose solutions with different concentrations were prepared to test the SPR sensor response to different bulk refractive indexes.

**Optical Fiber Experiments**

The surface plasmon resonance-based refractive index measurements were also realized using a bifurcated optical fiber (model BIF400-VIS-NIR from Ocean Optics) and bare optical fiber (OF) adapter (model F-AM-SMA from Newport). One arm of the fiber was illuminated from a white light source (model LS-1 from Ocean Optics), the second arm was connected to a spectrometer (model USB 2000 from Ocean Optics), and the sensing tip was a gold nanograting structure prepared using the same IL template-stripping procedure described above.

**Results and Discussion**

**Substrate Characterizations**

The IL template-stripping procedure, illustrated in Fig. 1, yielded one-dimensional grating nanostructures with a final patterned area of 1 in.² Figure 2 shows the SEM image of the patterned surfaces. The periodicity of the gratings was ~450 nm and the height of the ridges was 75 nm. Small morphological defects...
(roughness) can be noticed in Fig. 2, which partly justified the variation of the optical sensitivity on refractive index (RI) variations (substrate-to-substrate sensitivity variation was less than 20%—see below). Additionally, the roughness of the substrate was examined before and after the template-stripping procedure through atomic force microscopy (AFM). The AFM result, presented as Supplementary Information (Figure S1), shows that the overall roughness of the nanostructures was significantly reduced after the stripping procedure.

Zero-degree transmission spectrum through those large area patterned substrates led to clear peaks and dips at TM polarization (linear polarization perpendicular to the direction of the grating lines), as shown in Fig. 3a. The plasmonic response of nanoslit structures has been extensively studied by several research groups [8, 16]. Briefly, the transmission bands through periodic nanoslit structures have been assigned to contributions from different surface modes on the plasmonic grating [16]. These include contributions from (i) localized SPR from the nanostructures and roughness, (ii) cavity modes (Fabry-Perot type of effect), and (iii) coupling from the nearby nanograting features [16]. The transmission through a 200-nm thickness silver nanogratings presented in Fig. 3a agrees well with the optical transmission properties reported on the previous findings [8]. The features (peaks and valleys) in the transmission spectrum in Fig. 3b vanishes when the measurement was taken at TE (linear polarization parallel to the direction of the grating lines) polarization. The lack of features for TE excitation can be explained by the homogeneity of the electric field when the incidence polarization is parallel to the structures. The strong polarization dependence observed in Fig. 3 can potentially provide a control channel in chemical sensing experiments, for instance, to eliminate interferences from experimental variables that are polarization independent [17].

Surface Plasmon Resonance (SPR) Band Assignments

The SPR from an one-dimensional metallic nanogratings can be approximated through Eq. 1 [8, 16, 18]:

\[
\lambda_{spr} = \frac{P}{m} \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}; \quad m = 1, \quad (1)
\]

where \(\lambda_{spr}\) is the surface plasmon resonance wavelength, \(P\) is the periodicity of the nanogratings, \(m\) is the mode of the resonance, \(\varepsilon_d\) is the dielectric constant for the dielectric side of the interface, and \(\varepsilon_m\) is the dielectric constant for the metal side of the interface. The transmission spectrum from silver nanogratings in air was found to be significantly different as compared to that in water (refer to SI, Fig. S3). The calculated (using Eq. 1 for \(m = 1\)) SPR mode of a silver nanograting \((\lambda_{spr})\) is expected to shift from \(\sim 470\) nm (dielectric properties of Ag obtained from [19]) in air to about 585 nm in water. This
resonance in water matches reasonably to the observed transmission features in Fig. 3a. Another resonant mode in Fig. 3a should arise from the other interface between epoxy and silver. This resonance is expected to occur at ~630 nm (considering \( n_{\text{epoxy}} = 1.46 \)). This is, again, comparable to the observed transmission features in Fig. 3a.

The relative straightforward assignment obtained with Eq. 1 can be further confirmed experimentally by Fig. 4. Figure 4 shows the dependence of the transmission features with changes in the refractive index of the aqueous dielectric in contact to the metallic grating. It is possible to observe in Fig. 4 that the transmission wavelength redshifts in response to the refractive index changes (refer to Fig. 4) only for the transmission features at ~550 nm. In contrast, the resonant features at ~630 nm were almost unaffected by the changes of refractive indexes in the solution, as seen in Fig. 4. This can be explained by the consideration that the buried metal-epoxy interface is not significantly altered by the solution refractive index. On the other hand, the mode assigned to the water/analyte solution silver nanograting interface is expected to depend strongly on the optical properties of the aqueous solution.

