Nano- and microstructured plasmonic substrates for laser and spectral applications

T T H Nguyen1,3, S I Kudryashov1,2, P A Danilov1, A A Ionin1, R A Khmelnitskii1, A A Rudenko1 and I N Saraeva1

1Lebedev Physical Institute, Leninskiy prospect 53, 119991 Moscow, Russia
2ITMO University, 197101 St. Petersburg, Russia, Russia
3Moscow Institute of Physics and Technology, 141701 Dolgoprudny, Moscow Region, Russia
4Ha Tinh University, precinct Dai Nai, city Ha Tinh, province Ha Tinh, Viet Nam

E-mail: trang.nguyenthihuyen@htu.edu.vn

Abstract. Nano- and micro-structures of thin plasmonic films by focused femtosecond laser pulses was demonstrated as chemo- and bio-sensing substrates for surface-enhanced spectroscopies. As an example, large regular arrays of microholes (mm-sized laboratory-scale) of millions holes with variable periods were produced in thin films of diverse plasmonic metals or alloys, demonstrating surface plasmon-polariton enhanced extraordinary transmission.

1. Introduction

Plasmonic and all-dielectric functional nano- and micro-elements and their regular and irregular arrays as sensors, circuits and metasurfaces are invoking the growing attention in nanophotonics, photovoltaics and photo-catalysis, ultra-sensitive chemo- and bio-sensing, during the last decade [1-6]. Intricate morphology of advanced nano- and microstructures implies their versatile state-of-art, but elaborate, expensive, time-consuming and non-flexible fabrication procedures – electron, ion- and photolithography [7, 8]. In this lieu, the rapidly developing laser patterning technologies present a promising viable alternative for the current well-developed lithographic nano- and micro-fabrication routines in terms of fabrication costs, throughput, modalities, ecological shortcomings and flexibility. Furthermore, such laser patterning technologies are currently or potentially compatible with ultra-precise laser-induced additive – multi-photon polymerization, surface chemistry, displacive – thin-film dewetting, communicative – (sub)micro-scale bulk inscription and drilling in supporting transparent substrate materials, and many other functional laser-based and non-laser post-processing subtractive procedures – chemical etching, ion-beam polishing [9, 10].

Nano- and micro-structured plasmonic and dielectric films make use of nano- and micro-elements in the form of shaped nano- and micro-holes, which are the structures with their optical/plasmonic responses complementary to separate, “free-standing” nano- and micro-elements (or their arrays) in terms of transmittance, reflectance or absorbance [11, 12] (the “complementarity” principle in optics [6]). Owing to small – nano- or (sub)micro-scale dimensions, localized plasmon-polaritonic or pure polaritonic modes in metallic or dielectric structures, respectively, become dominating in their electromagnetic response irrespectively their “closed” (a nanoshaped piece matter) or “open” (a nanoshaped hole in metallic or dielectric film) morphology [13]. Moreover, comparing to nanoshaped
elements made of plasmonic materials with considerable dissipative losses, considerably increased optical strength is provided for “hollow” nano-elements because of the efficient heat sink to the surrounding reservoir metallic films, which is currently the crucial issue in plasmonic and all-dielectric nanophotonic sensing. Additionally, enhanced surface adhesion, chemical stability and mechanical robustness are characteristic of “hollow”-element arrays in thin non- and metallic films in comparison to those of shaped nano-elements [14].

In this work, we implicate thin films of diverse plasmonic metals (silver, copper, aluminum, gold-palladium alloy) as a starting point for fabrication of elaborate and multi-scale nano/micro-patterns through diffractive optical elements (DOE)-mediated femtosecond laser nano- and micro-scale ablative and displacive processes. The advanced patterning technology was also employed in ultrafast fabrication of mm-sized laboratory-scale of surface enhanced infrared absorption (SEIRA) sensors, comprised by regular arrays of ~1 million micro-holes in thin CaF$_2$-supported films with variable micro-hole period. These sensors allowed experimental IR-spectral studies of extraordinary transmission (EOT) effect in these micro-hole arrays and its many-fold surface plasmon-polaritonic (SPP) enhancement. Finally, label- and luminescence-free sensing of a mono-layer of highly luminescent Rhodamine 6G dye with many-fold (a few hundred times) analytical enhancements of its IR-absorption signals and the internal calibration of the deposited analyte concentration via IR-absorption measurements in the overtone range were demonstrated.

