Ablation-Free Laser Printing of Structural Colors in Reflection at 25,000 DPI

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Abstract. Using direct femtosecond laser patterning of metal-insulator-metal (MIM) sandwich designed to support Fabry-Perot mode in the visible spectral range we demonstrate new practically relevant strategy for high-resolution color printing. Irradiation of the MIM sandwich by tightly focused laser pulses allows to produce unique 3D surface nanostructures – hollow nanobumps and nanojets - locally modulating surface reflectivity. Laser processing parameters control the 3D shape of such nanostructures allowing to gradually tune the reflected color from reddish brown to pure green. Up-scalable ablation-free laser fabrication method paves the way towards various applications ranging from large-scale structural color printing to optical sensors and security labeling at a lateral resolution of 25,000 dots per inch.

1. Introduction
Unlike organic and inorganic pigments and dyes, structural colors originating from the interaction of broadband visible radiation with optically resonant nanostructures are non-fading and stable against UV radiation and thermal treatment [1,2]. Structural color technology is rather cheap in recycling, sustainable and durable, allowing to obtain vibrant (as compared to organic dyes) color tones with an extended gamut. Furthermore, utilization of optically resonant nanostructures paves the way toward high-quality imaging with the lateral resolution up to 100,000 dots per inch (DPI) that corresponds to the Abbe diffraction limit and makes the boundaries between neighboring pixels indistinguishable even with best dry microscope objectives. Lateral resolution of structural colors technology is two orders of magnitude higher comparing to those for best commercial printers. In the near future, structural colors are expected to revolutionize several technologically relevant areas as optical filters, next-generation displays, color marking and anti-counterfeiting of goods, etc. Moreover, a wide range of available materials for realization of optically resonant nanostructures makes the structural color technology potentially CMOS-compatible.

Despite the well-known physics of structural colors derived from standard bulk optics as prisms, thin films, photonic crystals or diffraction gratings, the interest in structural coloring of surfaces has recently refreshed. In part, this can be attributed to recent advances in such areas as nanophotonics, plasmonics and meta-optics, as well as the spreading of high-resolution planar nanofabrication technologies as electron- and ion-beam lithography that allowed to shrink the size of the structural colored pixel well below optical diffraction limit. Using semiconductor materials with high refractive index and low dissipative losses as well as plasmon-active metals [2,3], it is possible to fabricate sub-wavelength nanostructures with resonant optical response that can be tailored by varying characteristic geometry of nanostructures and their arrangement. Along with spectrally adjustable optical response, such nano-
resonators can be also fabricated to have polarization anisotropy and angular dependence allowing to realize various schemes of optical information encryption [5,6].

In spite of a new look borrowed from meta-optics, majority of works used rather classical schemes based on thin-film Fabry-Perot filters [5], percolated films [7] and diffraction gratings [8] being combined with standard planar nano-resonators like nanodics, and nanoholes, whose planar geometry and arrangement are determined by planar fabrication technologies. Additional functionality and controllability over the single-pixel color and brightness appears to be achieved using 3D optical nanostructures. However, the ability to vary the height of the optically resonant nanostructures in each individual pixel of a color-coded picture cannot be implemented using the time- and money-consuming planar lithographic fabrication technologies.

Pulsed laser radiation is known to drive ultrafast solid-liquid phase transition on the surface of the exposed material that allows its sculpturing and subsequent resolidification in the form of various surface nano-morphologies like nanoparticles, nanoripples and nanobumps [9,10]. The latter type of structures is of particular interest as the 3D geometry of the nanobumps can be easily controlled by varying only the laser fluence and focusing conditions. Such structures can be imprinted on the surface of all plasmon-active metal films without ablation (ejection of the nanoparticles) thus ensuring ultra-clean and reproducible fabrication. Previously, by taking advantage of geometry-dependent resonant scattering of isolated nanobumps we demonstrated the direct laser writing of plasmonic colors that can be observed in the dark-field back-scattering regime [9]. Here, we show that ablation-free laser patterning of the metal-insulator-metal (MIM) sandwich with nanobumps allows to realize high-resolution (up to 25,000 DPI) structural coloring in more practically relevant reflection regime at high lateral resolution.

2. Material and Methods

For preliminary estimation, structural colors in reflection were generated by patterning a specially designed with FDTD numerical simulations MIM film containing 50-nm thick Au top layer (transmission ~ 6.5%), 100-nm thick Al2O3 middle layer and 500-nm thick Ag bottom layer thermally evaporated above silica glass slide (inset in the Figure 1a). The as-fabricated MIM film has reddish (as compared to the ordinary 50-nm thick Au on glass) color and represents a Fabry-Perot cavity designed to have a sharp resonant feature at 540 nm in reflection spectrum (Figure 1a).

The top layer of the MIM cavity was directly patterned using second-harmonic (515 nm) 200-fs laser pulses generated by regeneratively amplified Yb:KGW laser system (Pharos, Light Conversion). Laser pulses were focused onto the surface of MIM top layer using dry microscope objective having the numerical aperture (NA) of 0.42. The laser system was synchronized with a PC-driven attenuator (Stand) and 3D nanopositioning stages (Aerotech Gmbh.) allowing to process the surface according to programmable trajectory and vary the incident pulse energy. Morphology of the laser-printed nanostructures was correlated with laser-processing parameters using scanning electron microscopy (SEM, Ultra 55+, Carl Zeiss).

