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Fabrication and characterization of three-dimensional copper metallodielectric photonic crystals

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Abstract: Three-dimensional metallodielectric photonic crystals were created by fabricating a micron-scale polymeric template using multi-photon direct laser writing (DLW) in SU-8 and conformally and selectively coating the template with copper (Cu) via nanoparticle-nucleated electroless metallization. This process deposits a uniform metal coating, even deep within a lattice, because it is not directional like sputter-coating or evaporative deposition. Infrared reflectance spectra show that upon metallization the optical behavior transitions fully from a dielectric photonic crystal to that of a metal photonic crystal (MPC). After depositing 50 nm of Cu, the MPCs exhibit a strong plasmonic stop band having reflectance greater than 80% across the measured part of the band and reaching as high as 95% at some wavelengths. Numerical simulations match remarkably well with the experimental data and predict all dominant features observed in the reflectance measurements, showing that the MPCs are structurally well formed. These data show that the Cu-based process can be used to create high performance MPCs and devices that are difficult or impossible to fabricate by other means.

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1. Introduction

Three-dimensional (3D) metal photonic crystals (MPCs) can exhibit intriguing electromagnetic properties such as ultra-wide photonic [1-5] or “plasmonic” [6-8] band gaps, selectively tailored thermal emission [9-11], extrinsically modified absorption [4], and negative refractive index [12]. Yet, visible and infrared (IR) wavelength 3D MPCs remain relatively unexplored due to the challenges posed by their fabrication. Optical wavelength MPCs have been created using planar semiconductor fabrication techniques coupled with vapor- and liquid-phase metallization [4,9]; sputtering gold (Au) or electro-plating nickel (Ni) onto polymeric photonic crystals (PCs) created by soft-lithography [5]; and infiltrating self-assembled PCs with metal [13,14]. These approaches have enabled pioneering explorations of MPCs, yet each is limited in its potential to extend development of MPCs for reasons that include: involving complex multi-layer patterning, layer-bonding, and planarization steps; requiring expensive lithographic equipment; restricting fabrication to a finite number of accessible crystal geometries; and not offering a direct means for including non-periodic functional defects. Among these, the last is particularly significant in that it limits the scope for incorporating MPCs into integrated photonic devices.

MPCs hold great promise for integrated photonics precisely because photons interact much more strongly with metals than with dielectrics. Devices may be designed with far fewer lattice periods so functional elements may be miniaturized or packed more densely. This approach, however, requires a fabrication methodology that can form arbitrarily shaped microscale metallic structures over large areas.

We [15-17] and others [18-20] have shown that multi-photon direct laser writing (DLW) coupled with electroless metallization is a promising technology for fabricating optical devices composed of metallodielectric structures. Free-standing, 3D photonic crystals (PCs) having virtually any geometry can be directly patterned in a single serial [21] or parallel [19] photo-patterning step onto a range of substrates. DLW can be implemented using relatively simple, commercially available instrumentation. Electroless metallization can then be used to deposit a wide range of metals onto the polymeric template using low-cost processes. As such, the method appears to provide a route to arbitrarily shaped 3D metallodielectric metamaterials [22], which are known to have intriguing and potentially useful optical properties, but are difficult to fabricate by other means.

Yet with only a few exceptions [16,20], previous accounts of this approach were limited to demonstrating the fabrication process and did not report the optical properties of the materials or explore how the processing conditions relate to the structure and resulting optical properties and performance. Additionally, most of these accounts reported processes based on fabricating the polymeric pre-forms by DLW in cross-linkable acrylates. Acrylates are poor materials for micro-fabrication because they shrink substantially when processed [23], compromising structural form, integrity, and adhesion to a supporting substrate. In contrast, the cross-linkable epoxide SU-8 is much better suited for fabricating micro- and nanophotonic structures and devices because it shrinks less upon polymerization (< 10%) [24]. We are aware of one report in which SU-8 was used to prepare an MPC perform [20]. In this case, the metallodielectric structure was obtained by electrolessly depositing Ni, but the metal deposition was non-uniform and non-selective. As a result the optical properties were poor, with the MPCs exhibiting no more than 65% reflectance in the stop band region (more typically 40–50%), and the experimental reflectance did not agree well with numerical simulations.

