**ABSTRACT:** We demonstrate plasmonic color printing with subwavelength resolution using circular gap-plasmon resonators (GPRs) arranged in 340 nm period arrays of square unit cells and fabricated with single-step electron-beam lithography. We develop a printing procedure resulting in correct single-pixel color reproduction, high color uniformity of colored areas, and high reproduction fidelity. Furthermore, we demonstrate that, due to inherent stability of GPRs with respect to surfactants, the fabricated color print can be protected with a transparent dielectric overlay for ambient use without destroying its coloring. Using finite-element simulations, we uncover the physical mechanisms responsible for color printing with GPR arrays and suggest the appropriate design procedure minimizing the influence of the protection layer.

**KEYWORDS:** Plasmonics, color printing, subwavelength optics, metasurfaces, gap surface plasmons

The manipulation of electromagnetic waves by plasmonic structures, in which propagating light couples to electromagnetic excitations associated with metallic nanostructures (i.e., surface plasmons), has been the subject of extensive studies at wavelengths spanning from microwave\(^1\)−\(^3\) and terahertz radiation\(^4\)−\(^5\) to infrared\(^6\) and visible light.\(^7\)\(^8\) Plasmonic structures potentially exhibit strong enhancement and confinement of electromagnetic fields. These properties enable the fabrication of efficient optical elements with subwavelength dimensions featuring unique properties such as, for example, facilitating light confinement beyond the (far-field) diffraction limit determined by the light wavelength.\(^9\)

Plasmonic nanostructures with closely controlled sizes and geometries have long been recognized as a means to tailoring absorption spectra, by locally controlling resonator dimensions on which the resonance frequency depends. This has been utilized, among others, to create meta-surfaces acting as color filters and absorbers in transmission,\(^10\)−\(^16\) reflection,\(^17\)−\(^20\) and, more recently, for phase-critical optical elements, such as waveplates.\(^21\)−\(^23\) Using this approach, color printing at the diffraction limit has recently been demonstrated.\(^17\)

However, the practicality of previously reported approaches to plasmonic color printing is limited, among others, by several factors. Configurations that have significant dependence of positions of spectral features on periodicity\(^10\)−\(^14\),\(^16\),\(^19\) are expected to exhibit strong angular dependence, which is a major disadvantage for printing purposes, as colors are desired to be stable under variations in the viewing angle. Some configurations feature strongly polarization-dependent spectra,\(^10\),\(^16\) while others are not supposed to be covered with commonly available dielectrics, either due to the absorption mechanism being dependent on the contrast in the refractive index between vacuum and incorporated dielectric structures\(^17\) or due to large shifts of spectral features.\(^18\) While being of major advantage for sensing applications,\(^24\),\(^25\) surface sensitivity is an obvious disadvantage for printing and filtering applications where color stability is of paramount importance and application-specific mechanical protection layers may be desired. Finally, printing techniques utilizing complex structures do not easily transfer to large-scale production techniques, such as nanoimprint lithography.

In this work we develop plasmonic color printing with subwavelength resolution that is based on the metal–insulator–metal (MIM) configuration capable of supporting gap-surface plasmons (GSPs). The uppermost metal layer is lithographically structured in a one-step process to consist of two-dimensional (2D) square arrays of circular gold nanodiscs (NDs). If desired, the sample can be protected with a transparent dielectric overlay without significantly influencing resonances, providing the sample with the chemical and mechanical stability necessary for use in exposed ambient color printing applications such as, for example, security certificates. This important feature is a direct result of the GSP field distribution that is almost entirely contained within the MIM structure itself.

It is well established that the Fabry–Perot (FP) resonance condition for the fundamental mode of a circular GSP-based resonator of diameter \(D\) is\(^26\),\(^27\)

\[
\frac{2\pi}{\lambda} n_{\text{GSP}} = \pi - \phi
\]

where \(n_{\text{GSP}}\) is the effective mode index for the GSP, \(\lambda\) is the vacuum wavelength, and \(\phi\) is the phase acquired upon reflection at the boundary of the ND. The spectral position

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**Supporting Information**

* Alexander S. Roberts,*\(^\dag\) Anders Pors, Ole Albrektsen, and Sergey I. Bozhevolnyi*

Department of Technology and Innovation (ITI), University of Southern Denmark, Niels Bohrs Allé 1, DK-5230 Odense M, Denmark

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of the resonance can thereby be controlled by changing the diameter of the gold NDs. Note that material and geometric choices also influence the effective index and the reflection phase.26