Reflectivity of the laser-patterned areas was studied using home-built microspectroscopy setup containing a bright-field optical microscope confocally aligned with a grating type spectrometer (Shamrock 303i, Andor) equipped with a thermo-electrically cooled CCD camera (Newton, Andor). Adjustable pinhole in the image plane was used to control the signal acquisition area. The reflection spectra were collected with an optical objective with NA=0.42 and normalized onto the signal from the bulk silver mirror. Reflection spectra were converted into the chromaticity coordinates of the hue-saturation-value (HCV) color space using the software package developed in [9].

3. Results and Discussions

Single-pulse ablation of “thermally” thin glass-supported Au films was extensively studied showing the formation of parabola- or cone-shaped hollow protrusions (nanobumps) at pulse energy E below the film ablation threshold [11]. Such behavior can be explained by a sequence of laser-induced phenomena as fast melting, acoustic relaxation at the film-substrate interface and resolidification [12]. Completely similar behavior was found for top Au layer of the MIM sandwich irradiated by tightly focused femtosecond laser pulses. In particular, similar nanobumps appeared upon laser irradiation with their lateral size and the height increases with a pulse energy E, as it is illustrated by a series of side-view SEM images (Figure 1b).

Remarkably, observation of the laser-patterned areas covered with nanobumps with an ordinary bright-field optical microscope revealed their structural colors (Figure 1c). More importantly, the color was found to be tuned from reddish brown to pure green upon increase of the nanobumps size as
illustrated by a series of bright-field optical images collected with microscope objective at NA=0.42. The nanobumps in all the arrays were printed at a periodicity of 1 µm that ensured the homogeneously colored surface where the isolated nanostructures can not be resolved. Reflection spectra of the laser-patterned areas allowed to correlate the change of the structural color with corresponding variation of the nanobump morphology (see Figure 1d). As can be see, the increase of the nanobumps height causes the gradual decrease of the reflectivity in the yellow-red part of the optical spectrum. In contrast, blue part of the spectrum shows slower decrease of the reflectivity versus the nanobump size that explains the resulting green color of the textured surfaces printed at pulse energy of 1.8 nJ.

Figure 1. (a) Diffuse reflectance spectra of MIM sandwich (red curve) and bare 50-nm thick Au film on a glass substrate (yellow curve). (b) Series of side-view SEM images of the MIM surface textured at elevated pulse energy (from 1.1 to 1.8 nJ). (c) Corresponding bright-field optical image of the square-shape laser-patterned areas (200 x 200 µm) processed at elevated pulse energies E as well as reflectance spectra (d) of these areas. (e) HCV color space with markers indicating the colors of the pristine MIM sandwich and the patterned areas from (c). (f) Bright-field optical image of the laser-patterned area (E=1.8nJ) visualized with microscope objective at NA=0.3 and 0.8. (g) Bright-field optical image of the patterned area (400 x 80 µm²) arranged to form “FEFU” letters. The nanobumps were imprinted at pulse energy E=1.8 nJ and periodicity of 1 µm.

Reflection spectra were further analyzed by converting them into the coordinates on the HCV color space to reveal the tuning range of the colors than can be reproduced using the developed laser-printing technique strategy. This data is summarized in Figure 1e illustrating that various rather pure colors can be reproduced via direct laser printing by changing the only experimental parameter – applied pulse energy. Noteworthy, imprinted structural colors of the laser-textured areas appeared similarly upon visualization with microscope objectives having variable NA that defines the collection angle of the reflected signal. Figure 1f compares the same laser-textured area produced at E=1.8 nJ upon its observation with low- and high-NA optics. As can be seen, visualization at NA=0.8 allowed to identify separate nanobumps that appeared as the green spots similarly to the whole laser-textured areas visualized at NA=0.3. In particular, this clearly illustrates possibility of the developed approach to imprint optical information and colored images at a lateral resolution up to 25,000 DPI. Finally, as an illustration of such possibility we imprinted
several micro-scale surface areas arranged to form “FEFU” letters visualized in the reflection mode of the optical microscope at NA=0.42 (Figure 1g).

4. Conclusion
In conclusion, we demonstrated a novel approach to structural coloring of surface using the ablation-free direct laser patterning of metal-insulator-metal films. Using the proposed method, we prepared a test sample and performed a preliminary evaluation of the spectral properties of the fabricated structures. The structured surfaces demonstrate colors from reddish brown to pure green in reflection spectra depending on the shape of the single nanobumps.

Overall, the tailoring of the laser pulse parameters, as well as the thicknesses and materials of metal and dielectric films, provides a potential opportunity to shift the Fabry-Perot mode supported by the MIM sandwich in the full visible spectral range, and, consequently, to obtain colors from violet to red. The relative simplicity of the proposed approach, as well as the high lateral resolution of 25,000 dots per inch, pave the way for applications in optical sensors, security labeling, etc.

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