In the present work we describe a new materials process for creating functional copper (Cu) metallodielectric photonic structures [25]. Our method combines DLW in SU-8 [21,26] with an approach for electroless deposition of Cu [18] that was modified to make it...
compatible with this polymer system. 3D templates were first prepared by DLW in SU-8 and then conformally coated with Cu by electroless deposition nucleated by surface-bound Au nanoparticles (Au-NPs). We demonstrate that the process selectively deposits Cu onto the SU-8 pre-form leaving the supporting substrate unmetallized. This feature makes the present method satisfactory for creating functional devices and integrated photonic structures, unlike non-selective routes [20]. We characterize the IR reflectance of the resulting metallodielectric structures and show that they behave like MPCs, exhibiting reflectance of ≥ 80% within the plasmonic stop band region and reaching as high as 95% at some wavelengths. Numerical simulations are presented and shown to compare remarkably well to the experimental measurements, which indicates that the fabrication process yields well-formed MPC structures. Finally, we provide insight into how the optical properties change during metallization and how the process can be used to achieve targeted metallodielectric properties. The latter point is particularly significant in that optical fabrication processes cannot become widely applied until there is deep understanding of how the properties and performance relate to the processing conditions and the resulting micro- and nano-scale structure.

2. Experimental
Polymeric PCs like those shown in Figs. 1(a)–(c) were fabricated onto cleaned coverslips by multi-photon DLW in thick films of an SU-8 based pre-polymer. DLW using SU-8 has been described by us and others previously [21,26]. An adhesion layer was applied by immersing the coverslips into 5 vol-% 3-glycidoxypropyl-trimethoxysilane (98%, CAS# 2530-83-8) in methanol for 24 hours at room temperature, rinsing with methanol, and drying for one hour at 100 ºC. The SU-8 pre-polymer consisted of 100 mg isopropylthioxanthone (ITX, CAS# 81-88-9, Aldrich) dissolved in 2.7 g of SU-8 2035 (MicroChem, 70–80 wt-% SU-8 in cyclopentanone and propylene carbonate). SU-8 2035 contains 3.4 wt-% of two triarylsulfonium photo-acid generators (PAGs, CAS# 89452-37-9 and 71449-78-0) that are the photo-initiators. ITX is a PAG sensitizer added to improve multi-photon sensitivity [27]. The pre-polymer was spin-coated onto adhesion-promoted coverslips (30 s at 2000 rpm) and baked to remove solvent (95 ºC, 30 min.) giving ~50 μm thick solid films. The SU-8 coated coverslips were mounted on a three-axis nanopositioner affixed to a microscope (Nikon TE2000-U). Photo-acid was generated in tightly confined 3D volumes within the sample by focusing the output of a mode-locked Ti:sapphire laser (Coherent-Mira, 800-nm center wavelength, 120 fs pulse duration, 76 MHz rep. rate) through the coverslip and into the pre-polymer film using a 60×/1.4 numerical aperture (NA) oil-immersion lens. The laser light was routed through a shutter and half-wave plate/polarizer combination to adjust the average power delivered to the sample (1–10 mW). To pattern the exposure, the sample was translated relative to the focal spot at 50 μm s⁻¹ as the shutter, attenuator, and nanopositioner were synchronously controlled from a microcomputer. Following exposure, samples were baked to activate cross-linking (95 ºC, 15 min.), immersed in propylene glycol methyl ether acetate to remove unexposed resin, rinsed with isopropyl alcohol, dried in air, then hard-baked (150 ºC, 15 min.), leaving a free-standing micro-structure remaining on the substrate.

