High transmission from 2D periodic plasmonic finite arrays with sub-20 nm gaps realized with Ga focused ion beam milling

Filippo Pisano\textsuperscript{1,\diamond}, Antonio Balena\textsuperscript{1,2,\diamond}, Muhammad Fayyaz Kashif\textsuperscript{3,\diamond}, Marco Pisanello\textsuperscript{1,\diamond}, Gaia de Marzo\textsuperscript{1,2,\diamond}, Luciana Algieri\textsuperscript{1,\diamond}, Antonio Qualtieri\textsuperscript{1,\diamond}, Leonardo Sileo\textsuperscript{1}, Tiziana Stomeo\textsuperscript{1,\diamond}, Antonella D’Orazio\textsuperscript{3,4}, Massimo De Vittorio\textsuperscript{1,2,4}, Ferruccio Pisanello\textsuperscript{1,4,\diamond} and Marco Grande\textsuperscript{3,4,\diamond}

\textsuperscript{1} Fondazione Istituto Italiano di Tecnologia, Center for Biomolecular Nanotechnologies, Arnesano (LE) 73010, Italy
\textsuperscript{2} Dipartimento di Ingegneria Dell’Innovazione, Università del Salento, Lecce 73100, Italy
\textsuperscript{3} Dipartimento di Ingegneria Elettrica e dell’Informazione, Politecnico di Bari, Bari, Italy

E-mail: filippo.pisano@iit.it

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Abstract

Fabricating plasmonic nanostructures with good optical performances often requires lengthy and challenging patterning processes that can hardly be transferred to unconventional substrates, such as optical fiber tips or curved surfaces. Here we investigate the use of a single Ga focused ion beam process to fabricate 2D arrays of gold nanoplatelets for nanophotonic applications. While observing that focused ion beam milling of crossing tapered grooves inherently produces gaps below 20 nm, we provide experimental and theoretical evidence for the spectral features of grooves terminating with a sharp air gap. We show that transmission near 10\% can be obtained via two-dimensional nano-focusing in a finite subset of 2D arrays of gold nanoplatelets. This enables the application of our nanostructure to detect variations in the refractive index of thin films using either reflected or transmitted light when a small number of elements are engaged.

Keywords: focused ion beam, nanoplatelets, plasmonic nanostructures

(Some figures may appear in colour only in the online journal)

1. Introduction

Research in the fabrication of metallic periodic nanostructures that support surface plasmon resonances (SPR) has received longstanding interest from both a fundamental and an applied perspective. In the past few years, the comprehensive knowledge of the resonant mechanisms in periodic arrays of sub-wavelength apertures \cite{1–5} has been widely applied in the detection of electro-chemical signals at extremely low molecular concentrations \cite{6–8}. This interest has been revived by the emergence of lab-on-fiber platforms, which have raised the demand for techniques to pattern unconventional substrates, such as the tip of an optical fiber, where conventional methods such as electron beam lithography cannot be applied \cite{9}. In this endeavor, focused ion beam (FIB) milling has been identified as a versatile technique to prototype
photonic structures and metasurfaces. However, while the effect of FIB milling on 1D periodic structures has been extensively studied, little work— to the best of our knowledge— has been dedicated to extend this concept to 2D structures with crossing corrugations. In this work, we describe the optical properties of finite subsets in 2D arrays of gold nanoplatelets (NPs) fabricated in a single Ga FIB patterning process. As FIB milling generates tapered slits, which have been shown to boost extraordinary optical transmission through adiabatic nano-focusing in 1D arrays, we numerically and experimentally expand this effect to comprehensively describe the optical performances of a finite subset of a 2D NP array.

