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FINAL LDRD REPORT: Directed-Assembly of Block Copolymers for Large-Scale, Three-Dimensional, Optical Metamaterials at Visible Wavelengths

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FINAL REPORT

Directed-Assembly of Block Copolymers for Large-Scale, Three-Dimensional, Optical Metamaterials at Visible Wavelengths

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Abstract

Metamaterials are composites with patterned subwavelength features where the choice of materials and subwavelength structuring bestows upon the metamaterials unique optical properties not found in nature, thereby enabling optical applications previously considered impossible. However, because the structure of optical metamaterials must be subwavelength, metamaterials operating at visible wavelengths require features on the order of 100 nm or smaller, and such resolution typically requires top-down lithographic fabrication techniques that are not easily scaled to device-relevant areas that are square centimeters in size. In this project, we developed a new fabrication route using block copolymers to make over large device-relevant areas optical metamaterials that operate at visible wavelengths. Our structures are smaller in size (sub-100 nm) and cover a larger area (cm^2) than what has been achieved with traditional nanofabrication routes. To guide our experimental efforts, we developed an algorithm to calculate the expected optical properties (specifically the index of refraction) of such metamaterials that predicts that we can achieve surprisingly large changes in optical properties with small changes in metamaterials' structure. In the course of our work, we also found that the ordered metal nanowires meshes produced by our scalable fabrication route for making optical metamaterials may also possibly act as transparent electrodes, which are needed in electrical displays and solar cells. We explored the ordered metal nanowires meshes' utility for this application and developed design guidelines to aide our experimental efforts.

Background and Research Objectives

Optics was long limited by the optical properties of materials found in nature, but the rise of metamaterials, which are designed composites with subwavelength periodic structures, over the last two decades has revolutionized what scientists believe is possible in the optics field. The optical properties of metamaterials are determined by the constituent materials and the details of their patterned subwavelength structures, and by simple changes in the geometry of subwavelength structures, their dimensions, or selection of constituent materials, the optical properties of metamaterials can be tuned to values even beyond those found in nature. For example, all naturally occurring materials have a positive index of refraction, but metamaterials can be designed to have a negative index of refraction, which can enable realization of structures previously considered impossible, like cloaking devices and perfect lenses (Shalaev, 2007; Smith, Padilla, Vier, Nemat-Nasser, & Schultz, 2000; Veselago, 1968). Since the first demonstrations in the early 2000s of such "cloaking" negative-index metamaterials at microwave wavelengths (Schurig et al., 2006; Smith et al., 2000), much effort has been dedicated to translating these results to visible wavelengths.

To this end, it was found that "fishnet structures" consisting of alternating metal and dielectric layers with a mesh-type of lattice structure with features on the order of 100 nm, as shown in Figure 1, can attain negative indices of refraction at visible wavelengths.[1-2] However, fabricating such subwavelength structures is challenging, typically requiring traditional nanofabrication techniques (i.e., electron-beam, focused-ion-beam, interference, and nanoimprint lithographies) that are not scalable to large areas or depths and thereby limit both the lateral size and dimensionality of potential structures (Soukoulis & Wegener, 2011). Thus, to realize the applications of optical metamaterials beyond the lab scale, novel fabrication approaches that provide structural control on the sub-100 nm length scale and over cm^2-areas are necessary, and our LDRD project addressed this challenge.

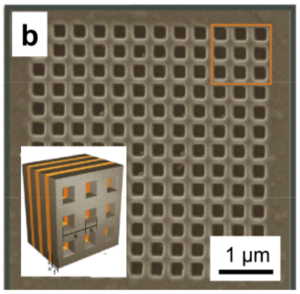

Figure 1. An example "fishnet" negative-index metamaterial operating in the visible (700-800 nm) and fabricated using focused ion beam milling. From Garcia-Meca C. *et al. Phys. Rev. Lett.* 2011, **106**, 067402.