Metallized PCs like those shown in Figs. 1(d)–(f) were created by: (a) functionalizing the surface of the polymeric micro-structure with alkylamino groups; (b) synthesizing Au-NPs at the aminated sites; and (c) depositing Cu onto the primed scaffold by immersing the sample into a Cu electroless deposition bath for a fixed period. Prior to metallization, SU-8 PCs were subjected to a 30 s O₂ plasma etch (100 mTorr, 35 cm³ min⁻¹, 100 W RF, 200 V DC bias) to remove organic residues adsorbed onto the substrate. This important step increases the selectivity of Cu deposition onto the micro-structure versus the substrate. The micro-structure surface was then aminated by immersing into 20 vol-% 1,2-diaminoethane (Acros, CAS# 107-15-3) in ethanol for two hours and rinsing with ethanol. Bis-amino-terminated n-alkanes were chosen for functionalizing the surface on the basis that one amino group could bind covalently via nucleophilic attack at unreacted epoxide groups, leaving the second amino group available for coordinating Au-NPs. Au-NPs were synthesized directly at the surface by immersing an aminated sample in 5.3 × 10⁻⁴ M HAuCl₄(aq) for 2 hrs, rinsing with water, immersing in
0.1 M NaBH₄(aq) for 120 s to reduce bound Au(III), then rinsing with water and drying in air. The Cu plating bath was prepared by dissolving 0.75 g of copper sulfate, 1 g of sodium hydroxide, and 3.5 g of sodium potassium tartrate in 25 mL of water. Immediately prior to use, the solution was filtered and 2.5 mL of aqueous formaldehyde (37%) were added with stirring [18]. Cu was deposited by immersing a Au-NP-functionalized structure into a fresh Cu bath at room temperature for 30–570 s, depending upon the desired metal layer thickness. Samples were then removed from the bath, rinsed with water, and dried in air.

Fig. 1. SEM images of SU-8 polymeric "stack-of-logs" PCs before (a–c) and after (d–f) Cu plating. The PCs were designed to have FCT symmetry and unit cell parameters \( b = a \sqrt{2} = 3.54 \mu m \) and \( c = 3.60 \mu m \), where \( a \) and \( c/4 \) are the center-to-center horizontal and vertical log-spacing, respectively. The conventional FCT unit cell is outlined in (b) with a white square of edge length \( b \). a, d) Perspective views of the PCs. b, e) Top views, looking along the <001> axis (normal to substrate). c, f) Side views, looking along the <110> axis (parallel to substrate). g) Energy dispersive x-ray (EDX) spectrum of a Cu-plated PC.

Uniform SU-8 thin films were prepared by spin coating pre-polymer onto coverslips, cross-linking by broad-band UV irradiation and post-exposure bake, then Cu coating as described above. Cu layer thickness was determined by applying micro-droplets of
concentrated nitric acid to the surface to etch sub-millimeter-wide pinholes in the Cu layer and then measuring the pinhole depth by stylus profilometry (Tencor Alpha Step 200).

The reflectance of electrolessly deposited Cu was compared against that of a uniform thick Cu film prepared using a physical vapor deposition system (AJA International). The Cu metal was vapor deposited to a thickness of 150 nm onto a silicon substrate using two guns (99.995% purity) at 200 W DC power for 280 s under an argon atmosphere (20 sccm, 4 × 10⁻³ Torr). The physically deposited Cu film was stored under an inert atmosphere of nitrogen.

The IR reflectance of PCs and uniform films was measured under ambient atmosphere using a Fourier-transform infrared (FTIR) spectrometer coupled to a microscope (Perkin Elmer Spectrum One, 4 cm⁻¹ resolution). IR radiation was focused onto and collected from the sample using a 0.6 NA Cassegrain objective whose optical axis was parallel to the <001> axis of the PC. A field-stop situated before the objective was adjusted to match the size of the PCs. The Cassegrain optic illuminated the sample with a hollow cone of light having inner and outer cone-angles of 16° and 32°, respectively. The reflectance was referenced to a Au mirror. Optical transmission at visible and near-IR wavelengths was measured using an Agilent 8453 spectrophotometer.

Reflectance was simulated using a newly developed Slice Absorption Method (SAM) shown to be highly accurate and efficient for modeling periodic structures with high volumetric complexity [28]. This method breaks large problems down into slices composed of a single layer of grid cells in a manner that retains only a few slices in memory at any given time. Adjacent slices are connected using simple matrix algebra rather than eigen-system computations and scattering matrices, so the SAM scales more favorably than other computational methods. A Fourier-space SAM was used to model the purely dielectric photonic crystals, while a real-space SAM was used for the metallodielectric devices. To fully benefit from the SAM, a realistic lattice geometry was incorporated into the simulations by modeling the multi-photon DLW process [29,30] and comparing to SEM images like those obtained in Figs. 1(a)–(c). The refractive index of the polymer was taken to be \( n = 1.56 \pm 0.009 \) [31]. Because the experimental reflectivity of the electrolessly deposited Cu was found to be high, the metallized PCs were modeled using literature values of the complex permittivity for bulk Cu [32]. To model the sample being interrogated by a Cassegrain optic, total reflectance was computed by integrating the zero-order reflectance of circularly polarized light over the full range of incidence angles produced by this optical system. Due to symmetry, these angles were restricted to \( 16° \leq \theta \leq 32° \) and \( 0° \leq \phi \leq 45° \) where \( \theta \) represents elevation angle and \( \phi \) the azimuth angle.