**Sensing Measurements**

The polarization dependence observed in Fig. 3 was used to correct for polarization-independent background, such as, for instance, the effect of room temperature variations. The transmission spectra were then expressed using the following equation [17] (Eq. 2):

\[
T_{\text{corrected}} = \frac{I_\perp - I_{\parallel}}{I_\perp + I_{\parallel}}
\]

where \( I_\perp \) is the transmission intensity at TM polarization and \( I_{\parallel} \) is the transmission intensity at TE polarization.

The transmission measurements for the sensing experiments were taken using an ordinary UV/Vis/NIR spectrometer. A thin PDMS cell was fabricated and used to expose the nanograting substrates to aqueous solutions with different refractive indexes. The refractive index of glucose solutions of different concentrations ranged from 1.3354 to 1.3550. Normalized transmission spectra (according to Eq. 2) from different glucose solutions are presented in Fig. 4.

The SPR wavelength shifts with refractive index changes were then quantified using the integrated response (IR) method [20]. In this case, the whole visible spectrum, from 400 to 700 nm, were taken into account. Previously, our group and collaborators have employed this IR method to quantify nanohole SPR sensing and demonstrated an improvement of up to 90% to the signal-to-noise ratio [24]. The IR equation is given below (Eq. 3):

\[
IR = \sqrt{\int_{\lambda_1}^{\lambda_2} \left( D(\lambda) \right)^2 d\lambda},
\]

where \( D(\lambda) \) is the difference in signal between a reference and a measured spectrum and \( D(\lambda) \) is the average of the difference in signal over the entire spectrum. In our particular case, the spectrum obtained from the aqueous solution with the lowest refractive index \( (n = 1.3354) \) was used as reference.

The normalized IR response for 200-nm-thick Ag nanogratings was plotted against the solution refractive index in Fig. 5. The calibration sensitivity of the large area SPR substrates, calculated from the slope of Fig. 5, were in the range between 50 and 160 IR/RIU, depending on the type of metal (Ag or Au) and on the thickness of the metal film. A summary of the experimental sensitivity values are shown in Fig. 6. Typically, in the literature, calibration sensitivity of plasmonic sensors are given in nanometers/RIU. Therefore, for sake of comparison, the calibration sensitivity was also recorded in the nanometer/RIU scale. In this case, the wavelength shifts of the SPR band (in the region between 545 and 560 nm, see Fig. 4) were quantified. The shifts were measured at the full width of half maximum (FWHM) of the SPR bands of the normalized transmission spectra. The first transmission spectrum in the series (i.e., in solution medium of the smallest refractive index) was used as reference, and the wavelength shifts were read relative to that reference spectrum. The wavelength shifts as a function of refractive index changes are also shown in Fig. 5. The values of the calibration sensitivity (slope of the line in Fig. 5) were between 500 and 600 nm/RIU (again depending of parameters, such as nature of the metal and film thickness; see Fig. 6). This calibration sensitivity range is comparable to values that has been reported from other grating-based plasmonic substrates [6].

![Fig. 4 Transmission spectra for the silver nanogratings under perpendicular polarization of the incidence light in solutions of different refractive indexes. a 1.3354. b 1.3401. c 1.3453. d 1.3523](Image)
The structure reported here was prepared in a large area using a relative simple and inexpensive procedure. Another figure of merit to compare plasmonic sensor is the sensor resolution, defined as the minimum refractive index change detectable by the device. The resolution was calculated from the calibration sensitivity values and the experimental variation measured by our detection system (either in wavelength or in IR), obtained from multiple measurements from the same sample [6]. Figure 6 shows the calibration sensitivity and resolution of nanogratings of different types of metal (silver or gold) and thickness of the metal film (100 or 200 nm). The reproducibility of our fabrication procedure is represented in Fig. 6 as an error bar in the sensitivity values, which were calculated from the average of three samples. The 100-nm-thickness silver nanogratings demonstrated the sensor resolution (8.35 × 10^{−5}/RIU) in Fig. 6. The 100-nm-thickness gold nanogratings exhibited the best sensing reproducibility of ~15%, which might be related to the chemically inert properties of gold metal. In order to further rationalize our findings in Fig. 6, the substrates were examined by AFM (refer to SI Fig. S2). It was observed that the 100-nm Ag nanograting presented more crack lines on the surface and consistently showed more random roughness, as compared to 200-nm Ag nanogratings and 100-nm Au nanogratings (Fig. S2 in SI). This might explain the larger variation shown (substrate-to-substrate reproducibility) observed in Fig. 6 for the 100-nm Ag nanograting. On the other hand, the thinner Ag film should allow better transmission through the interaction between the plasmonic interfaces [21], which in turn improves the sensitivity of the system.