2. Extraordinary transmission in arrays of nano- and micro-holes

EOT is mediated by SPP and localized plasmonic effects on the metal surfaces (in thin films – both front and rear ones [6]) and on hole edges, respectively, effectively increasing the actual hole size available for transmission and revealing, e.g., a few resonant transmission bands for different directions in square arrays of holes as 2D photonic crystals [15]:

$$v_{SP}(i,j) = \frac{\sqrt{i^2+j^2}}{n_{SP}D} = \frac{\sqrt{i^2+j^2}}{P} \frac{\varepsilon_M+\varepsilon_D}{\varepsilon_M\varepsilon_D}$$

where $i,j$ are the integer indexes for different directions $(i,j)$ in the array (grating), $n_{SP}$ is the effective refractive index for surface plasmon-polaritons, $\varepsilon_M$ and $\varepsilon_D$ are the dielectric functions of the metallic and the dielectric media [15].

In this study, we harnessed the advantage of large-scale, high-throughput laser patterning of thin plasmonic films to comprehensively characterize IR-range transmission in large (~10$^3$-10$^6$ holes per array) arrays of micro-holes of variable periods in thin films with thickness 50 nm from diverse plasmonic materials (silver Ag, copper Cu, aluminum Al and gold-palladium (Au-Pd, 80%/20%) alloy.

Equation (1) based on the SPP-mediated transmission model for hole arrays in metal films [6, 15] enables to assign the main peaks in the transmittance maximum in Fig.1 to different directions in the gratings as 2D photonic crystals. In Fig.1 such normalized transmittance spectra are presented for different materials (Ag, Al, Cu, Au-Pd alloy) and different grating periods $P$. In agreement with this equation, the corresponding (1,0), (1,1) and (2,0)-peaks blue-shift monotonously versus decreasing $P$ with their particular experimental spectral positions in the quantitative agreement with the predicted ones, considering the metal-dielectric (CaF$_2$, IR dielectric constant $\varepsilon_{CaF_2} \approx 2$), rather than metal-air (IR dielectric constant $\varepsilon_{air} \approx 1$), interface of the gratings. Previously, such air-metal interface of nano-hole gratings was also demonstrated as predominating in their transmission [15].

Moreover, since both localized surface plasmons on micro-hole edges/walls and SPP propagating on the metal-air and metal-CaF$_2$ film interfaces are considered to be involved in the EOT phenomenon, it is instructive to evaluate their relative contributions from our experimental data for the thin metallic films, supporting waveguide-like transmission. Similarly, in Figure 1 the fixed 4-μm hole diameter (perimeter, square) is favorable for increasing amplitudes (contrast) of the (1,1)- and (2,0)-
peaks at increasing P, as the corresponding surface density of hole decreases versus P, decreasing the surface corrugation.

**Figure 1.** Normalized transmittance spectra of micro-hole gratings with the diameter $D \approx 4 \mu m$ on the 50 nm thick Ag (a), Al (b), Cu (c) and Au-Pd alloy (d) films on the CaF$_2$ substrates with the variable periods (shown by the same colors as the corresponding spectra), the colored numbers showing the spectral positions of their (1,0), (1,1) and (2,0)-peaks and the red dashed lines showing their evolution versus P. Insets: (a) top-view SEM images of the gratings with the diameters shown in the frames (scale bars can vary).

Finally, the abovementioned SPP enhancement of the IR-transmittance appears differently for the micro-hole gratings with the fixed 4-$\mu m$ hole diameter and different similar periods on the films of the diverse metals used in this study. Specifically, the micro-hole gratings on the Au-Pd alloy film demonstrate considerably – by almost 50% – lower (1,0)-peak transmittance, comparing, e.g., to the similar gratings on the Ag-film (Fig.1a). Likewise, in the whole series of gratings the 4-$\mu m$ hole diameter with similar periods of 6 and 7 $\mu m$ in Figure 1, the ranking of metals according to (1,0)-peak amplitude is 1) Cu (0.75/0.6), 2) Al (0.7/0.5), 3) Ag (0.45/0.3) and 4) Au-Pd (0.3/0.2), indicating the best plasmonic response for copper and aluminum, the medium one for Ag and the worst one for the Au-Pd alloy (80%/20%), which has indeed main transport characteristics strongly – five-fold – diminished due to the high Pd-impurity concentration. In the case of silver films, their grain-like (island) structure and minor surface oxidation during low-vacuum (10$^{-2}$ bar) magnetron sputtering can hamper the usual outstanding plasmonic properties of this metal.