3. Results and discussion

3.1. Metallization process

Uniform SU-8 thin films were used to optimize the Cu plating process and characterize the physical properties of the electrolessly deposited metal. Figure 2(a) shows how the metal layer thickness increased versus total Cu bath immersion time. Under the conditions used, Cu deposition proceeded at an average rate of approximately 0.15 nm s⁻¹ with no apparent initial induction period. A 90 nm thick film was obtained after an immersion time of 570 s. At this point, the rate of deposition is only marginally decreased, which indicates that thicker Cu layers could be obtained with longer immersion times. The mid-IR reflectance was monitored versus film thickness at a vacuum wavelength of \( \lambda_0 = 3.5 \mu m \). The reflectance increased rapidly and exceeded 95% for Cu layers thicker than 50 nm (> 180 s bath immersion time). This is comparable to the optical skin depth of bulk Cu (~22 nm at \( \lambda_0 = 3.5 \mu m \)) [33]. Figure 2(b) shows the reflectance measured at \( \lambda_0 = 0.2–22 \mu m \) for a pristine SU-8 film, one that was electrolessly Cu plated for 180 s, and a 150 nm thick film of Cu that was physically deposited onto a silicon substrate. The electrolessly deposited Cu increases the reflectance of an SU-8 film to greater than 80% for \( \lambda_0 > 700 \) nm, and it is greater than 90% across the mid-IR region. The reflectance decreases sharply at \( \lambda_0 = 650 \) nm and remains low across much of the visible spectrum, consistent with the orange-red reflectance characteristic of bulk Cu [34]. The reflectance spectra of the physically and electrolessly deposited Cu films are similar in
shape, although the absolute reflectance of the electrolessly deposited Cu is lower at all wavelengths. Four-point probe measurements indicate that the deposited Cu had a DC conductivity of $\sigma_0 = 2.6 \times 10^7 \, \Omega^{-1} \, \text{m}^{-1}$, which is $\sim 45\%$ that of bulk Cu [35].

The electromagnetic characteristics can be expected to depend on the nanoscale morphology of the electrolessly deposited metal [36,37]. The surface morphology was characterized by AFM and found to consist of densely packed pseudo-spherical grains having diameters of 50 nm or less and a root-mean-squared surface roughness of 15 nm. This morphology implies a large number of grain boundaries in the conduction path and may explain why the plated Cu is less conductive than bulk Cu. The nanoscale roughness will also increase diffuse scatter and intrinsic losses causing the optical reflectance to be somewhat lower than that of bulk Cu, as observed. Nonetheless, the data show that this process deposits Cu having high reflectance and conductivity comparable to that of the bulk metal [34].

![Graph](image1.png)

**Fig. 2.** a) Metal layer thickness and reflectivity of an SU-8 thin film at $\lambda_0 = 3.5 \, \mu\text{m}$ versus Cu bath immersion time. The uncertainty in the measured reflectivity and thickness are $\pm 3\%$ and $\pm 15$ nm, respectively. b) Spectral reflectivity of physical vapor deposited Cu (150 nm thickness) and an SU-8 thin film before and after 180 s of electroless Cu plating.