In this project we sought to (1) develop a new block copolymer derived method to fabricate fishnet optical metamaterials with sub-100 nm features over large areas and (2) model the expected index of refraction of our targeted structures to understand how changes in the dimensions and thickness of optical metamaterials affect the index of refraction. We have achieved both these objectives for the project; we plan to submit a paper on objective 1 and have published a paper on objective 2. Furthermore, in the course of fabricating our fishnet optical metamaterials, we realized that the metal layer of the fishnet structure by itself has significant potential utility as a transparent electrode material. To evaluate the potential of our block copolymer-derived metal nanowire meshes for transparent electrode applications became our additional objective 3. Transparent electrode materials are necessary in any electrical devices that either absorb light (i.e., solar cells, photodetectors) or emit it (i.e., electronic displays). A replacement transparent electrode material for indium tin oxide (ITO), the most widely used transparent electrode on the market, is highly desired because indium is a critical material with limited supply. We have published an additional paper on this potential transparent electrode application of our structures and have submitted a patent application on it, as well.

Scientific Approach and Accomplishments

Objective 1: Develop Scalable Approach to Make Fishnet Metamaterials Over Large Areas

We proposed a novel fabrication scheme to make fishnet metamaterials using block copolymers (BCPs), as outlined in Figure 2. BCPs consist of two chemically dissimilar but covalently linked polymers or blocks that microphase separate to form one of several patterns, like spheres, cylinders, or lamellae, with ca. 10-100 nm features (Bai & Ross, 2016). While BCPs do not naturally form the kind of long-range straight line patterns needed to create a fishnet pattern, it was previously demonstrated that applying shear force to block copolymers can cause them to rearrange into line-patterns oriented in the direction of applied shear with long-range ordering (Angelescu et al., 2004; Kim, Gwyther, Manners, Chaikin, & Register, 2014). Repeating this process in two layers creates a fishnet-type mesh, and stacking multiple such layers atop one another allows for the construction of the targeted fishnet metamaterial structure. As proposed, we successfully leveraged this technique to create over cm^2-areas subwavelength metal lattices (see Figures 3a and 3b) that can be layered atop one another with dielectric layers in between to produce the fishnet architecture.

We chose to use the commercially available block copolymer poly(styrene)-*b*-poly(2-vinylpyridine) (PS-P2VP) since the P2VP phase complexes with metal salts (Chai, Wang, Fan, & Buriak, 2007), thereby providing a means of directly creating metal nanowires from the shear-aligned block copolymer rearranged into lines. We found that the dimensions and periodicity of the nanowire arrays produced from block copolymers can be easily tuned by the degree of polymerization (i.e., molecular weight) of the block copolymer, as shown in Figure 3c. Furthermore, the type of metal nanowires formed can be varied simply by selection of the metal salt (Chai et al., 2007). We found that the quality of shear alignment and resulting nanowires depends on several factors, including the block copolymer molecular weight, the thickness of the film, and the shearing time, and we optimized these conditions to attain high quality metal nanowires meshes with few defects over ca. 4-cm^2 areas with tunable sub-100 nm dimensions and geometry. We have a manuscript forthcoming that details these results. Furthermore, we designed and developed at LLNL a pneumatic-based shear-aligning system that is capable of handling 4" wafers, thereby allowing us to scale to yet larger areas.