The investigated samples consist of arrays of square unit cells of gold NDs, fabricated with EBL, on an insulator-on-metal structure consisting of continuous gold and SiO2-layers (Figure 1), deposited by electron beam (e-beam) evaporation of 100 nm gold and subsequent radio frequency (RF) Ar+-sputtering of an SiO2-insulator layer onto a Si-substrate. Adhesion layers are deposited by e-beam evaporation prior to each layer. The e-beam lithographic process of the top gold layer consists of spin-coating a 100 nm thick layer of positive tone 950 kDa PMMA resist onto the sample and exposing the design in a scanning electron microscope (SEM, model: JEOL JSM-6490LV) with an acceleration voltage of 30 kV, a working distance of 6 mm and an area dose of 350 μC/cm2. The writefield size is 100 × 100 μm2 with a step size of 2.0 nm. After exposure the resist is developed for 30 s in a 3:1 mixture of 2-propanol/methyl isobutyl ketone (MIBK) and subsequently rinsed in 2-propanol. Three nanometer titanium and 30 nm gold is then deposited by thermal evaporation, and lift-off is performed in a 10 h acetone bath without ultrasonic activation, yielding ND structures of which representative optical and SEM images can be seen in Figure 1b–d. The SEM images reveal arrays with well-defined circular discs and periodicity with a small amount of edge roughness while the optical images reveal a high degree of color homogeneity. In order to achieve independence of individual pixels it is necessary to minimize diffraction close to normal incidence. A subwavelength unit cell periodicity of 340 nm is chosen, with NDs ranging in diameter from 80 to 270 nm.

We characterize the reflection of the sample arrays by means of optical bright-field reflection spectroscopy in the visible range (400–800 nm). Reflection spectra are measured with an optical microscope (Olympus, BX-51 Research System) with halogen illumination through a ×50 objective (numerical aperture 0.75). Reflected light is collected by the objective and collimated by a pinhole allowing for definition of the circular area from which light is collected, and subsequently directed to a fiber-coupled spectrometer (Ocean Optics QE65000), with sensitivity in the visible and near-infrared. Reflection spectra measured on the samples are normalized against the reflection (Rref) of the homogeneous MI-surface, i.e., before the fabrication of gold ND-arrays. It has previously been established that the geometry chosen in the present work does not exhibit polarization dependence.27 Size measurements, geometry, and quality inspection are performed in-system on the SEM used for fabrication.

We produce quadratic gold ND arrays with a periodicity of 340 nm and disc diameters that increase from bottom to top, as seen in Figure 2a. The ND arrays are produced on samples with SiO2 spacer layer thicknesses of 20 nm (Figure 2a, left) and 50 nm (Figure 2a, right). All array geometries exhibit bright colors. CCD images are captured with a ×20 objective and a color average over a square area of 10 × 10 μm2 is performed, the result of which is seen in Figure 2a. The arrays on 20 nm SiO2 are examined in bright-field reflection spectroscopy, as described above, yielding the selection of spectra shown in Figure 2b. We perform finite-element simulations of the

![Figure 1](image1.png)

**Figure 1.** (a) Schematic views of the 340 nm unit cell of a rectangular array of circular gold NDs and continuous gold layer (yellow) and SiO2 layer (blue) forming a MIM structure. (b–d) Example SEM images of NDs with average sizes of 80, 120, and 270 nm, respectively. Insets: Optical reflection microscopy images of the entire 27 × 27 μm2 arrays. It is seen that the colors produced are visually highly uniform. Edge roughness can be seen on several gold NDs. Scale bars: 250 nm (b–d).

![Figure 2](image2.png)

**Figure 2.** (a) Colors of rectangular arrays of gold CL-GPR arrays fabricated on an MI-structure with a 20 nm (left) and 50 nm (right) SiO2 insulator layer against the color of the MI-surface itself. Colors used for color printing (Figure 3a) are marked with dotted boxes and correspond to ND diameters of 80, 120, and 270 nm. (b) Reflection spectra from NDs with increasing diameters on 20 nm SiO2, collected with a ×50 objective (NA = 0.75) and normalized against the reflection from SiO2-on-gold. (c) Finite-element simulation of the reflection spectrum normalized against the SiO2-on-gold surface, shown for SiO2 thicknesses 20 and 25 nm. Inset: Electric field enhancement normalized against the incoming field amplitude for a 120 nm ND illuminated at its first order FP resonance at 780 nm.
reflection spectra of ND arrays in COMSOL Multiphysics, with a Floquet-bounded unit cell and plane wave, normal incidence. The simulated spectra (Figure 2c) are normalized against the analytically calculated reflection of the SiO2-on-gold surface. We use interpolated optical properties from tabular values for gold. For the gold nanodiscs we multiply the imaginary part of the dielectric function with a factor of 4, so as to take into account the increased grain boundary and surface effects for thin films and the additional losses due to the titanium layer. The influence of different factors multiplied onto the imaginary part of the dielectric function can be seen in Figure S1 in the Supporting Information. The dielectric indexes used for SiO2 and air are \( n_{SiO2} = 1.45 \) and \( n_{air} = 1 \), respectively.