### 3.2. Photonic crystal fabrication

All micro-structures discussed here are face-centered-tetragonal (FCT) “stack-of-logs” PCs [38], as in Fig. 1. The PCs consist of parallel logs spaced center-to-center within a layer by $a$. Logs in adjacent layers are oriented perpendicularly and spaced vertically by $c/4$. Logs in alternate layers are parallel, but offset laterally by $a/2$. The resulting structures have FCT symmetry with a two-crossed-log basis and a unit cell base-length and height equal to $b = a\sqrt{2}$ and $c$, respectively. The PCs in Fig. 1 were designed to have 62.5 $\mu$m long logs, $b = 3.54 \, \mu\text{m}$ ($a = 2.50 \, \mu\text{m}$), $c = 3.60 \, \mu\text{m}$, and a total height corresponding to six complete unit cells. Close inspection of Figs. 1(a)–(c) reveals the resulting PCs have actual dimensions within $9\%$ of design parameters, indicating they are well formed and highly ordered. The constituent logs have an ellipsoidal cross-section (Fig. 1(c)) that results from the shape of the polymerized volume element or “voxel” generated by multi-photon DLW [21]. For the conditions used here, the voxel had transverse and vertical dimensions of 0.6 $\mu\text{m}$ and 1.80 $\mu\text{m}$, respectively, resulting in a PC volumetric fill factor of $\sim 0.3$.

Polymeric PCs were metallized using a Cu bath immersion time of 180 s, generating the structures shown in Figs. 1(d)–(f). This plating time was chosen to achieve a metal layer thickness of $\sim 50$ nm, which based on the data of Fig. 2 appears to be close to the apparent optical skin depth for this morphology of Cu. Comparison of Figs. 1(a)–(c) and 1(d)–(f) shows the metallized PCs retain the uniformity and structural fidelity of the polymeric scaffolds. Moreover, close inspection of Figs. 1(e)–(f) reveals the process conformally deposits Cu throughout the entire structure, even deep within the lattice. The energy dispersive X-ray (EDX) spectrum of the metallized PC (Fig. 1(g)) consists of a dominant peak at 0.93 keV and a smaller peak at 8.04 keV. These energies are characteristic of Cu [39] and confirm that the lattice surface is metallized. The absence of significant deposition on the
substrate (Fig. 1(d)) indicates that the process is truly selective toward Cu plating the polymer surface. This stands in contrast to the Ni-based approach [20], for which metal deposited on both the polymeric template and the substrate, making it unsuitable for fabrication of integrated metallodielectric devices.

3.3. Photonic crystal characterization

As Cu deposits onto the polymeric lattices, the structures transition from purely dielectric PCs to metallodielectric meta-materials. This transition was characterized by monitoring the visible and mid-IR reflectance of PCs of the type shown in Figs. 1(a)–(c) at various stages throughout the metallization process. These data are compiled in Fig. 3. Figures 3(a)–(d) are optical microscopy reflection images recorded while viewing along the PC <001> direction. Figures 3(e)–(f) are corresponding IR spectra that were also recorded with the PC oriented such that its <001> axis was parallel to the optical axis of the illuminating/collecting Cassegrain objective.

![Image](https://via.placeholder.com/150)

Fig. 3. a) - d) Optical reflection microscopy images of SU-8 PCs (same type as in Figs. 1(a)–(c)) at subsequent stages of the Cu deposition process. The scale bars correspond to 20 μm. e) and f) FTIR reflection spectra of PCs at various stages of Cu deposition. The spectra in (e) are offset vertically from one another by 10%. Those shown in (f) are superimposed (same reflectance scale), but plotted on an expanded wavelength scale.

The FTIR spectrum of the pristine SU-8 PC consists of weak reflection peaks (< 20%) and a stronger reflection band approaching 60% centered at λ₀ = 4.30 μm. In interpreting these features, it is helpful to compare the spectrum to that obtained from a uniform SU-8 film (Fig. 2(b)). The weak features, particularly those at λ₀ > 8 μm, can be assigned as intrinsic absorptions due to vibrational normal modes of the polymer. In contrast, the strong reflectance at λ₀ = 4.30 μm is not seen in the uniform film spectrum, and can be assigned as a photonic stop-band resulting from the micron-scale periodicity of the PC. Consistent with theory, the stop-band center-wavelength is comparable to the dimensions of the unit cell [31,40]. The stop-band is spectrally narrow (0.5 μm full-width at half-maximum, FWHM), mainly because the refractive index contrast of the polymeric lattice versus air is small (Δn = 0.6). Additionally, the peak reflectance is this high because of the large number...
of unit cells in the \(c\)-direction and the structural uniformity of the lattice. The simulated spectral reflectance of the PC (Fig. 3(f)) is in excellent agreement with the experimental measurement. These findings are consistent with other previously reported experimental observations and theory for polymeric PCs [31,41].