We found that FIB milling of crossing tapered grooves inherently generates sub-20 nm gaps. This is an interesting aspect since a spacing of less than 40 nm between nanostructures has been previously shown to strongly contribute to surface enhancement of Raman scattering (SERS). While observing that the orientation of such gaps with respect to the polarization of the incoming light influences the array’s performance, we measured transmissivity peaks approaching 10% in the VIS–NIR region. As a possible application, we experimentally and numerically demonstrate that illuminating a subset of the array results in the detection of refractive index (RI) changes with a sensitivity of \( S_R = 620 \text{ RIU}^{-1} \) and a figure of merit (FOM) of \( \text{FOM}_R = 7 \text{ RIU}^{-1} \) using reflected light and \( S_T = 445 \text{ RIU}^{-1} \) and \( \text{FOM}_T = 29 \text{ RIU}^{-1} \) using transmitted light. These values are consistent with previous reports for this class of devices.

## 2. Results and discussion

We fabricated NP arrays in a gold film deposited on a quartz microscope coverslip (Ted Pella), following the design shown in figures 1(a) and (b). The patterning process involved two steps. First, a 5 nm thick adhesion layer of Cr and a 180 nm thick layer of Au were deposited by electron beam deposition. Second, the NPs were carved in the gold layer by milling thin slits of metal with a Ga+ FIB system (FEI dual-beam HeliosNanoLab600i). The ion beam current was set at 7.7 pA, with 30 kV voltage. The beam spot (12 nm in diameter) was sequentially scanned in the two milling directions (from edge to edge), horizontal (H) and vertical (V) covering one gap at a time across the full array length, with minimal line overlap (5%–10%). The fabrication of a single array, 30 \( \mu \)m \( \times \) 30 \( \mu \)m wide, lasted for approximately 30 min. We first performed a morphological characterization of the final device via scanning electron microscope (SEM) (figure 1(b)). Interestingly, we found that the milling order influences the groove shape. This is shown in figure 1 for arrays where vertical (V) slits were milled before horizontal (H) ones. Once the set of V slits is carved, milling in the H direction produces a redeposition of sputtered material that narrows the V groove at the NP corners (figure 1(b)-inset). At the same time, the H groove widens at the platelet corners (figures 1(b)-inset, (c), and (d)). As highlighted in the SEM images, this process produces gaps approaching 10 nm in width (figure 1(b)-inset and (d)). This effect was confirmed by reversing the fabrication order of the slits (figure 3(a)). We attribute this phenomenon to the combination of the edge effect and the redeposition of sputtered material.

As expected, FIB milling resulted in tapered grooves. In details, we milled grooves with a bottom aperture of \( \sim 30 \text{ nm} \) at the NP center and \( \sim 10 \text{ nm} \) at the corner, with an air gap extending down to \( \sim 30 \text{ nm} \) below the substrate surface (figures 1(c) and (d)).

We then characterized the spectral response for two array periodicities, A and B with \( P_A = 550 \text{ nm} \) and \( P_B = 630 \text{ nm} \). For each periodicity, we produced arrays with reversed milling order A1 (B1), starting from the V direction, and A2 (B2) starting from the H direction. As shown in figures 3(a) and (d), the milling order influences the orientation of the narrow gaps at the NP corners. We acquired reflectance and transmittance spectra using a modified upright microscope.

The experimental setup is shown in figure 2. We used a broadband light source (500–900 nm) that was spatially filtered with a 100 \( \mu \)m pinhole. After passing through a linear polarizer, the illumination beam was relayed on the sample, at normal incidence, using a lens (focal length 250 mm), two beam splitters (non-polarizing, 50/50) and an infinity corrected objective (5\( \times \), NA = 0.16). We then collected reflected
light with the same objective and the transmitted signal with a 20 × objective (NA = 0.50). Spectra were recorded with a spectrometer equipped with a 300 l/mm grating (Horiba Scientific iHR320, EMCCD camera Horiba Scientific Synapse, 1600 × 1200 pixels).