3. Advanced chemo-sensing with mm-sized laboratory samples of micro-structured IR-sensors

Chemo-sensing of the produced 4×4 mm$^2$ gratings of micro-holes (approx. half-million of micro-holes) on the 30-nm thick silver film on the IR-transparent CaF$_2$ substrate (Fig.2a,b) was investigated in terms of their resonant EOT-enhanced IR-transmission as surface-enhanced IR-absorption (SEIRA) [3]. FT-IR transmission spectra of the pristine CaF$_2$ substrate, as-deposited Ag-film and the micro-hole grating (D $\approx$ 4 $\mu m$, P $\approx$ 6 $\mu m$) with an analyte – Rhodamine 6G molecules, was measured in vacuum in the near-mid IR range of spectral wave-numbers $\nu = 400$-$5000$ cm$^{-1}$, using a FT-IR spectrometer V-70 (Bruker). These spectra normalized to the CaF$_2$ transmittance near the cut-off wavenumber $\sim$ 1000 cm$^{-1}$ are presented in Fig.2c,d, indicating the very minute characteristic fingerprint dips in the spectra in
the ranges $\nu = 900$-$1300 \text{ cm}^{-1}$ and $2800$-$3000 \text{ cm}^{-1}$, as R6G analytical signals. The extra-large micro-hole array with its SPP-enhanced EOT provide strong and robust transmission signals, enabling enlightening studies of the R6G distribution (i.e., potential pre-concentration or dis-concentration effects) and spectral characteristics on the array surface owing to different ultrafine physio- and chemisorption interaction with the structured Ag surface and the CaF$_2$ substrate.

The large-hole sensor with monolayer R6G demonstrates a few much stronger absorption lines for $\nu = 900$ – $1300 \text{ cm}^{-1}$ (the strongest one at $1261 \text{ cm}^{-1}$) (Fig.2c). In comparison with this sensor, similar surface density of R6G molecules on the bare CaF$_2$ substrate indicates much stronger absorption in the range of $2800$ – $3000 \text{ cm}^{-1}$, while, surprisingly, much less absorption in the mid-IR range of $900$ – $1300 \text{ cm}^{-1}$. Comparison of the mid-IR absorbance for the sensor- and CaF$_2$-supported R6G molecules demonstrates the analytical SEIRA enhancement $-40 \pm 11$, $47 \pm 19$ and $455 \pm 230$ times for the mid-IR spectral bands at 1024, 1097 and 1261 cm$^{-1}$, respectively (Fig.2c). However, being normalized to the six-fold enhancement of the absorption in the near-IR range (see above), the spectrally sensitive physical SEIRA enhancement appears to be more moderate $-7 \pm 2$, $8 \pm 3$ and $76 \pm 38$ times at 1024, 1097 and 1261 cm$^{-1}$, respectively. Furthermore, the limit of R6G detection for the sensor, taken for the most SEIRA-enhanced band at 1261 cm$^{-1}$, at the 3σ-level is equal to LOD $= \Delta/A1261 \approx 10^{-2}$ monolayer.

**Figure 2.** (a) Optical image (general view) of the 11-mm wide CaF$_2$-slab with the top 30-nm thick Ag-film and a number of micro-hole gratings (typical square – $4 \times 4 \text{ mm}^2$). b) Top-view SEM image of the grating with $D = 4 \mu\text{m}$ and $P = 6 \mu\text{m}$ (inset: its magnified view). c) Normalized FT-IR transmission spectra of the grating with $D = 4 \mu\text{m}$ and $P = 6 \mu\text{m}$ (G, (1,0), (1,1) and (2,0) – resonance transmission peaks) and of the grating with the R6G monolayer atop (G+R6G); FT-IR transmission spectrum of the CaF$_2$ substrate with the R6G monolayer is given for comparison. Inset: the magnified view of their normalized low-$\nu$ transmittance with the assignment of the R6G absorption bands on the CaF$_2$ substrate and the grating (see the different top and bottom scales) discussed in details in the text. d) Magnified view of their normalized high-$\nu$ transmittance in the overtone region with the assignment of the composition R6G absorption bands.

