NEGATIVE INDEX MATERIALS

J. A. Rogers, D. Chanda, and co-workers use a nanotransfer printing technique to fabricate large-area visible 3D negative index metamaterials. Alternating silver and dielectric layers are printed over a large area on a flexible substrate, and deposition conditions are introduced such that nearly ideal geometries with excellent optical properties are obtained.
Materials Selections and Growth Conditions for Large-Area, Multilayered, Visible Negative Index Metamaterials Formed by Nanotransfer Printing

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Negative index metamaterials (NIMs) are engineered structures that exhibit negative permeability and permittivity. From early demonstrations in the microwave[1,2] and terahertz[3,4] regimes, to more recent work at optical wavelengths,[5-9] designs have evolved from split-ring and U-shaped resonators to metallic cut-wire pairs and dielectric-metal multilayers in open mesh (i.e. fishnet) layouts. This last geometry represents a multilayered construct that not only allows low loss operation at near infrared (NIR) and visible wavelengths, but is also compatible with large area fabrication strategies based on nanotransfer printing (nTP).[10] A critical step in this type of fabrication involves colloidal physical vapor deposition (PVD) of alternating layers of metals and dielectrics onto substrates with features of relief that define the fishnet layouts. Detailed mechanisms for film growth depend strongly on materials properties, such as surface mobility, sticking coefficient, crystallinity and grain structure[11,12] and on conditions for deposition, such as rate and base pressure. A behavior of particular relevance here is that the films grow often in a direction that is not entirely perpendicular to the patterned substrate surface (stamp), even for normally incident flux of material. As a result, angled sidewall profiles develop at the edges of deposits near features of relief on the substrate. Although such effects can be useful in the fabrication of silicon nanodome arrays,[13] Spindt-type field emitters,[14,15] nanocones of metals with sharp tips[16] and other related structures, they can be detrimental in the fabrication of metamaterials by nTP. For the case of NIMs that consist of multilayer stacks of silver (Ag)/magnesium fluoride (MgF₂) formed by nTP for operation in the NIR, the sidewall slopes are ∼6–12°[10] depending on deposition conditions. This value is comparable to or slightly larger than those observed in otherwise similar structures formed by traditional focused ion beam machining techniques.[8] This angle can be included explicitly in the design and modeling steps, to enable NIMs with excellent and predictable transmission values, with high figures-of-merit for near-IR operations.[9] For operation in the visible, however, the required dimensions of the openings in the fishnet structures can be as small as 200 nm.[17-19] As shown subsequently, in such cases, angular growth can lead to substantial or even complete elimination of the fishnet geometry at the top surfaces of the multilayer stacks. In the following, we explore aspects of PVD growth in previously reported materials for multilayered fishnet NIMs, and introduce alternative dielectrics and deposition conditions that enable nearly ideal geometries by nTP. Demonstrations include large-area, uniform NIMs with excellent characteristics in the visible range, along with modeling results that capture the key behaviors.

Figure 1 provides schematic illustrations of the key steps for fabricating multilayered NIMs by nTP, as implemented here. A silicon wafer with a square array of periodic holes (period, P, edge-to-edge separation, W, and depth, H) serves as a stamp which appears in Figure 1a. The schematic shows the top view of fishnet features of relief and the cross sectional view of this relief cut at the red dash line. Electron-beam evaporation forms multilayer stacks of metals and dielectrics (Figure 1b) on the top and bottom regions of relief, with negligible deposition on the sidewalls. Transfer of material from the top regions to a target substrate, here facilitated by a photocurable polymer as an adhesive, completes the process (Figure 1c). Previous multilayered fishnet NIMs formed by nTP exploited Ag as the metal and MgF₂ as the dielectric,[18] due to their favorable plasmonic properties and established uses in optical coatings, respectively. Although Ag deposited by electron-beam evaporation with a material flux collimated in a direction perpendicular to the substrate surface grows in a nearly vertical fashion, MgF₂ exhibits angular growth with columnar grain structure.[10] This latter behavior defines the overall growth profiles of the Ag/ MgF₂ multilayers. Figure 1b illustrates the key parameters: the angular profile of the growth, θ, and the characteristic widths at