For the practical usability of the proposed plasmonic color printing, a weak angular dependence of the reflection spectra is necessary. Furthermore, spectra collected as described above are the result of weighted average of the response of the structures at the incidence angles in question (angles up to 49° in Figure 2b). We have performed finite-element simulations of the reflection spectra for varied angles of incidence (Figure S2 in the Supporting Information) and optical measurements with different magnifications (Figure S3), both showing that the influence of incidence angle is indeed negligible.

All measured reflection spectra (Figure 2b) exhibit at least one of two distinct absorption features. One absorption feature occurs at 610 nm for 80 nm diameter discs. This dip in reflectance red-shifts almost linearly with regard to the disc diameter and has a near constant fwhm width of approximately 110 nm, which is consistent with a FP type resonance. Simulations of the electric field distribution support this assumption regarding the resonance type (Figure 2c, inset). Returning to Figure 2b, it can furthermore be seen that the resonant absorption increases rapidly for disc diameters up to approximately 120 nm, after which it is saturating and red-shifting out of the visible part of the spectrum. For small diameters, the increase in absorption for increasing diameters can simply be related to an increase in the filling factor, i.e., to an increase of the ND area resulting in stronger absorption by a unit cell. At larger diameters, however, the GSP excitation efficiency becomes weaker due to stronger overlap of neighboring GSP mode fields, resulting in a reduced cross-section per GPR. A second absorption feature, located at 500 nm wavelength, exhibits a fundamentally different behavior: this absorption is very broad and its location is insensitive to the GPR diameter. The absorption strength is weak for discs up to 120 nm in diameter but grows in strength with growing disc size. For disc diameters up to 220 nm, the position of the feature is largely constant, while spectra obtained from the two largest discs show an additional higher order mode located at a wavelength of 540 nm for \( D = 270 \) nm diameter GPRs. The invariance of the spectral position to \( D \) and the position of the absorption feature indicate nonresonant absorption, due to the interband-transitions in gold at short visible wavelengths, leading to increased skin depth and nonresonant Ohmic losses within the gold. Below 450 nm the reflection increases for decreasing diameter, presumably the result of scattering on the ND surface and edge irregularities acting as Rayleigh scatterers with a scattering cross-section that scales with \( k^2 \), where \( k = 2\pi/\lambda \) is the vacuum wavenumber. As is immediately clear from the spectra, the GSP-based absorption feature lies outside the visible spectrum for \( D > 150 \) nm, making nonresonant Ohmic absorption the fundamental feature determining the color of the largest disc arrays. With higher resolution of fabrication, however, eq 1 allows for resonant absorption in a larger part of the spectrum. The decreasing absorption strength of the resonance (with decreasing diameter) can readily be compensated for by increasing the number of NDs per unit cell.

Comparison of the simulated and measured spectra gives qualitatively good correspondence (Figure 2b,c). One should keep in mind that ND edge and surface irregularities are not included in the simulations, and therefore, the steep increase in the reflection at low wavelengths cannot be expected to show in the simulated spectra. However, quantitative analysis reveals that the position of the simulated resonance features are red-shifted by 50 nm with regard to the observed spectra. This is presumably due to inaccuracies in the thickness of the RF-
sputtered SiO₂ layers. The effect of changing the spacer layer thickness on the effective refractive index is demonstrated in Figure 2c, where simulations of the reflection spectra have been performed for an SiO₂ thickness of 25 nm for otherwise equal parameters. Finally, the adhesion layers of 3 nm titanium, which are not included in the finite-element simulation, potentially contribute to further deviation from measured reflection spectra.

