Continuous metal plasmonic frequency selective surfaces

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Abstract: In the microwave part of the spectrum, where losses are minimal, metal films regularly patterned (perforated) on the sub-wavelength scale achieve spectral selectivity by balancing the transmission and reflection characteristics of the surface. Here we show for optical frequencies, where joule losses are important, that periodic structuring of a metal film without violation of continuity (i.e. without perforation) is sufficient to achieve substantial modification of reflectivity. By engineering the geometry of the structure imposed on a surface one can dramatically change the perceived color of the metal without employing any form of chemical modification, thin-film coating or diffraction effects. This novel frequency selective effect is underpinned by plasmonic Joule losses in the constituent elements of the patterns (dubbed 'intaglio' and 'bas relief' metamaterials to distinguish indented and raised structures respectively) and is specific to the optical part of the spectrum. It has the advantage of maintaining the integrity of metal surfaces and is well suited to high-throughput fabrication via techniques such as nano-imprint.

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Frequency selective surfaces (FSSs) are a well-established paradigm for filtering electromagnetic waves, particularly in the microwave and radio frequency bands [1], and are recognized as the foundation of the modern field of metamaterials [2]. They commonly comprise either cascaded partially transmitting boundaries (akin to distributed Bragg reflectors in optics) or, like their metamaterial counterparts, resonant periodic arrays of conducting elements in a dielectric matrix or apertures in a conducting screen. In such systems, functionality relies on manipulation of the balance between reflected and transmitted waves. We report here on a contrasting class of FSS operating in the visible/near-infrared spectral domain, where the plasmonic response of metals facilitates the modification of reflection spectra via the sub-wavelength patterning of single, continuous (i.e. non-perforated) surfaces. It is found that absorption resonances can be engineered through the formation of arrays of nanoscale elements inscribed into or raised above the surface to a depth/height of the order 100 nm. These 'intaglio' (inscribed) and 'bas-relief' (raised) metamaterials can radically change a metal's reflection spectrum and, in the visible range, its perceived color (Fig. 1) without recourse to chemical modification (e.g. anodization) or application of secondary coatings (paints, dielectric multilayers, etc.). The colors produced can, by design, be polarization-dependent or -independent and are largely insensitive to viewing angle.

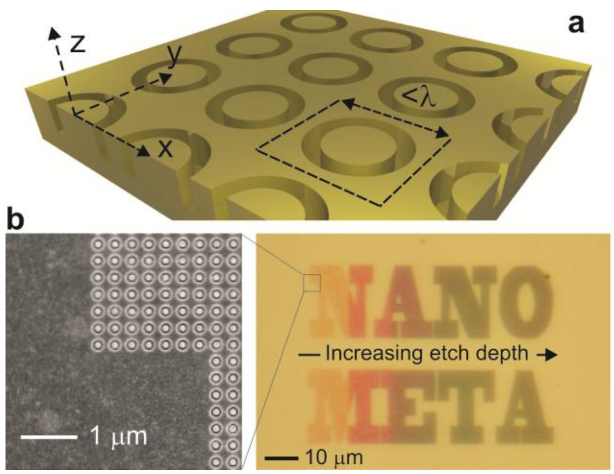

Fig. 1. Metallic structural color[†]: (a) Artistic impression of a generic intaglio metamaterial array of sub-wavelength single ring meta-molecules inscribed into a metal surface; (b) The realization of this concept in gold: The words 'NANO META' seen under an optical microscope on the right are formed from arrays of 170 nm diameter rings (as shown in the electron microscope image, left) milled to a depth that increases in six steps from 60 to 200 nm across the sample.

In the natural world, many plants and animals display dramatic 'structural colors' derived from astonishingly intricate three-dimensional assemblies of intrinsically colorless bio-materials [3] and while the physics of these colors is increasingly well understood, replicating them remains a significant challenge [4–6], typically requiring complex (multi- or atomic) layer deposition and etching fabrication procedures. In contrast, the intaglio/bas-relief metamaterials provide a flexible paradigm for structural coloring of pure metals that can be applied equally to bulk and thin-film surfaces and may ultimately be implemented via a single-step imprint process.