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the bottom, \( W \), and top, \( W' \), of a multilayer stack with trapezoid height \( t \). The thickness, \( T \), corresponds to the distance from the base to the highest point on the top surface. The thickness-averaged value of \( \theta \) is, therefore, simply given by \( \tan \theta = \frac{W' - W}{2t} \). For purposes of fabricating fishnet NIMs by nTP, the ideal stack should have \( \theta = 0 \). All observations in real systems show \( \theta > 0 \), dominated by angular growth in the dielectric material. Figure 1d-f presents scanning electron microscope (SEM) images of cross sectional and top views of films and multilayers deposited onto silicon stamps with \( P = 300 \) nm. Figure 1d corresponds to single layer of \( MgF_2 \) with \( T \sim 300 \) nm, where angular growth is evident, i.e., \( W \sim 77\pm2 \) nm and \( W' \sim 228\pm6\) nm, \( t \sim 219\pm3 \) nm, with \( \theta \sim 19.1\pm0.6^\circ \). Similar studies indicate that \( \theta \) for \( Ag \) is close to zero.\(^{[10]}\) This behavior in angular growth of \( MgF_2 \) directly affects the geometry of multilayer stacks of \( Ag \) (35 nm) / \( MgF_2 \) (15 nm) (Figure 1e), where \( t \sim 224\pm3 \) nm, \( W \sim 117\pm3 \) nm, \( W' \sim 249 \pm 15 \) nm, and \( \theta \sim 15.3\pm1.6^\circ \). Here, the diameters \( (D) \) of the holes in the fishnet evaluated at the top surface of the deposited multilayers are smaller than the value set by the geometry of the stamp, i.e. \( \sim 220 \) nm, and exhibit a large variance, i.e. between 25 nm and 85 nm (Figure 1f). The values of \( \theta \), inferred from \( D \), \( t \) and the geometry of the stamp, lie within the range of 16^\circ-23^\circ which is somewhat larger, but comparable to, those determined from the cross sections. Although these effects can be manageable in fishnets with relatively large geometries for operation in the IR and NIR,\(^{[10]}\) they severely limit designs in the visible, where the period of the fishnet can be in the range of 300 nm or less. These dimensions derive from linear scaling between surface plasmon induced light transmission and structure period.\(^{[17-19]}\) For instance, the structures of Figure 1 have an optical transmission of less than \( \sim 1\% \) at a wavelength, \( \lambda = 650 \) nm, due mainly to small values of \( D \). Experiments show that control over physical collimation and other examined conditions associated with deposition offers only limited utility in reducing \( \theta \). In our setups, the source for evaporation has a diameter of \( \sim 2.5 \) cm, and the distance from source to sample is \( \sim 60 \) cm; for a sample size of \( \sim 2 \) cm placed perpendicular to the source, the incident material flux front has almost zero angular distribution over \( W \sim 117 \pm 3 \) nm linewidth. Further efforts to enhance the degree of collimation using tubes placed between the source and sample dramatically reduce the deposition rates, but without significant benefits in angular growth (Figure S1). Other techniques, such as ion beam assisted electron-beam deposition, also do not decrease \( \theta \) appreciably (Figure S2). (We note that \( \theta \) can depend slightly, although not significantly, on the geometry of the relief on the substrate. See Figure S3.) Other inorganic dielectrics with suitable optical properties, such as silica\(^{[14]}\) and alumina,\(^{[17,18]}\) exhibit similar
Al₂O₃ with polycrystalline morphologies tend to grow with large angles on structured surfaces. [14, 17, 18] The results of Figure 2 suggest that thermally evaporated MG systems [20, 21] provide an attractive class of dielectric for NIMs formed by nTP, likely due to their lack of grain structure and non-columnar growth. Cross sectional and top view SEM images in Figure 3 provide additional evidence that θ is ∼2°, not only for a different MG but also for multilayer stacks with Ag. (The slight negative angle observed near the top of the stack arises from the focused ion beam preparation techniques used to enable the cross sectional views.) Figure 3a shows that with a MG thickness \( T \sim 300 \text{ nm} \), where \( t \sim 220 \text{ nm} \), \( W \sim 110 \text{ nm} \) and \( W' \sim 130 \text{ nm} \), \( \theta \sim 2.2 \pm 0.2^\circ \). For this geometry, the hole diameter decreases from the base to the top, from ∼185 nm to ∼159 nm (Figure 3c). (We note that the value of θ inferred from \( D \) is ∼3.5°). To ensure suitability of MG as a good optical dielectric behavior. Organic small molecule materials, many of which can be thermally evaporated, represent alternatives.