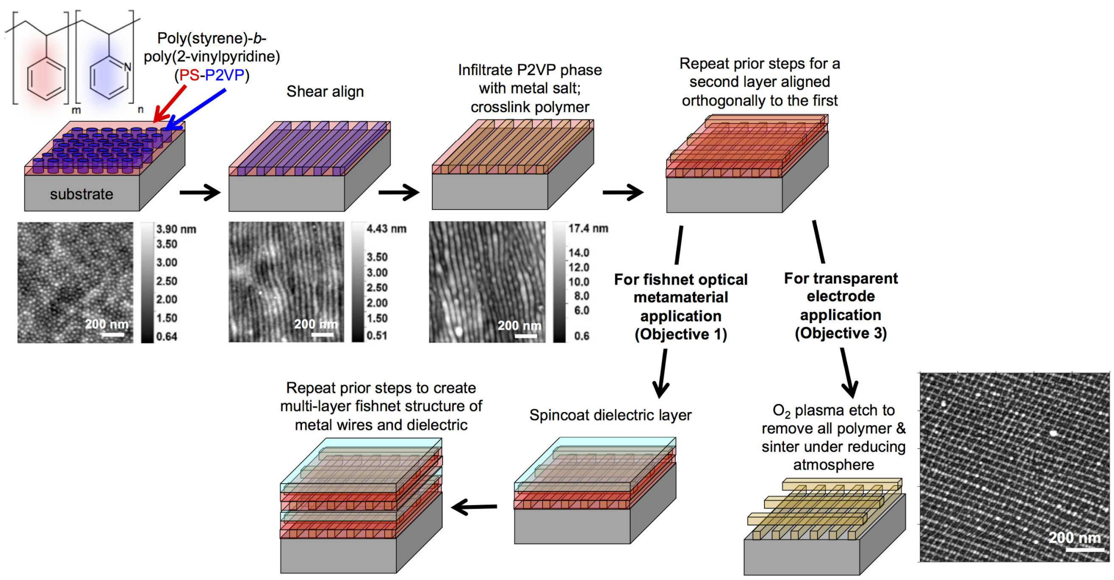

Figure 2. Schematic of the scalable process developed to create metal nanowire meshes that can be used either as the basis for fishnet optical metamaterials or transparent electrode materials. Atomic force microscopic height images of samples accompany select figures.

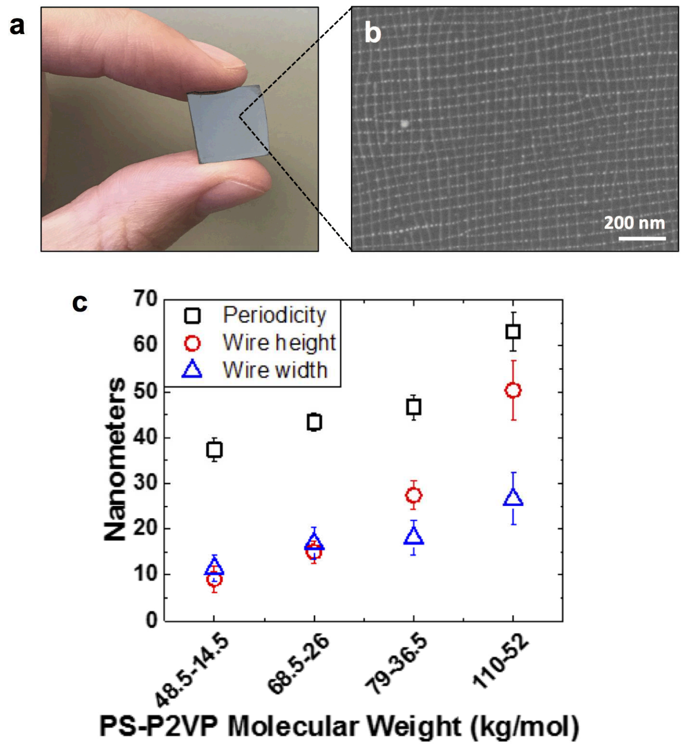

Figure 3. (a) Photograph of a silicon sample that we fabricated whose surface is coated with a transparent platinum nanowire mesh. **(b)** Scanning electron microscope image of the silicon sample surface showing the platinum nanowire mesh with sub-100 nm periodicity and wire dimensions. **(c)** The periodicity (black squares), height (red circles), and width (blue triangles) of platinum nanowire arrays as a function of PS- P2VP number-average molecular weight, demonstrating the ease of tuning the geometry of a nanowire mesh.