To demonstrate the suitability of the presented technique for use in color prints and related applications, we prepare a colored bitmap of the University of Southern Denmark logo with a resolution of 287 × 290 pixels. Each pixel is represented by a quadratic unit cell with 340 nm periodicity, yielding an exposure pattern approximately 98 × 99 μm in size (Figure 3). Color pixels are represented by a unit cell comprising one ND (Figure 3d), while black pixels are represented by a composite unit cell containing four NDs of two different sizes (Figure 3e), drawing inspiration from previous work.²⁷ We chose colors that correspond to disc diameters of 80, 120, and 270 nm (Figure 2a). For each pixel the most appropriate disc size and geometry is found by matching the desired pixel color with the three chosen colors, using a computerized script.

The fabrication steps are as described above for periodic square arrays. The resulting print is displayed in Figure 3. The optical image (Figure 3a) reveals a high quality color print with several desirable properties. First, the colors are bright and stand out well against each other and the background due to high color saturation. Second, colored areas exhibit a high contrast in refractive indexes at the Au/PMMA interface, resulting in a larger part of the entire visible spectrum, while at the same time increasing the absorption in the long wavelength range and colors with very high saturation, in this case yielding a dark blue.

Figure 4. Optical microscopy images (×50 magnification, NA = 0.75) comparing an uncovered color print (left) and the same print (right) after covering the sample with 100 nm of PMMA. It is seen that while the PMMA layer does have an influence on the perceived colors, color printing is still very much feasible, mainly influencing the red content of the image. Inset (left): The unit cells used for printing the green leaf is exchanged with a unit cell of double periodicity (170 nm) and equal nominal disc diameter. Scale bar: 10 μm.

The flexibility in terms of unit cell geometry is demonstrated in the inset of Figure 4, where we have used a periodicity of 170 nm instead of 340 nm, which leads to highly increased absorption in the long wavelength range and colors with very high saturation, in this case yielding a dark blue.

To demonstrate how this color printing procedure can be passivated for ambient use, opening the door towards practical applications, we mechanically and chemically protect the sample by spin-coating a 100 nm thick PMMA layer, using the EBL recipe described above. Figure 4 shows a direct comparison between an uncoated sample (left) and the resulting PMMA-coated sample (right). The extra layer of PMMA does have limited influence on the resulting colors, effectively reducing the red content of all the colors. This is due to weakening of the nonresonant absorption caused by a lower contrast in refractive indexes at the Au/PMMA interface compared to an Au/air interface, resulting in a larger part of the field situated in the (near lossless) dielectric. It should be noted that the resonant behavior is largely unchanged and that both sample geometry and color values were originally designed for use in air. It should therefore be possible to achieve better color production by designing the GSP structures specifically for use with PMMA coverage.

Several improvements to the geometry can be made. The influence of the dielectric protection layer can be further minimized by using NDs with increased film thickness and thereby confining the GSP modes within the intermediate dielectric to an even larger extent. Furthermore, the use of smaller discs in smaller unit cells (which can be achieved with thinner spacer layers) would also increase the GSP mode confinement and could make the FP resonances available in the entire visible spectrum, while at the same time increasing the angle at which diffraction begins to occur. A rough estimate using eq 1 for the spacer thickness of 15 nm, gives the range of ND diameters with first order FP resonances in the visible regime as approximately 45 nm < D < 155 nm, which is well within the resolution range of current EBL and NIL procedures. This would allow a reduction in unit cell size to roughly 200 nm, further reducing the influence of diffraction and allowing for wider viewing angles.

We would like to point out that the color printing demonstrated above is very well suited for practical applications, such as security marking, as several requirements are simultaneously met. The design is flexible and can easily be reprogrammed, while fabrication incorporates expensive and specialized equipment (as well as knowledge). Furthermore, the print can readily be inspected with standard low-magnification microscopes while being small enough to hide from plain view. Finally, the security stamp should be stable under mechanical and chemical influence from the environment. As demonstrated, a transparent dielectric cover layer provides aforementioned protection, with negligible influence on the plasmonic resonances.

Summarizing, we have demonstrated that, using continuous-layer gap surface plasmon resonators, in which only the top layer is structured, it is possible to produce clear color prints with subwavelength resolution that exhibit low dependence on incidence angle and surface coverage (by dielectric materials). We demonstrate this by fabricating effectively an MIM structure that to a large extent produces the same colors as the uncovered (MIM) sample. Furthermore, it should be noted that the developed approach can easily be implemented using fabrication with scalable techniques, such as nanoimprint lithography.
ASSOCIATED CONTENT

Supporting Information
Finite element simulations and reflection spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors
* (A.S.R.) E-mail: asro@iti.sdu.dk.
* (S.I.B.) E-mail: seib@iti.sdu.dk.

Notes
The authors declare no competing financial interest.

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