Reflectance and transmittance spectra show clear resonance signatures for both A and B arrays (figures 3(b) and (c) for array A and figures 3(e) and (f) for array B). Besides a grat- ing state sharp peak at the array periodicity (indicated as II in figure 3), we observed a blue-shifted peak (I) and a broad red-shifted resonance (III) for both A and B arrays [14]. As outlined in [14], periodic metallic gratings show a num- ber of peculiar features in their spectra that depend mainly on the geometrical parameters of the structure. In particular, the dip shown as II corresponds to the excitation of a leaky mode that propagates on the metal grating and causes a sharp dip in the reflection spectrum while the other dip, indicated as III, is a hybrid state related to the availability of a Fabry–Pérot mode inside the cavity which propagates in the metal-insulator-metal (MIM) waveguide [14]. The presence of the MIM waveguide is responsible for the high transmission in figure 3. Interestingly, we found that the milling order influences the spectral response by shaping the NP morphology. For both A and B arrays, we measured a higher transmittance when the impinging light was polarized along the first-milled direction: V for A1 and B1 and H for A2 and B2 (figures 3(b) and (c) for array A and figures 3(e) and (f) for array B). We also observed that the transmittance is maximized (∼10%) when the optimal illuminating polarization—V for A1 and B1, H for type A2 and B2—encountered narrow gaps in the perpendicular direction.

To describe the physical origin of the measured spec- tra we developed a theoretical model of the FIB-milled NP-arrays. We modelled the nano-platelets with a trapezoidal gold patches placed on top of the glass substrate, following figure 1(a).

The width w of the V grooves was set as 32 nm at the bottom (glass–gold interface) and 67 nm and 103 nm for vertical and horizontal milling, respectively. The gold thickness was set as 180 nm. This resulted in grooves with opening angles of α = 11.1° for vertical milling and α = 22.3° for horizontal milling. We did not take into account milling artifacts such as rounded corners.

The device optical response was studied by means of finite difference time domain (FDTD) and rigorous coupled-wave analysis (RCWA) methods (FullWave and DiffactMODE software from RSoft). We used a Drude–Lorentz model for gold consisting of a Drude pole and two Lorentz poles [17] for both numerical methods.

The relative complex permittivity is described in equation (1), where \( \varepsilon_{\infty} \) is metal dielectric constant at the high frequency regime in the Drude model, \( \omega_D \) and \( \gamma_D \) are the plasma and collisions frequencies of free electron gas related to Drude model, whereas \( \delta_i, \omega_i \) and \( \gamma_i, i = 1, 2 \), are amplitude, resonant angular frequency and damping constant of

Figure 2. Sketch of the experimental system. White light is filtered with a 100 μm pinhole and linear polarizer (Pol). The image of the pinhole is projected on a subset of the NP array using a lens (L1, focal 250 mm) and an infinity corrected objective (O1, 5 ×, NA = 0.16). An imaging path is used to align the focal spot with the sample. Reflected light is collected by O2, NA = 0.5) and focused in an MMF with an achromatic doublet lens (L3, focal 40 mm). The MMF conveys the signal to the spectrometer. The inset shows an enlarged with of the excitation beam recruiting a finite number of NPs.

Figure 3. (a) Nano-gap orientation in array A1 and array A2, milled at period \( P_A = 550 \) nm with V–H and H–V order, respectively. (b) Reflectance (black) and transmittance (red) spectra for A1 (solid line) and A2 (dashed line) for H-polarized light. (c) As in (b) for V-polarized light. (d) Nano-gap orientation in array B1 and array B2, milled at period \( P_B = 630 \) nm with V–H and H–V groove order, respectively. (e) As in (b) for B1 and B2 arrays. (f) As in (c) for B1 and B2 arrays.
each Lorentz-like oscillator, respectively.

\[
\varepsilon_m(\omega) = \varepsilon_\infty - \frac{\omega_D^2}{\omega^2 + j\omega\gamma_D} - \sum_{k=1}^{2} \frac{\delta_k\omega_k^2}{\omega^2 - \omega_k^2 + 2j\omega\gamma_k}
\] (1)

A recent experimental study reported that the dielectric function of the metals is determined by their structural morphology and it strongly depends upon the film thickness [16].