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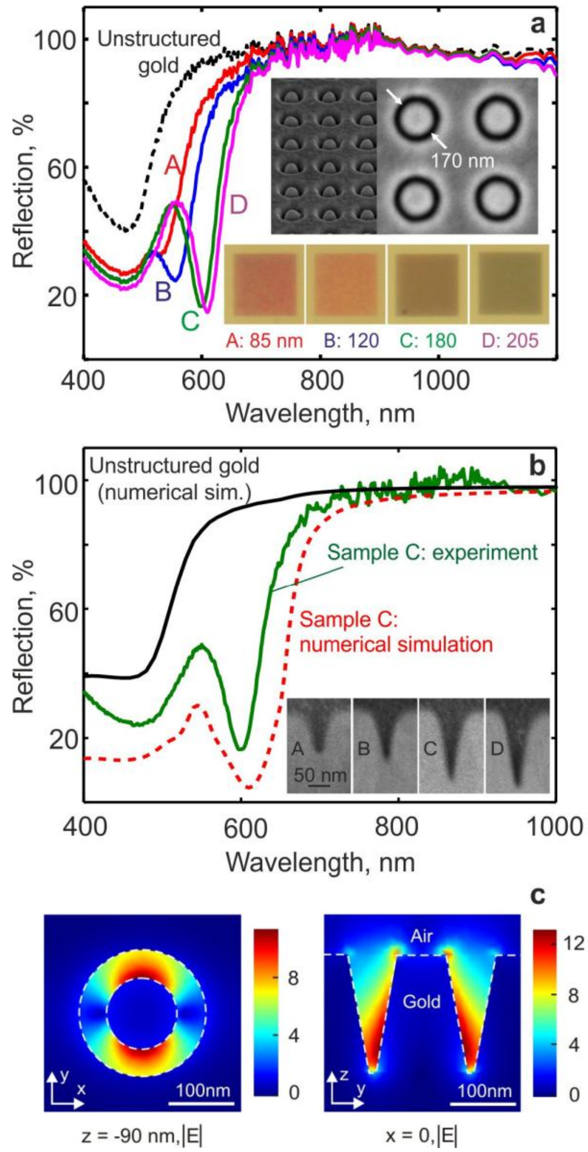

Fig. 2. Changing the color of gold[†]: (a) Normal incidence reflection spectra for an unstructured gold surface and for the same surface patterned with intaglio metamaterial arrays of 170 nm diameter rings cut to depths ranging from 85 to 205 nm (as labeled, depths derived from FIB calibration). The insets show electron microscope images of the design (at oblique incidence and in plan view) and optical microscope images of the different patterned domains; (b, c) Numerical modeling of gold intaglio metamaterials: (b) Comparison between simulated and experimentally measured reflection spectra. For clarity, data for one of the four designs presented in part (a) are shown on a magnified wavelength axis; (c) Maps of total electric field intensity in a z-plane 90 nm below the top surface of the metal (left) and in the x-plane diametrically bisecting a ring (right). The structure is illuminated at normal incidence with y-polarized plane waves at 610 nm.

In experiment, a microspectrophotometer (CRAIC QDI2010) was employed to measure normal incidence reflection spectra for a variety of gold and aluminum intaglio and bas-relief metamaterial designs: Gold intaglio metamaterial patterns were fabricated by focused ion beam milling (FEI Helios NanoLab 600) on 250 nm thick gold films evaporated on optically polished quartz substrates. Figure 2a shows spectra for square metamaterial arrays of 170 nm

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single rings milled to four different depths into a gold film, alongside the reflection spectrum for the adjacent unstructured gold surface. The red-shift of absorption resonance with increasing etch depth is clearly seen and the associated changes in the color of gold are strikingly illustrated by the inset optical microscope images.

These intaglio metamaterial designs have been numerically modeled using a fully three-dimensional finite element technique (in Comsol MultiPhysics), employing dielectric parameters for gold from Ref [7]. With account taken of the characteristic v-shaped slot profile produced by focused ion beam milling, there is excellent agreement between experimental and simulated reflection spectra. This is illustrated in Fig. 2b, which presents curve C from Fig. 2a alongside the corresponding simulated spectrum for an array of 180 nm deep, 170 nm diameter single rings and the simulated reflection spectrum for unstructured gold. Detail of the model meta-molecule geometry is shown in Fig. 2c, which shows horizontal and vertical cross-sections of the field distribution within the plasmonic ring resonator mode responsible for the 610 nm absorption resonance.

Aluminum bas-relief structures were fabricated at an interface between the metal and an optically polished fused silica substrate using electron beam lithography and anisotropic reactive ion etching: A 100 nm PMMA resist layer on the substrate was patterned by electron beam exposure at 100 keV via a high-resolution vector beam pattern generator (Vistec Lithography VB6HR) to form a mask for reactive ion etching in a fluorine-based plasma