Such internal calibration was performed, considering the waveguide-like transmission through the array in the mid-IR range of 2800-3000 cm$^{-1}$ at the transmittance level $\approx 0.08$ (8%) in the clean array.
and ≈0.069 (6.9%) in the array with the R6G monolayer. The corresponding transmittance dips of R6G bands are 0.11% (≈2850 cm⁻¹), 0.35% (≈2920 cm⁻¹) and 0.2% (≈2960 cm⁻¹) on the CaF₂ substrate, representing combination CH-stretching modes of the main xanthene ring (XR), phenyl, ethyl and methyl groups with the lower-wavenumber external group modes (EGM), but with the overall wave-numbers less than those of C-H stretching overtones (Fig. 2d). On the array, these R6G absorption bands demonstrated, on average, much – almost 7-fold – lower signals of 0.04% (≈2850 cm⁻¹), 0.03% (≈2920 cm⁻¹), while the R6G absorbance at 2960 cm⁻¹ unexpectedly appears even two-fold higher (0.4%). Comparing to the 13-fold stronger IR-transmission through the CaF₂ substrate – 92% vs 7% (this array), such 7-fold lower R6G absorbance on the array effectively means its 2-fold, on average, enhancement of R6G absorbance, with the corresponding 26-fold enhancement of the absorption band at 2960 cm⁻¹. Generally, such enhancement could occur due to plasmonic (spectrally homogeneous over the narrow range of 2800-3000 cm⁻¹) or chemical (R6G-Ag-complexing, spectrally-selective for the different R6G bonds) factors, which will be discussed below during the analysis of the characteristic absorption bands. Meanwhile, taking the minimal enhancement conditions at ≈2920 cm⁻¹, 13-fold difference in the R6G absorbance on the CaF₂ and the grating could be expected over the entire IR spectrum at the absence of the relevant plasmonic and chemical enhancement factors.

4. Conclusion
DOE+MHz fs-laser through easy, green and low-cost high-throughput fabrication of complementary nano- and micro-structures – large arrays of plasmonic (or even dielectric) nano- and micro-elements. Enable advanced studies of topology- and material-dependent physical phenomena in metasurfaces by common laboratory spectroscopic tools, but also label- and luminescence-free laboratory-scale, robust and high-sensitivity sampling of chemicals and biosamples via plasmonic and chemical contributions, uneven and structurally-sensitive regarding different functional groups of the analyte molecules and band structure of the plasmonic metal.

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References
[1] Baikova T V et al 2017 AIP Conference Proceedings 1874 040052
[2] Baikova T V et al 2016 Las. Phys. Lett. 13 (7) 070602
[3] Danilov P A et al 2016 Laser Phys. Lett. 13 055602
[4] Emelyanov V I 2014 JETP Letters 99(9) 518
[5] Zayarny D A et al 2014 JETP Lett. 100 295
[6] Klimov V 2014 Nanoplasmonics (Boca Raton, FL: CRC Press)
[7] Im H et al 2010 ACS Nano 4 947
[8] Qiuming Yu et al 2008 Nano Lett. 8 (7) 1923
[9] Danilov P A et al 2014 Quantum Electron 44 540
[10] Kulchin Yu N, Vitrik O B, Kuchmizhak A A, Nepomnyashchii A V, Savchuk A G, Ionin A A, Kudryashov S I and Makarov S V 2013 Opt. Lett. 38 1452
[11] Masatoshi Osawa, Masahiko Ikeda 1991 J. Phys. Chem. 95(24) 9914
[12] Hartstein A, Kirtley J R and Tsang J C 1980 Phys. Rev. Lett. 45 201
[13] Kuchmizhak A A, Ionin A A, Kudryashov S I, Makarov S V, Rudenko A A, Kulchin Yu N, Vitrik O B and Efimov T V 2015 Opt. Lett. 40 1687
[14] Ionin A A, Kudryashov S I, Makarov S V, Levchenko A O, Rudenko A A, Saraeva I N, Zayarny D A, Nathala C R and Husinsky W 2015 Laser Phys. Lett. 13 025603
[15] Ghaemi H F, Thio, Tineke, Grupp D E, Ebbesen T W, and Lezec H J 1998 Phys. Rev. B. 58(11) 6779