We tuned a parameter \(\gamma_D (1.66938 \times 1015 \text{ rad s}^{-1})\) called damping rate (or scattering loss) in order to analyze the influence of film thickness on the optical absorption and adjust the fitting parameters. First, we considered a periodic structure with array B1 parameters illuminated by a plane wave impinging at normal incidence. The structure had periodic boundary conditions along the \(x\)-axis and absorbing boundary conditions along the \(z\)-axis (figure 1(a)). Figure 4(a) shows the reflectance and the transmittance spectra of the periodic grating structure from FDTD simulations. A dip can be observed at a wavelength of 630 nm in the reflection spectrum. RCWA simulations for the infinite structure revealed that the spectra are based on contributions from all the grating orders (0, \pm 1).

However, the measured spectra (figure 3) showed another dip near 600 nm (shown as I in figure 3) which is not visible in the spectra shown in figure 4(a). We believe this first dip is due to missing diffraction orders \(\pm 1\). This is because the experimental setup exploits a spot that illuminates a finite number of NPs (inset of figure 2). Hence, under normal incidence, the diffracted higher order modes could not be collected by the lens.

In order to match the experimental setup, the numerical model—based on real device dimensions—considered a limited number of grating periods and employed absorbing boundary conditions in all four directions in the \(XZ\) plane for FDTD simulations. The grating structure was illuminated by a normally incident Gaussian pulsed source with a Gaussian spatial profile (transverse magnetic (TM) polarization, electric field along the \(x\)-axis—\(E_x\)—as in figure 1(a)) centered at 600 nm. Figures 4(b) and (c) show the numerical reflectance and transmittance spectra when the Gaussian illumination diameter covers 20 NPs (beam waist equal to 10 periods). As it can be inferred from the plot, when considering a finite-size device, the shape and features of the simulated spectra match the experimental results and a dip (I) emerges at the blue side of the reflection spectra for both arrays \(A(p = 550 \text{ nm})\) and \(B (p = 630 \text{ nm})\). In particular for arrays B, FDTD simulations confirm that the first dip (I) is due to the first-order diffraction that is not collected in the experimental setup. Also, the simulated transmission agrees well with the experimental results, while previous work reported that ion beam bombardment increases the optical density of glass, reducing the transmission for wavelengths in the 500–600 nm range [18]. We suggest that the effect of ion beam bombardment is mitigated by the limited exposure of quartz during the milling process.

It can be furthered observed from figure 4(d) that under increasing width of the illuminating beam waist from 5 to 40 periods, dip I is red-shifting and decreasing in intensity eventually matching the results for an infinite structure. Conversely, the dip II is blue shifted and moves towards \(\lambda = p\) as for the infinite structure (figure 4(b) and (c)).

To fully account for the effect of variations in the NP geometry, we modelled the reflectance and transmittance spectra while varying the array period and the gap size. As expected, a variation of the array periodicity shifts all the spectral features consistently (figure 4(e)). On the other hand, an increase on the gap width \(w\) (figure 1(a)) from 0 to 50 nm only alters the magnitude and position of the dips around 600 nm (I) and 800 nm (III) (figure 4(f)). This can explain the small difference in the position of the peaks in the range 750–800 nm in the experimental spectra. Overall, these numerical results confirmed our hypothesis, since simulations are in very good agreement with the measurements.

On the strength of the theoretical model developed, we predicted and validated the performances of the NPs array as a refractive index sensor. To do this, we first simulated the reflectivity spectrum for a NP array with \(p = 630 \text{ nm}\) covered...
in a thin layer of distilled water (RI = 1.33) and isopropyl alcohol (IPA) (RI = 1.37). Figure 5(a) shows that the numerical reflectance spectrum in IPA is red-shifted when compared to the reflection in water. The wavelength shifts (20 nm) results in a predicted sensitivity $S_R = 500$ nm RIU$^{-1}$ and FOM, defined as $FOM = S/\Delta \lambda$ where $\Delta \lambda$ is the full width at half-maximum and $FOM = 10$ RIU$^{-1}$.