Objective 2: Evaluate the Optical Properties of Metamaterials

Given that 1) our block copolymer-derived method of creating fishnet metamaterials provides tunability over the dimensions of the structure and that 2) the dimensions we can access are approximately an order of magnitude smaller than those previously explored, we were next interested to perform simulations to understand how the optical properties of these structures change as a function of their subwavelength dimensions. The techniques reported in literature to calculate metamaterials' effective index of refraction treat the metamaterials as "black boxes." However, we found that these techniques are not robust as they yield erroneous and not realistic indices of refraction if the right constraints are not chosen, and the right constraints are not necessarily apparent *a priori*. Thus, rather than treat the metamaterial as a black box, we developed a more robust method to extract the index of refraction of metamaterials by tracking the phase of the primary propagating mode of light through the structure. This phase tracking algorithm also allows us to easily study how changing various structural parameters, like the number of layers in the optical metamaterial, affects the effective index of refraction, as shown in Figure 4. We published this approach and results in the *Journal of Optics*.

Using this phase tracking algorithm, we found that most of the metamaterials in the dimensional range that we can fabricate yield a highly tunable index of refraction. This is an exciting finding since materials with tunable indices of refraction are desired for gradient-index optics to make, for instance, flat lenses that would enable more compact and lighter weight optics; the tunability achievable from our metamaterial structures far surpasses that attained with more traditional methods (Shingyouchi & Konishi, 1990; Urness, Anderson, Ye, Wilson, & McLeod, 2015; Visconti & Bentley, 2013), and importantly, can be achieved over thin samples ~100 nm-thick.

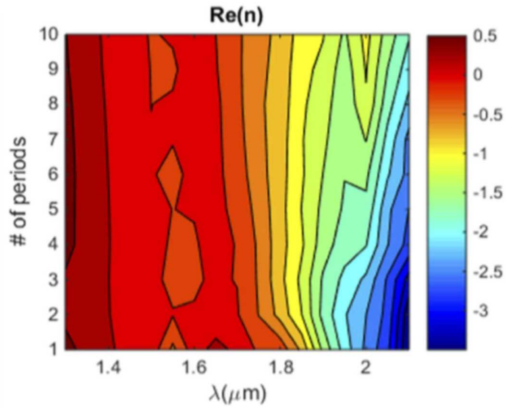

Figure 4. The effective index of refraction (i.e., Re(n)) deduced using our phase accumulation tracking algorithm is depicted by color as a function of both the number of periods (i.e., film thickness) of the fishnet metamaterial structure and the wavelength of incident light. These results demonstrate the high tunability of the index of refraction that can be achieved, even to values beyond those observed in nature, like a negative index of refraction. The modelled fishnet structure to which the algorithm was applied here had features that were hundreds of nanometers in size – larger than what we can attain with block copolymers – and thus this specific metamaterial is active at longer wavelengths in the IR regime.

Objective 3: Evaluate the Materials for Transparent Electrode Applications

In fabricating these metal nanowire meshes to ultimately produce fishnet metamaterials, we realized that the metal nanowire meshes by themselves may have significant utility as transparent electrodes – an idea for which we recently filed a patent application. An important topic in the display and solar cells industries is finding substitute transparent electrode materials for the defacto standard – indium tin oxide (ITO) – because indium's supply is limited (considered near-critical material by DOE's Critical Materials Institute) and ITO has poor robustness in flexible devices (Ellmer, 2012; Hecht, Hu, & Irvin, 2011; Hu, Wu, & Cui, 2011). The most promising alternative materials demonstrated to-date are randomly dispersed networks of Ag nanowires, but the random-nature of these networks means that electrical junctions between wires are not maximized, which limits the network's conductivity (Hecht et al., 2011; Hu et al., 2011; Lee, Connor, Cui, & Peumans, 2008).

Thus, our ordered metal nanowire meshes, which have ordering to increase conductivity yet are also sub-100 nm in size to give high transparency, are promising alternatives. Based on optical simulations and conductivity calculations, we have devised design guidelines for metal nanowire meshes to maximize their conductivity and transmissivity (see Figure 5), which we have recently published as a paper in *ACS Applied Materials & Interfaces*. We found that the ordered nature of the nanowires significantly decreases the average nanowire length required to maintain high conductivity, increasing defect tolerance. Furthermore, we evaluated and extracted relationships for how introducing anisotropy by changing nanowires' periodicity or resistivity affects both electrical and optical performance. Having explored the TCNs' parameter design space using numerical calculations, these design rules can help guide future fabrication and experimental studies.