The SU-8 uniform films and PCs do not absorb at visible wavelengths, so pristine and plasma etched polymeric PCs appear faint and colorless in optical reflection (Fig. 3(a)). Optical and scanning electron microscopy (SEM) imaging show that the brief plasma etch does not compromise the structural integrity of the PCs. Consistent with this claim, the FTIR spectra of etched and pre-etched PCs are nearly indistinguishable.

At visible wavelengths, uniform films and PCs take on a pink-red hue when functionalized with Au-NPs (Fig. 3(b)). This coloration is caused by scatter and absorption due to Au-NP plasmon resonance, which peaks near \(\lambda_0 = 520\) nm for spherical particles of \(\sim 20\) nm diameter or less [42]. Plasmon resonance near this wavelength was confirmed by visible transmission spectroscopy for Au-NP functionalized films. Binding Au-NPs to the PCs red-shifts the stop-band to 4.46 \(\mu\)m and slightly decreases the reflectance without changing the stop-band width (Fig. 3(c)). Such changes were consistently observed in repeated experiments, although the magnitude of red-shift varied between samples. The red-shift is thought to result because highly polarizable NPs increase the effective refractive index of the PC lattice. The decrease in stop-band reflectance may be due to increased scatter and absorption from the NPs at the lattice resonance.

After 60 s of Cu deposition, uniform films and PCs take on a green-purple hue with metallic reflectance (Fig. 3(c)). In the mid-IR, the stop-band red-shifts further to 4.68 \(\mu\)m, decreases in reflectance to 30%, and broadens to a FWHM of 0.58 \(\mu\)m. The weak reflection peaks within \(\lambda_0 = 8\)–15 \(\mu\)m broaden and decrease in intensity, presumably because the incident field interacts only weakly with the underlying polymer.

Following 120 s total Cu deposition, uniform films and PCs (Fig. 3(d)) exhibit the familiar orange-red reflectance of bulk Cu, approaching that in Fig. 2(b). In the mid-IR spectrum, the narrow stop-band is now absent and in its place we see an abrupt transition from low (< 15%) to high average reflectance (~30%). With further Cu deposition, the transition near \(\lambda_0 = 4\) \(\mu\)m continues to sharpen. Concomitantly, the average reflectance increases at wavelengths longer than the transition, peaking at 75% near \(\lambda_0 = 6\) \(\mu\)m after 360 s of Cu plating. The data of Figs. 2 and 3(e) suggest that plating times of 180 s and longer generate a Cu layer that exceeds the mid-IR optical skin depth, so IR radiation interacts with these thickly Cu-coated PCs as though they were pure metal structures. This observation was also confirmed by simulation. Consistent with this interpretation, mid-IR features associated with the underlying SU-8 scaffold are absent from the reflectance spectra. For \(\lambda_0 > 7.0\) \(\mu\)m, the reflectance oscillates increasingly with wavelength. This feature vanishes, however, when the lateral size of the PCs is increased. For example, the black curve in Fig. 4 shows the IR reflectance recorded for a PC having the same symmetry and unit cell dimensions as those associated with Fig. 3, but with the base area enlarged from \((62.5\ \mu\m)^2\) to \((250\ \mu\m)^2\). The modulations are nearly absent for large-area PCs, and in its place we observe a spectrally flat, high reflectance. It can be concluded then that because the PCs have finite area, each acts as a small diffractive aperture, introducing modulations in the reflectance spectra that are more prominent when their lateral dimensions are comparable to the mid-IR probe wavelengths [43].

The mid-IR properties observed for thickly Cu-coated PCs are consistent with the formation of MPCs. Characteristically, MPCs comprised of unbroken logs are highly reflective across a broad spectral region that extends, in theory, from infinite wavelength down to a cut-off comparable to and determined by the lattice geometry [3-5,7]. Some investigators have referred to the long-wavelength reflective region as a “plasmonic band-gap”, in direct analogy with pure metals [6-8]. Although the physical origin of this phenomenon continues to be a subject of investigation, we adopt such terminology here for simplicity. At wavelengths shorter than the plasmonic band-edge, MPCs exhibit a complex structure of multiple allowed and forbidden bands in which the reflectance alternates between low and high, respectively [4]. If the rapid transition in reflectance observed for the Cu-plated
PCs discussed here is due to a plasmonic band-edge, it should red-shift as the PC unit-cell is enlarged. Figure 4 presents the IR reflectance measured for a homologous series of Cu-plated PCs for which the unit-cell was progressively enlarged. We see that each of these PCs exhibits a plasmonic band-gap region, with multiple forbidden and allowed bands at higher energy. Importantly, the feature assigned as the plasmonic band-edge shifts to longer wavelength with increasing unit-cell size as expected.

