Demonstration of Al:ZnO as a plasmonic component for near-infrared metamaterials

Gururaj V. Naik^a, Jingjing Liu^a, Alexander V. Kildishev^a, Vladimir M. Shalae^{a,b}, and Alexandra Boltasseva^{a,c,1}

^aSchool of Electrical and Computer Engineering, and Birk Nanotechnology Center, Purdue University, West Lafayette, IN 47907; ^bThe Russian Quantum Center, Moscow 119991, Russia; and ^cDTU Fotonik, Technical University of Denmark, Lyngby 2800, Denmark

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Noble metals such as gold and silver are conventionally used as the primary plasmonic building blocks of optical metamaterials. Making subwavelength-scale structural elements from these metals not only seriously limits the optical performance of a device due to high absorption, it also substantially complicates the manufacturing process of nearly all metamaterial devices in the optical wavelength range. As an alternative to noble metals, we propose to use heavily doped oxide semiconductors that offer both functional and fabrication advantages in the near-infrared wavelength range. In this letter, we replace a metal with aluminum-doped zinc oxide as a new plasmonic material and experimentally demonstrate negative refraction in an Al:ZnO/ZnO metamaterial in the near-infrared range.

transparent conducting oxides | heavily doped semiconductors | low-loss metals

The recent emergence of plasmonics (1, 2) and metamaterials (3) has led to the demonstration of optical devices with many unconventional functionalities such as subdiffraction imaging (4, 5), cloaking (6), and optical magnetism (7). These novel functionalities have been demonstrated through exciting proof-of-principle experiments performed in the ultraviolet (UV), infrared (IR), or microwave frequency ranges (4–6, 8). The experimental demonstrations of similar devices in the visible and near-IR ranges would have a significantly larger impact owing to the technological importance of these frequency ranges. However, the major problem impeding the realization of efficient devices in these important spectral ranges is the optical loss associated with the metallic constituents in metamaterial building blocks (9–11). The development of new constituent materials for low-loss, metamaterial-based devices is therefore required for realistic applications of metamaterials in the visible and near-IR (10, 12, 13). Previously, we reported that heavily doped oxide semiconductors like transparent conducting oxides could serve as good alternatives to metals for the realization of many classes of metamaterials, including metamaterials with hyperbolic dispersion (14, 15) in the near-IR (16). Here, we have designed, fabricated, and characterized a nonresonant, plasmonic, metamaterial device in which the noble metal acting as the constituent plasmonic building block has been replaced by aluminum-doped zinc oxide (Al:ZnO, hereinafter referred to as AZO). As a proof-of-concept demonstration, we experimentally show that, similar to traditional metal-dielectric structures, a device built of alternating subwavelength AZO/ZnO layers exhibits negative refraction in the near-IR range. We also show that the performance of the AZO/ZnO device is significantly better than that of conventional metal-based devices.

Optical metamaterials typically use nanostructured metals and dielectrics as their building blocks. The geometry of the unit cell and the optical properties of the constituent materials form the parameter space for the device design. In the near-IR and shorter wavelength ranges, the geometry is restricted by nanofabrication capabilities since unit cells cannot be made arbitrarily small. Thus, the optical properties of the constituent natural materials form an important set of design parameters. The optical properties of bulk natural materials are described only by their complex-

valued and dispersive permittivities or dielectric functions (ϵ), as their permeabilities are unity at optical frequencies. The real part of the dielectric function (ϵ' or $\text{Re}(\epsilon)$) signifies the electrical polarization response of the material, while the imaginary part (ϵ'' or $\text{Im}(\epsilon)$) describes the material losses. When designing a low-loss, high-performance metamaterial, one can choose dielectric materials (for an $\epsilon' > 0$ contribution) having negligible losses. However, metals that offer negative real permittivity ($\epsilon' < 0$) exhibit strong optical dispersion, which is accompanied by large losses. Even noble metals like silver and gold (the metals with the highest DC conductivities) exhibit excessive losses at optical frequencies that seriously restrict the experimental realization of metamaterial devices in the optical frequency range. Furthermore, for noble metals, the real part of their permittivity is very large in magnitude. Due to the fact that many devices based on transformation optics (TO) (17) require the polarization responses of the metallic and dielectric constituents to be nearly balanced (18), the extreme contrast in magnitude between the negative (metallic) and positive (dielectric) real parts of the constituent permittivities could cause additional problems in the fabrication of metamaterial devices. The robust fabrication of balanced TO structures requires that the volume fractions of the metal and dielectric components are comparable along with comparable magnitudes of the real parts of their dielectric functions. At optical frequencies, ϵ' of dielectrics is on the order of 1 to 10 (e.g., ϵ' of Al_2O_3 is about 3 at 1.5 μm), while ϵ' of noble metals is about one or even two orders higher (~ 115 for Ag at 1.5 μm). Such a large magnitude discrepancy necessitates that the geometrical scale of the subwavelength metallic elements should be up to 100 times smaller than the dimensions of the dielectric elements (18–20), which can pose severe fabrication challenges. Another significant drawback when working with conventional metals like Au and Ag is that their optical properties are not tunable and cannot be adjusted to fit the requirements of a specific metamaterial design. An even worse disadvantage of using traditional metals for metamaterial devices and their applications is the issue of compatibility and integration: The processing of noble metals is not compatible with standard silicon nanofabrication technology. This fabrication incompatibility precludes the integration of plasmonic structures and metamaterials with nanoelectronics; hence, this is a serious threat to the development of real-life metamaterial applications. In contrast, alternative plasmonic materials such as heavily doped semiconductors provide adjustability through doping properties and lower optical loss combined with well-established fabrication methods and straightforward integration into complex device geometries.