Figure 2 provides top view SEM images of stamps coated with various candidate materials, including alumina (Al₂O₃; \( T \sim 340 \text{ nm} \); electron-beam evaporation) (Figure 2a), silica (SiO₂; \( T \sim 300 \text{ nm} \); electron-beam evaporation) (Figure 2b), titania (TiO₂; \( T \sim 320 \text{ nm} \); electron-beam evaporation) (Figure 2c), a molecular glass (MG; 5 5' 6 6'-tetrahydroxy-3 3' 3'-tetramethyl-1 1'-spirobisindane; \( T \sim 350 \text{ nm} \); thermal evaporation) (Figure 2d) and pentacene (\( T \sim 300 \text{ nm} \); thermal evaporation) (Figure 2e) (organic materials like MG and pentacene were deposited thermally to avoid electron-beam chamber contamination). The results clearly show that only MG yields deposits with \( W \sim W' \). Specifically, the inferred values of θ from the images of Figure 2 are: ∼25° for Al₂O₃; ∼30° for SiO₂; ∼25° for TiO₂; ∼3° for the MG. The θ for pentacene is large, but difficult to estimate due to the grain structures. Such behaviors are qualitatively consistent with previous observations that dielectric materials such as SiO₂ and Al₂O₃ with polycrystalline morphologies tend to grow with large angles on structured surfaces.[14, 17, 18] The slight negative angle observed near the top of the stack arises from the focused ion beam preparation techniques used to enable the cross sectional views.) Figure 3a shows that with a MG thickness \( T \sim 300 \text{ nm} \), where \( t \sim 220 \text{ nm} \), \( W \sim 110 \text{ nm} \) and \( W' \sim 130 \text{ nm} \), \( \theta \sim 2.2 \pm 0.2^\circ \). A multilayer stack of Ag/MG yields a even slightly smaller angle (Figure 3b), where \( t \sim 205 \text{ nm} \), \( W \sim 115 \text{ nm} \) \( W' \sim 125 \text{ nm} \), and \( \theta \sim 1.4 \pm 0.3^\circ \).
we performed spectroscopic ellipsometry and experimentally obtained refractive indices ($n$, $\kappa$) which verifies almost no absorption loss over the visible band (Figure S4) and closely matches with previously reported ($n$, $\kappa$) values of such materials.

Deposits like those of Figure 3 can be transferred, by nTP, to a target substrate to complete the fabrication. Here, a layer of a liquid prepolymer (Norland, NOA 63) spin-casted onto a glass plate ensures strong adhesion and high fidelity in the transfer. Photocuring the prepolymer by passing ultraviolet light through the glass and then removing the stamp yields a high quality NIMs structure, without observable defects. Figure 4 shows large area SEM images of Ag/MG multilayer stacks on a stamp (Figure 4a) and transferred to NOA/glass (Figure 4b). NIMs with macroscopic sizes (∼4 cm$^2$), limited only by the available overall dimensions of the stamp, and with uniform properties are routinely possible (Figure 4c). Optical measurements indicate, however, low transmission in the range of wavelengths of interest, i.e., less than 1% at $\lambda = 650$ nm, as can be seen in Figure 5a. This low transmission is a direct consequence of the small $\theta$ because, in the absence of angular growth, the incident flux of Ag can lead to formation of grains and particles on the sidewalls of the multilayer stacks especially when deposited with thermal evaporation. The effect is visible in Figure 3b. Such deposits can electrically short adjacent Ag layers in the stack, thereby diminishing the excitation of strong magnetic responses that underpin the behavior in the NIMs structure. Immersing the sample in a wet chemical etchant for Ag can reduce or eliminate this problem. For etching times between 15 s to 30 s, the peak transmission increases from 18% to 40%, as shown in Figure 5b. Beyond 30 s, the etchant begins to remove significant amounts of Ag from the multilayer stacks themselves. The excessive removal of Ag causes damage to the desired metal–dielectric–metal LC resonant circuit and the electro-magnetic resonance diminishes and consequently less light transmits out of the structure, thereby leading to a decrease in transmission from 23% to 12% for times of 45 s and 60 s, respectively.