3.4. Numerical simulation

Figure 4(b) shows the experimentally measured and simulated IR reflectance of the Cu-MPC designed for \( b = 5.90 \mu m \) and \( c = 6.00 \mu m \). The simulated and experimental data are in good agreement in several key respects. Both show high reflectance at long wavelengths which decreases rapidly in the region around the plasmonic band edge (~6.0 \( \mu m \)). Multiple forbidden and allowed bands are present beyond the band edge that modulate the reflectance from high to low with decreasing wavelength. Both spectra show two distinct stop bands near 3.2 \( \mu m \) and 4.7 \( \mu m \) for which the reflectance decreases at shorter wavelengths. Discrepancy between the simulated and experimental data is most likely due to non-periodic defects and distortions in the real lattice and metal coating that are not accounted for in the simulation. We note that for both the experimental and simulated spectra, the forbidden and allowed bands would be sharper and deeper in modulation if the MPC were probed with an idealized uniform plane wave, rather than illuminated with a Cassegrain optic, the latter of which averages the spectral response over a range of incident angles. The good agreement between the simulated and experimental reflectance indicates that the MPCs exhibit the optical behavior expected theoretically and are thus structurally uniform. In particular, the intended periodicity and lattice dimensions must be consistent throughout the interior of the 3D structure or the dominant reflectance peaks would be significantly broadened and/or absent altogether. The overall form of the experimental reflectance spectra (particularly the modulations around the plasmonic band edge) are similar to those reported by Fleming et al. for FCT tungsten MPCs created using a multi-step semiconductor fabrication process [4]. Collectively, the data confirm that the Cu-plated PCs behave optically like MPCs and the fabrication process reported here provides a route to MPCs and related metalodielectric photonic materials with controllable feature sizes and periodicity.

It is noteworthy that the large-area MPCs of Fig. 4 exhibit reflectance exceeding 80% across plasmonic stop band and reaching 95% at some wavelengths. These values approach the theoretical limit of 100% reflectance expected for a perfect-conductor MPC. The shortfall is likely due to intrinsic losses and diffuse scatter originating from the nanoscale roughness of the metal that is not captured by the Cassegrain optic. The performance of these...
Cu-MPCs greatly exceeds that of recently reported Ni-MPCs [20] created by DLW-electroless deposition. These Ni-MPCs exhibited peak reflectance of only 65% and more typically 40–50% across the plasmonic stop band. Reflectance modulations expected near the plasmonic band edge were not observed and numerical simulations only roughly predicted the position of the plasmonic band edge. SEM images of the Ni-MPCs show clearly that the metal coating did not deposit uniformly and there were regions where metal had either not deposited or had delaminated during processing. This non-uniformity may well account for the lower overall reflectance of these MPCs and differences between the experimental and simulated reflectance. Even perfectly formed Ni-MPCs would not be expected to perform as well as their Cu counterpart because the intrinsic losses at mid-IR wavelengths are higher for Ni [44]. Lastly, the reflectance spectra may have been compromised by the fact that the Ni deposition process used is non-selective, so Ni deposited on both the lattice and the underlying substrate. By comparison then, the Cu-based process discussed in this work provides a better route to high-performance functional MPCs.

4. Conclusion

We have developed a method for fabricating and modeling truly 3D Cu-coated microstructures based on electroless metallization of chemically functionalized SU-8 templates created by DLW. Experiments show this approach can be used to deposit sub-micron layers of Cu conformally throughout highly micro-porous 3D structures. The resulting Cu-coated structures are reflective and conducting, so the method can be used to create functional photonic, electronic, electro-mechanical and microfluidic structures. We show further that the approach can be used to transform conventional dielectric PCs into Cu-MPCs. As such, the method provides a flexible new route to novel metalldielectric structures, metallized photonic materials, and integrated devices having optical function in the mid- and near-IR region of the electromagnetic spectrum.

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