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¹To whom correspondence should be addressed. E-mail: aeb@purdue.edu.

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calculated reflectance spectra (34) for the multilayer stack. The calculations use material properties extracted from ellipsometer measurements, as shown in Fig. 1A. The reflectance spectra from measurements and calculations are in good agreement, confirming the correctness of the ellipsometric extraction procedure for the optical parameters. The transmittance plots can be found in the supplementary information (Fig. S2).

In order to visualize negative refraction in the wavelength range from 1.84 μm to 2.4 μm in the fabricated slab, simulations were carried out using the extracted material parameters for AZO and ZnO. The field maps of the simulations in TM and TE polarizations are shown in Fig. 3. The TM-polarized Gaussian beam incident at an angle of 40° to the sample normal undergoes negative refraction inside the sample, producing a beam shift toward the incident side of the sample normal. This dramatic effect is observed only in the case of TM-polarized (*p*-polarized) incident light because only in this polarization is the electric field component of the incident light able to probe both components of the dielectric function and thus experience the material's hyperbolic dispersion. In the case of TE-polarized (*s*-polarized) incident light, the medium behaves as an isotropic dielectric with a real permittivity given by $\epsilon_{\parallel}$. Since observing the anomalous beam shift in the TM case would provide evidence for negative refraction, transmittance measurements were performed on the multilayer stack with half of the transmitted beam blocked by a razor blade. Fig. 4A shows the schematic of the experimental setup for observing negative refraction in our ZnO-based HMM. The details of the experimental set-up are shown in *SI Text*, Fig. S3. The position of the razor blade was adjusted to block the transmitted beam intensity exactly at 50% at normal incidence. We then increased the incidence angle and recorded the beam shift by measuring the relative transmittance (ratio of transmittance with and without the blade). It may be noted from Fig. 4A that the relative transmittance should dip if negative refraction were to occur. Fig. 4B plots the ratio of the transmittance with and without the beam-blocking blade (referred to as "relative transmittance"). The figure also compares the measured curves with the theoretically predicted results. The theoretical predictions were carried out using the exact dispersion equation for a bulk, planar, multilayer stack (31) (see Fig. S1). The relative transmittance dips around 1.8 μm wavelength in the TM polarization due to negative refraction. No similar dip in the relative transmittance is observed for any incident angle in the TE-polarization (see

Fig. S4). The theoretical predictions agree well with the experiments, thus confirming our observation of negative refraction in the AZO/ZnO metamaterial.

The performance of HMMs can be characterized by a figure of merit (FoM). For a negatively refracting slab such as the device in this work, Hoffman et al. introduced the FoM as (21): $\text{FoM} = \text{Re}(\beta_{\perp})/\text{Im}(\beta_{\perp})$, where $\beta_{\perp}$ is the propagation vector in the direction perpendicular to the layers. A large FoM requires smaller $\text{Im}(\beta_{\perp})$ (i.e., lower losses) and larger $\text{Re}(\beta_{\perp})$ (i.e., higher effective index). The FoM for our AZO/ZnO HMM was found to be about 12, which is at least three orders of magnitude larger than that of HMMs with a similar design using silver or gold (35). In fact, the FoM in our sample is the highest FoM achieved so far in the optical range for any negatively refracting HMM (4, 29). This conclusively shows that ultrahighly doped semiconductors can serve as good alternatives to metals for certain metamaterial applications in the near-IR.

Conclusions

In summary, we designed and fabricated a semiconductor hyperbolic metamaterial in the near-IR and in which AZO replaced conventional metals. Using the AZO/ZnO metamaterial, we successfully demonstrated negative refraction in the near-IR and showed that the figure of merit of this multilayered stack is about three orders of magnitude larger than that of its metal-based counterpart.