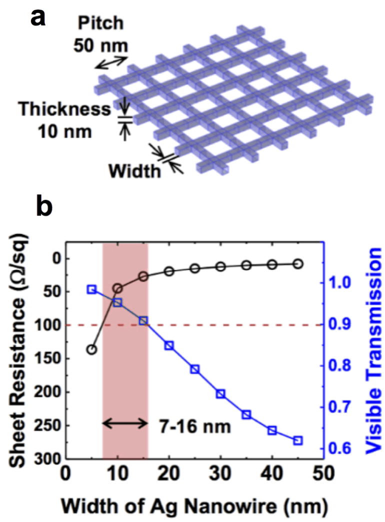

Figure 5. (a) Schematic of a modelled silver nanowire network having dimensions similar to those that we can access using our block copolymer method. **(b)** Sheet resistance (left axis, black) and visible transmission (right axis, blue) calculated for the modelled silver nanowire network as a function of the nanowire width. The dashed red line represents the performance criterion (<100 ohms/square and >90% visible transmission) for transparent conductive electrodes, and the region in red indicates the nanowire width needed to achieve this performance criterion. This nanowire width is well within the dimensions we can achieve.

Impact on Mission

This project is directly relevant to the Laboratory's focus on advanced materials and manufacturing techniques for optical and energy applications. We have demonstrated a new fabrication route to make over large areas subwavelength structures needed for optical metamaterials at visible wavelengths with tunable properties and for transparent electrodes used in solar cells and photodetectors. We have also developed computational tools for evaluating and guiding the development of these materials for their target applications. The project helped introduce a number of students and recent graduates to LLNL, including: a postdoc who also gained project management experience as the principal investigator of the project; two post-collegiate appointees, one of whom converted to a staff position; three summer undergraduate students; and one graduate student.

Conclusion

Our method of fabricating these fishnet metamaterials and transparent electrode nanowire meshes represents a fundamentally new and different approach, and attracted significant interest from both academic partners and large industrial firms (who were primarily interested in the transparent electrode applications) when we presented these preliminary results at the 2017 Materials Research Society Spring Meeting. We are currently exploring potential collaborations with both academia and industry to further evaluate and develop these materials.

Publications and Presentations

- Eyal Feigenbaum, Anna M. Hiszpanski. "Phase accumulation tracking algorithm for effective index retrieval of fishnet metamaterials and other resonant guided wave networks." *J. Optics*, 2017, *19*, 075103. LLNL-JRNL-703042. http://dx.doi.org/10.1088/2040-8986/aa751b
- Juan J. Diaz Leon, Eyal Feigenbaum, Nobuhiko P. Kobayashi, T. Yong-Jin Han, Anna M. Hiszpanski. "Design parameters for subwavelength transparent conductive nanolattices." *ACS Appl. Mater. Interfaces*, 2017, *9*, 35360-35367. LLNL-JRNL-732399. http://dx.doi.org/10.1021/acsami.7b08446
- Anna M. Hiszpanski, Carla L. Watson, Timothy D. Yee, Juan J. Diaz Leon, Eyal Feigenbaum, T. Yong-Jin Han. "Nanometer-Scale Metal Meshes Across Device-Relevant Areas for Transparent Electrodes and Optical Metamaterials." 2017 Spring Materials Research Society (MRS) Meeting. Phoenix, AZ. April 17-21, 2017. LLNL-POST-729139.
- Eyal Feigenbaum, Anna M. Hiszpanski. "Index retrieval of finite thickness fishnet metamaterials: tracking the phase accumulation." SPIE, Optics + Photonics, Nanoscience + Engineering, Conference. San Diego, CA. August 6-10, 2017.
- Anna M. Hiszpanski, T. Yong-Jin Han, Carla L. Watson, Timothy D. Yee. "Fabrication of Metal Nanowire Meshes Over Large Areas by Shear-Alignment of Block Copolymers." Patent Application, 2017. IL-13111 LLNLP165.

Notes to the Editors

cm^2 (2 superscripted) is used throughout the report.

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