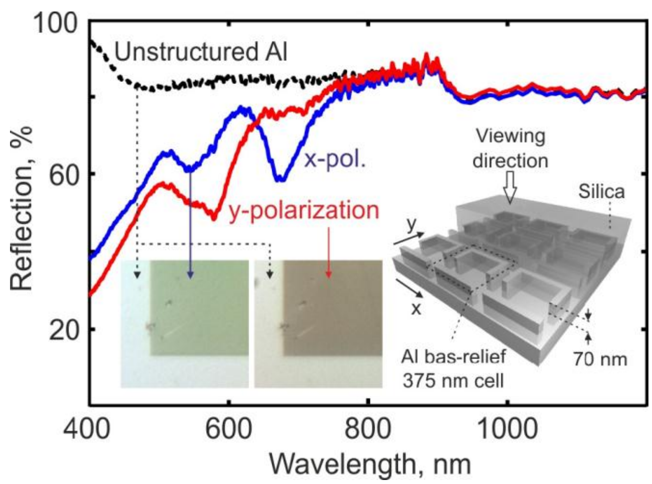

Fig. 3. Anisotropic color control on aluminum[†]: (a) Normal incidence reflection spectra for an unstructured aluminum/silica interface and for the same surface patterned with a bas-relief metamaterial array of 375 nm asymmetric split rings having a height of ~70 nm. Data are presented for two orthogonal incident polarizations parallel [x] and perpendicular [y] to the split in the rings. The insets show a schematic of the sample structure [with part of the silica layer cut away] and optical microscope images of the patterned domain under the two incident polarizations.

(Oxford Plasma Technology System90). The metamaterial design was etched into the silica to a nominal depth of 70 nm then coated by evaporation with a 250 nm layer of aluminum. Figure 3 shows spectra for an aluminum bas-relief design of asymmetric split rings (ASRs). Such patterns are routinely employed in conventional (discrete resonator) photonic metamaterials where they deliver collective ‘closed-mode’, polarization-sensitive transmission/reflection/ absorption resonances [8]. In the bas-relief form they provide dramatic changes in color from that of the unstructured metal, which are by virtue of the design anisotropy dependent on the polarization of incident light.

The functionality of intaglio/bas-relief designs, wherein sub-wavelength periodicity excludes diffraction effects, relies on the resonant plasmonic properties of the meta-molecules and as such is best realized via good ‘plasmonic’ metals (i.e. gold, aluminum, silver in the visible range). As in any plasmonic system from conventional photonic metamaterials [8] to

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sub-wavelength holes displaying extraordinary optical transmission [9], periodically perforated films supporting ‘spoof’ surface plasmons [10] and noble metal nanoparticles [11], resonances are a strong function of geometry and size [12]. The colors achieved by continuously metallic meta-surfaces in the present case are derived from the selective enhancement of absorption in the visible spectral range via the coupling of energy to plasmonic modes of the structures. While the existence of such modes is known (Vesseur *et al.* for example, have reported in detail on the whispering gallery modes of individual gold plasmonic ring resonators probed via electron-induced emission spectroscopy [13]) the spectral characteristics of dense metamaterial arrays of such meta-molecules has not previously been studied.

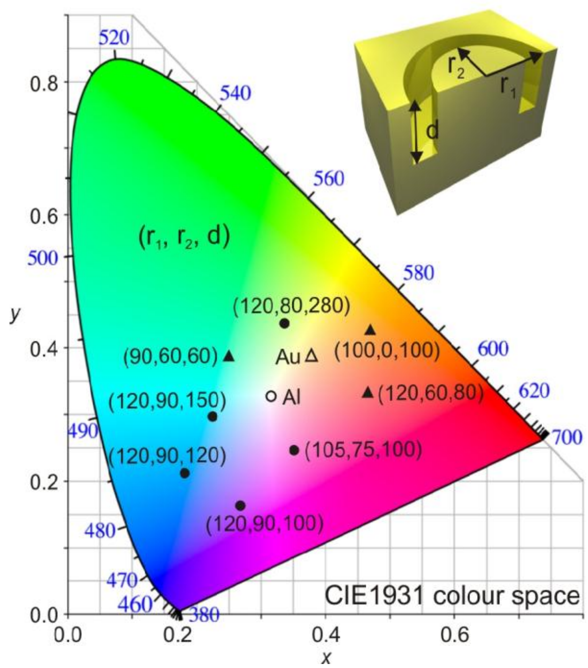

Fig. 4. Metallic color palette†: CIE1931 chromaticity diagram overlaid with points corresponding to the simulated reflected colors of single ring intaglio metamaterial designs in aluminum (circular symbols) and gold (triangles), labeled according to their structural parameters (external radius r_1, internal radius r_2, depth d, array period = 300 nm in all cases). Points for the unstructured metals are indicated by open symbols.

Figure 4 presents a numerical analysis (based on material parameters from Ref [7].) of various single-ring intaglio designs and illustrates that one can achieve a wide palette of colors through structural engineering of the metamaterial design. In this two-dimensional representation of the CIE1931 color space, perceived color coordinates are derived directly from reflection spectra using Judd-Vos-modified CIE 2-deg color matching functions [14–16] assuming in all cases an illuminating light source with the spectral radiant power distribution of a 6500 K black body and a normalized observational brightness level.