Comparing experimental and finite difference time domain (FDTD) results enables extraction of the effective optical properties of the NIMs. It has been firmly established in the optics community that full-vectorial FDTD prediction of index is sufficiently accurate to experimental observations.$^{[22–24]}$ Interferometric measurements to verify FDTD predictions of negative refractive index have been previously demonstrated for similar fishnet metamaterials.$^{[9,25]}$ Transmission and reflection spectra are calculated using experimental parameters for the printed multilayered NIMs structures, with commercial FDTD software package (Lumerical FDTD, Lumerical Solutions Inc.). A Drude model was used for the dielectric parameters of silver in the FDTD simulation, with plasma frequency 9.0 eV and scattering frequency 0.054 eV. The scattering frequency is increased by a factor of three compared to that of the bulk silver in order to account for the additional surface scattering loss in fabricated structures.$^{[26]}$ These simulation results were used to retrieve the impedance ($z$) and refractive index ($n$) of the samples. The retrieval exploited effective medium approaches, as described elsewhere.$^{[22–24]}$ For calculation, we use $W = 120$ nm, $W' = 140$ nm and $T = 285$ nm, with $\theta = 2^\circ$ respectively. Optical characterization reveals a broad-band transmission peak of 40.1% at 802 nm after an etching time of 30 s. The results exhibit good agreement with FDTD prediction (Figure 6a). The origin of the shoulder at around 0.6 $\mu$m is due to the partial infiltration of polymer inside the open hole of
The loss for these types of structures branches of the Re(n) which are labeled as ‘Mode 1’ and ‘Mode 2’ flow rate 110 sccm) formed a cross-linked polymer on the surface of the etch rate 1 μm/0.1 W, SF6/C4F8 flow rate 35 sccm/110 sccm for constant ICP power of 600 W; etch rate 1 μm/0.1 W, ICP power ∼500 nm. A 20 nm thick layer of SiO2 deposited by electron-beam evaporation (AJA International) on the top layer of Ag served as a resist to wet etching of the Ag from the sidewalls. Removing Excess Ag by Wet Etching: A mixture of sodium thiosulfate (anhydrous, 1.581 g), potassium ferricyanide (0.042 g), potassium hexacyanoferrate (0.329 g) dissolved in DI water (100 ml) served as the etchant. Immersion times were 15, 30, 40, and 60 s, each followed immediately by rinsing in DI water.

**Optical Measurements:** Transmission spectra were collected using an Alpha-3000 spectrophotometer where the photo-detector is changed right at 800 nm where a small step-like response is always artifically added to the measured spectrum by the instrument. The data is typically reported in terms of a figure of merit (FOM) defined by –Re(n)/Im(n). The results suggest a high FOM for the visible P = 300 nm Ag/MG NIMs of 7.4 at 654 nm as shown in Figure 6c, consistent with low loss (higher transmission). The good agreement between experiment and FDTD results that assume ideal geometries of the fishnets provides additional evidence of the high structural quality of the samples.

The results described here reveal some important effects of film growth in the formation of fishnet NIMs by large area processing techniques such as nTP. A key finding is that the film growth characteristics in MG systems make them attractive alternatives to more widely explored inorganics for the dielectric layers. The outcomes enable fabrication of multilayered NIMs with excellent optical characteristics in the visible regime and they appear to have implications in other areas of optical application of nanotransfer printing.