**Sensing with Optical Fiber Tips**

In order to demonstrate the potential of the stripping procedure to transfer pattern to different types of flat substrates, a plasmonic nanograting was fabricated on an optical fiber tip (OFT). There are several reports in the literature focused on the transfer of nanostructure to optical tips [22]. Yang et al. has reported an in situ IL fabrication on OFTs, but that requires a complex substrate-hosting setup to achieve the transfer [23]. Template-stripping procedure [24, 25] offers an easy and efficient solution to the setup complications of conventional lithography fabrication. In this case, the pattern from the IL template can be transferred onto optical fiber facet with the aid of an optical adhesive [25, 26] or some intermediate medias such as flexible polymeric structures [24]. Similarly, in this work, the IL-generated large area nanograting structures were template stripped onto the fiber facet with the aid of epoxy adhesive. Specifically, the IL template was first deposited with 100 nm of gold film using electron beam.

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**Fig. 5** Normalized integrated response (y-axis at left) and wavelength shift (y-axis at right) plot as a function of the refractive index of the solution for 200-nm-thick Ag nanogratings

**Fig. 6** Comparison of the refractive index calibration sensitivity and resolution. Left, 200-nm Ag nanograting; middle, 100-nm Ag nanograting; and right, 100-nm Au nanograting.
evaporator. A drop of epoxy was added to the gold-nanostructured face of the IL substrate. The polished end of the OF, which had been held in a simple plastic holder to fix the fiber end at normal position, was brought to contact with the epoxy-gold nanogratings. The system was then allowed overnight exposure to 100-W white light source to ensure that the epoxy was cured completely. The photoresist template was then stripped from the fiber end, as demonstrated in Fig. 7. Scanning electron micrographs of the resulting structures are available as supporting information (Fig. S5 in SI). The plane cut of the fiber core was achieved by connectorizing the OFT to a commercially available ceramic ferrule and polished extensively. The connectorized fiber tip was modified using the template-stripping method. The patterned tip of the optical fiber was then used as a refractive index-sensing element. In this case, the detection was done in reflection (backscattering) mode, using a bifurcated OF. As shown in Fig. 7, one arm of the bifurcated fiber carried the white light while the other arm took the reflected signal to a miniaturized spectrometer. Either the patterned tip or a bare fiber tip can be connected to the system through an OF adapter purchased commercially. The measurements were done by immersing the fiber tip (either the patterned or the bare tips) into solutions with different refractive indexes. The solutions with different refractive indexes were placed in 5-mL disposable vials. A lab-lift was used to control the immersion of the fiber end of the optical setup into the analyte solutions. The system was equilibrated for ~5 min before obtaining backscattered spectra using the spectrometer. The equilibration time was particularly important during solution changes. It allowed the system to settle and ensured a good degree of stability during the measurements. All measurements were done in a dark room to minimize background noise contributions.

The backscattered measurements carried information regarding the SPR mode excited on the metal nanograting tip. The SPR waves on the metal-solution interface were very sensitive to the refractive index changes (i.e., intensity changes and wavelength shifts). The recorded spectra in the region from 400 to 850 nm were then smoothened, polynomial fitted, and subjected to the IR calculation, as shown in Eq. 2. An example of the wavelength shifts observed in response to the changes of refractive index from a nanograting-patterned tip is shown in the SI file (Fig. S4(a)). The bare fiber’s backscattered spectra remained unchanged for all the refractive indexes tested (Fig. S4(b)). Figure 8 shows a comparison of the sensing performance of a Au nanograting-patterned optical fiber tip to a bare optical fiber. The non-patterned (bare) fiber showed almost no response as compared to the patterned tip. In addition, since the measurements were taken with a bifurcated fiber setup, the results from Fig. 8 illustrate the potential for application of this setup in an optrode geometry [27], which could be useful for in-line monitoring of chemical process, for instance. This relative simple and inexpensive procedure to modify the OFT with plasmonic nanostructures has also the potential to be utilized in other plasmonic sensing applications; i.e., surface-enhanced Raman spectroscopy.

It is worth to mention that the polarization-dependent characteristic of the nanograting structures has not been utilized in the fiber setup reported here. The manipulation of the polarization effect, using a polarization maintaining fiber, for instance, is a potential future improvement that can be implemented for the application of this type of OFT-modified plasmonic device.
Conclusions

Summarizing, we successfully utilized the IL template stripping to prepare SPR substrates on both large area (1 in.²) and on small surfaces (50-μm core OPTs). These plasmonic substrates were used for bulk refractive index sensing. The successful integrations of the IL procedure have clearly demonstrated flexibility for the fabrication of good quality plasmonic substrates with different dimensions. This allows tailoring the fabrication for different applications. For instance, the realization of refractive index sensing using the optical fiber setup illustrated the potential of the procedure to prepare miniaturized (small area) plasmonic structures, suitable to accommodate remote sensing applications. Lastly, the substrates patterned with nanogratings demonstrated strong polarization dependency. This property has the potential to be used as an additional control in refractive index-sensing applications. For instance, polarization controlled self-referencing can be implemented to eliminate non-polarization-dependent interferences and backgrounds, such as stray illuminations and temperature variations.

References