It is worth highlighting that numerical results show that similar performance, in terms of sensitivity and FOM, can be achieved by considering a lower number of the illuminated nanoplatelets ($N = 5$ or 10). However, for smaller launch widths, a flattened dip arises and this could increase the measurement uncertainty. We verified this prediction experimentally by acquiring the reflection spectra when the array ($p = 630$ nm) was covered by a thin layer of distilled water or IPA. The spectra in figure 5(b) show a clear red shift of the resonance when substituted with IPA ($\Delta \lambda = 24.9 \pm 5.3$ nm). As IPA was very volatile upon illumination of the array, the acquisition was limited to 3 s per analyte. The spectral shift was measured with the aid of visual eye-guides obtained by interpolating the data with second order Fourier series (figure 5(b)). When compared with the variation of refractive index unit (RIU), the wavelength shift translates to a sensitivity of $622 \pm 134$ nm RIU$^{-1}$, compatible with the simulated value. The experimental figure of merit results as $FOM = 7$ RIU$^{-1}$ for a FWHM of $88$ nm.

To provide evidence of a fast, alternative detection method, we used dark field (DF) microscopy to image the array immersed in air or IPA. Using an upright microscope in DF configuration (Nikon Eclipse 2000), we illuminated the sample with oblique light: while the zeroth diffraction order was blocked, the first order reached the detector. We acquired DF images with the sample ($p = 550$ nm) covered in air and in IPA (figure 5(c)). It is apparent that only the patterned area produces a diffraction spectrum, as no signal arises from the gold layer around the platelets, apart from scattering from small particles deposited on the sample.

Similarly, we characterized the sensing performances using transmitted light. Figure 5(d) shows the numerical model for transmitted light when a 3 $\mu m$ thick drop of water (blue) or IPA (red) covers the array ($p = 630$ nm). The change in refractive index induces a shift of the transmittance peak of $\Delta \lambda = 24$ nm; this shift implies that the array has a theoretical sensitivity of $S_T = 600$ nm RIU$^{-1}$ and a $FOM_T = 24$ RIU$^{-1}$ in transmission once the FWHM = 25 nm of the water peak is taken into account. The experimental measurements, shown in figure 5(e), produced a shift of $\Delta \lambda = 17.8 \pm 0.5$ nm that reflects a sensitivity of $S_T = 445 \pm 12$ nm RIU$^{-1}$ and a $FOM = 29$ RIU$^{-1}$, once the FWHM = 15.4 nm of the water peak is taken into account. While we attribute the differences between simulations and experiments to a mismatch in the thickness of simulated and actual layers of water and IPA, we observe that the measured values are consistent with literature reports on similar sensor architectures [8].

3. Conclusions

We have provided a comprehensive experimental and theoretical description of the combination of plasmonic and diffractive effects in finite, 2D arrays of NPs with sub-20 nm gaps fabricated with Ga FIB milling. Notably, we observed that high optical transmission (approaching 10%) can be achieved by illuminating a small number of elements (illumination beam diameter covers 20 periods). We have also proven that our arrays can serve as an effective refractive index sensors using either reflected or transmitted light. We envision that our work will favour future research on the fabrication of metallic nanostructures, on the fundamental investigation of their optical properties as well as on the application of these tools as advanced biosensors.

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**Conflict of interest**

L.S., M.D.V. and F. Pisanello are founders and hold private equity in OptogeniX, a company that develops, produces and sells technologies to deliver light into the brain.

**ORCID iDs**

Filippo Pisano https://orcid.org/0000-0002-5499-160X

Antonio Balena https://orcid.org/0000-0003-4314-4314

Muhammad Fayyaz Kashif https://orcid.org/0000-0002-7837-6679

Marco Pisanello https://orcid.org/0000-0003-2179-7883

Gaia de Marzo https://orcid.org/0000-0002-8073-9395

Luciana Algieri https://orcid.org/0000-0002-1906-8772

Antonio Qualtieri https://orcid.org/0000-0003-5655-3104

Tiziana Stomeo https://orcid.org/0000-0002-8073-9395

Ferruccio Pisanello https://orcid.org/0000-0002-1489-7758

Marco Grande https://orcid.org/0000-0002-1906-8772

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