**Experimental Section**

**Fabrication of the Silicon Stamp:** The silicon was etched using a Bosch process (94 mTorr, etch/passivation: cycle time, 5 s/5 s; RIE power 20 W/0 W, SF6/C4F8 flow rate 35 sccm/110 sccm for constant ICP power of 600 W; etch rate 1 μm/80 s) with SF6 gas, to a depth of ~500 nm. A layer of photoresist patterned by soft nanoimprint lithography served as the resist. Exposure to CF4 in an ICP-RIE system (STS Inc., RIE power = 0 W, ICP power = 600 W, 15 s, chamber pressure = 94 mTorr, CF4 flow rate 110 sccm) formed a cross-linked polymer on the surface of the silicon to facilitate release in the transfer process by reducing the degree of adhesion between the deposited multilayer stacks and the substrate.

**Collimated Deposition of Multilayer Stacks:** Multilayer stacks of Ag and MgF2, and single layers of MgF2, Al2O3, SiO2, and TiO2 were deposited using a six-pocket electron-beam evaporation system (AJA International). The sample was mounted close to the center of the dome in the chamber; where the distance between the sample (~2 cm) and source (~2.5 cm) was maximized (~60 cm). The angle between the sample and source was estimated to be less than 5°. Due to the evaporation profile and the spherical dome shape, the incident flux was considered to be uniform over the 2 cm × 2 cm sample area. During deposition of Ag, MgF2, Al2O3, SiO2 and TiO2 the average base pressures and growth rates were 1 × 10⁻⁸ Torr and 0.1–0.15 nm/s, respectively. The chamber pressure increased by about one order of magnitude during evaporation for most dielectrics except for titania, where the increase was more than two orders of magnitude. Experiments with physical collimators involved a Temescal (FC-1800) six-pocket electron-beam evaporation system, with the sample at one end of a cylindrical metal tube whose other end aligned to the source. The chamber geometry and sample orientation were similar to AJA International electron-beam evaporation system. Sequential thermal evaporation formed stacks of Ag and the MG alpha, alpha, alpha'-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene system. Sequential thermal evaporation formed stacks of Ag and the MG alpha, alpha, alpha'-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene with a base pressure of 1.0 × 10⁻⁶ Torr and rate 0.05–0.1 nm/s using a thermal evaporator (TCI International). The other MG material, 5′ 6′-tetrahydroxy-3 3′ 3′-tetramethyl-1 1′-spirobisindane, was deposited in similar fashion. Pentacene was deposited at 0.03–0.05 nm/s. All samples were mounted perpendicular to the flux in the thermal evaporator. The distance between the sample (~2 cm) and source (~1 cm) was ~50 cm and the angle between them was less than 2°. A 20 nm thick layer of SiO2 deposited by electron-beam evaporation (AJA International) on the top layer of Ag served as a resist to wet etching of the Ag from the sidewalls.

**Removing Excess Ag by Wet Etching:** A liquid pre-polymer to polyurethane (NOA 63, Norland Inc.) spin-casted onto a clean glass plate served as an adhesive. A silicon stamp coated with multilayer stacks was pressed into contact with this substrate. Passing UV light (Osram Sylvania 100 W MV PAR38, power density 8.4 mW/cm²) through the glass for 1 h cured the NOA into a solid form, to form a strong bond with the multilayer stack. Removing the stamp completed the process.

**Optical Measurements:** Transmission spectra were collected using Varian Cary 5G UV-Vis-NIR spectrophotometer where the photo-detector was changed right at 800 nm where a small step-like response is always artifically added to the measured spectrum by the instrument. The data
was collected over a slit with a diameter of 2 mm. Transmission spectra were normalized using a glass substrate with cured NOA.

**FDTD Simulations:** Transmission spectra were calculated using experimental parameters for the printed NIMs structures, with a commercial FDTD software package (Lumerical FDTD, Lumerical). A Drude model was used for the dielectric parameters of Ag in the FDTD simulation, with a plasma frequency of 1.37 × 10^{16} s\(^{-1}\) and scattering frequency of 8.5 × 10^{13} s\(^{-1}\). The scattering frequency was increased by a factor of 3 compared with that of bulk Ag to account for the additional surface scattering loss. The FDTD simulations used averages of transmission separately computed with plane wave sources of TE and TM polarizations, to compare with the unpolarized light used in the spectrometer. These simulations used precise geometries and scattering frequency of 8.5 \times 10^{13} \text{s}^{-1}. The scattering frequency was

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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