Unstructured aluminum, which uniformly reflects more than 80% of light across the range from 400 to 800 nm, occupies a position in the central white region of this map at (0.315, 0.327) [open circle symbol], while unstructured gold is found at (0.383, 0.399) [open triangle]. Metamaterial arrays of intaglio ring-resonators on these metals introduce strong absorption resonances at wavelengths dependent on the structural parameters of the meta-molecules thereby modifying the reflection spectrum, i.e. perceived color, of the surface. A selection of geometries have been assessed through numerical simulation (as shown by the filled symbols in Fig. 4, labeled according to the outer/inner radii and depth of the rings) illustrating that this simple design alone can provide access to a significant proportion of color

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space. The available parameter space for meta-molecule design and distribution is obviously almost unlimited and, as the above experimental results show, one has the option of introducing anisotropy through design asymmetry.

It should be emphasized that the experimentally observed colors presented in Figs. 1-3 cannot be mapped directly to colors in Fig. 4 because neither the illumination spectrum nor the uniform observational brightness assumed in this 2D chromaticity diagram correspond to experimental conditions. Nevertheless, *(x, y)* chromaticity coordinates derived from experimental spectra on the basis of an assumed light source (i.e. a 6500 K black body) do provide an approximate quantitative measure of structurally induced color change: For example, sample *A* in Fig. 2 has coordinates of (0.419, 0.362) and at progressively decreasing brightness sample *B* = (0.415, 0.342); *C* = (0.340, 0.374); *D* = (0.342, 0.386); the coordinates of the unstructured gold surface are (0.383, 0.385).

While spectrophotometric experiments are instrumentally restricted to normal incidence illumination, numerical analyses are readily extended to oblique incidence configurations. These reveal, as shown in Fig. 5, that the colors derived from metamaterial relief structuring

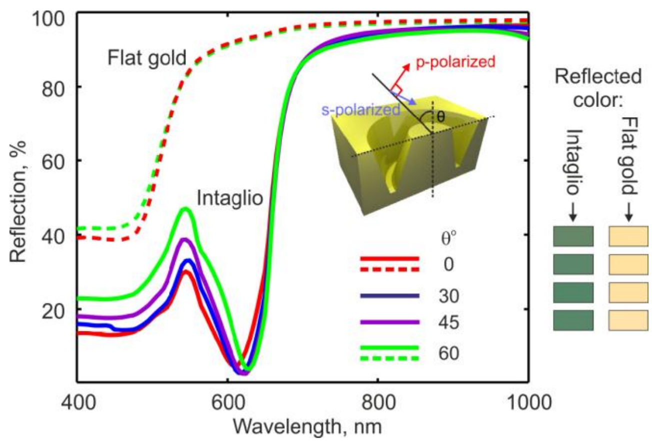

Fig. 5. Color invariance with viewing angle: Numerically simulated reflection spectra and associated perceived colors for a gold intaglio metamaterial array of 170 nm diameter rings with a depth of 180 nm viewed at normal incidence and a selection of oblique angles (as labeled, averaged over incident s- and p-polarizations). For comparison, the corresponding perceived color of an unstructured gold surface is shown for each viewing angle and reflection spectra for the unstructured metal at 0° and 60° angles are plotted.

are essentially independent of viewing angle, with variations in color being no larger than those observed for the unstructured metal. This angle invariance results from the fact that absorption is linked to localized plasmon modes of the metamaterial unit cells rather than diffraction effects or the coupling of incident energy to propagating surface plasmon polaritons (both excluded by the sub-wavelength periodicity of the metamaterial arrays).

Intaglio/bas-relief photonic metamaterials offer a robust and flexible paradigm for engineering the spectral response of metals in the *visible* domain, with potential applications ranging from aesthetic (e.g. jewelry) to optical sensing and security (e.g. in banknote/document anti-forgery features that must be difficult to imitate without substantial up-front investment in design and fabrication technology). In contrast to conventional (discrete meta-molecule) metamaterial forms demonstrated for absorption control in infrared sensing/imaging applications [17, 18]; to metallic films structured via micro-sphere lithography for broadband omnidirectional near-infrared absorption [19]; and to surfaces laser-roughened to suppress reflection below a monotonically tunable cut-off wavelength [20], continuously metallic intaglio and bas-relief designs offer a highly controllable mechanism for engineering and manipulating diffraction-free, angle-invariant absorption resonances that may ultimately be implemented using simple, low-cost scalable fabrication techniques (the proof-of-principle demonstrations reported here rely on focused ion beam milling and electron beam

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lithography but the patterns may be produced via nano-imprint or template stripping techniques), even on non-planar surfaces.

† Color presentation

The color balance of optical microscope images is referenced to a test pattern of RGB-specified sample colors (ColourChecker Mini by X-Rite). Readers should be aware that their monitor and/or printer settings may affect color rendering (Fig. 6 shows reference colors with specified RGB values for comparison).

Fig. 6. Reference colors.

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