Furthermore, alternative plasmonic materials such as AZO overcome the bottleneck created by conventional metals in the design of optical metamaterials and enable more efficient devices. This demonstration opens up approaches to engineer optical metamaterials and customizes their optical properties in order to develop optical devices with enhanced performance. We anticipate that the development of new plasmonic materials and nanostructured material composites such as AZO/ZnO will lead to tremendous progress in the technology of optical metamaterials, enabling the full-scale development of this technology and uncovering many new physical phenomena.

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- Maier SA (2007) *Plasmonics: Fundamentals and Applications* (Springer, New York).
- Lal S, Link S, Halas NJ (2007) Nano-optics from sensing to waveguiding. *Nat Photonics* 1(11):641–648.
- Smith D, Pendry J, Wiltshire M (2004) Metamaterials and negative refractive index. *Science* 305(5685):788–792.
- Liu Z, Lee H, Xiong Y, Sun C, Zhang X (2007) Far-field optical hyperlens magnifying sub-diffraction-limited objects. *Science* 315(5819):1686.
- Fang N, Lee H, Sun C, Zhang X (2005) Sub-diffraction-limited optical imaging with a silver superlens. *Science* 308(5721):534–537.
- Schurig D, et al. (2006) Metamaterial electromagnetic cloak at microwave frequencies. *Science* 314(5801):977–980.
- Soukoulis CM, Linden S, Wegener M (2007) Negative refractive index at optical wavelengths. *Science* 315(5808):47–49.
- Kehr SC, et al. (2011) Near-field examination of perovskite-based superlenses and superlens-enhanced probe-object coupling. *Nat Commun* 2:249.
- Boltasseva A, Atwater HA (2011) Low-loss plasmonic metamaterials. *Science* 331(6015):290–291.
- West P, et al. (2010) Searching for better plasmonic materials. *Laser Photon Rev* 4(6):795–808.
- Khurgin JB, Sun G (2010) In search of the elusive lossless metal. *Appl Phys Lett* 96(18):181102.
- Noginov M, et al. (2011) Transparent conductive oxides: plasmonic materials for telecom wavelengths. *Appl Phys Lett* 99:021101.
- Frölich A, Wegener M (2011) Spectroscopic characterization of highly doped ZnO films grown by atomic-layer deposition for three-dimensional infrared metamaterials [Invited]. *Opt Mater Express* 1(5):883–889.
- Podolskiy VA, Narimanov EE (2005) Strongly anisotropic waveguide as a nonmagnetic left-handed system. *Phys Rev B* 71(20):201101.
- Jacob Z, Alekseyev LV, Narimanov E (2006) Optical hyperlens: Far-field imaging beyond the diffraction limit. *Opt Express* 14(18):8247–8256.
- Naik G, Boltasseva A (2010) Semiconductors for plasmonics and metamaterials. *Physica Status Solidi RRL: Rapid Research Letters* 4:295–297.
- Pendry JB, Schurig D, Smith DR (2006) Controlling electromagnetic fields. *Science* 312(5781):1780–1782.
- Kildishev A, Shalaev V (2008) Engineering space for light via transformation optics. *Opt Lett* 33(1):43–45.
- Yagil Y, Deutscher G (1987) Transmittance of thin metal films near the percolation threshold. *Thin Solid Films* 152(3):465–471.
- McCarthy S (1976) Optical properties of ultrathin Ag films. *J Vac Sci Technol* 13(1):135–138.
- Hoffman A, et al. (2007) Negative refraction in semiconductor metamaterials. *Nat Mater* 6(12):946–950.
- Panish M, Casey H, Jr (1967) The solid solubility limits of zinc in GaAs at 1000. *J Phys Chem Solids* 28(9):1673–1684.
- Neave J, Dobson P, Harris J, Dawson P, Joyce B (1983) Silicon doping of MBE-grown GaAs films. *Appl Phys A: Mat Sci Process* 32(4):195–200.
- Wolfe C, Stillman G (1975) Self-compensation of donors in high purity GaAs. *Appl Phys Lett* 27(10):564–567.
- Yoon M, Lee S, Park H, Kim H, Jang M (2002) Solid solubility limits of Ga and Al in ZnO. *J Mater Sci Lett* 21(21):1703–1704.
- Naik GV, Kim J, Boltasseva A (2011) Oxides and nitrides as alternative plasmonic materials in the optical range [Invited]. *Opt Mater Express* 1(6):1090–1099.
- Ashcroft NW, Mermin ND (1976) *Solid State Physics*, (Saunders College, Philadelphia), 1, pp 16–20.
- Lindell IV, Tretyakov S, Nikoskinen K, Ilvonen S (2001) BW media—media with negative parameters, capable of supporting backward waves. *Microw Opt Technol Lett* 31(2):129–133.
- Yao J, et al. (2008) Optical negative refraction in bulk metamaterials of nanowires. *Science* 321(5891):930.