12th International Congress on Artificial Materials for Novel Wave Phenomena – Metamaterials 2018
Espoo, Finland, Aug. 27th – Sept. 1th, 2018

Extraordinary properties of chalcogenide metamaterials

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***Abstract* – Fascinating opportunities are offered by metamaterial nanostructures fabricated from materials with highly-dispersive optical properties, between those of ideally plasmonic (e.g. noble metal) and transparent dielectric media. Chalcogenide semiconductors are excellent examples – their optical properties can be engineered by controlling alloy composition and phase state to provide high and low refractive indices, plasmonic, dielectric and epsilon-near-zero characteristics at near-ultraviolet to near-infrared wavelengths. We report here on the application of chalcogenide materials to photonic metasurfaces.**

I. INTRODUCTION

Chalcogenides – binary, ternary and quaternary alloys based upon group-16 'chalcogen' elements (sulfur, selenium and tellurium; not oxygen) have long been recognized in the field of optics and photonics for their exceptional transparency at infrared wavelengths and as highly optically nonlinear materials. They are also commercially established as the enabling 'phase-change material' foundation of rewritable optical and electronic data storage technologies (i.e. CD/DVD/Blu-ray discs, and P-RAM), and have played a notable role in the evolution of active plasmonic and photonic metamaterial technologies, predominantly as functional (phase-change) dielectric media hybridized with noble metal nanostructures [1-3], but also as a platform for all-dielectric nanostructured and laser-rewritable metasurfaces [4, 5].

In recent work, we have shown that germanium antimony telluride ($Ge_2Sb_2Te_5$ or GST) can be converted between amorphous and crystalline states that are respectively, at UV/VIS frequencies, dielectric and metallic (i.e. plasmonic) enabling the realization of optically-switchable 'structurally colored' metasurfaces; that amorphous bismuth telluride (Bi:Te) can serve as a compositionally-tunable, CMOS-compatible material platform for plasmonics in the ultraviolet-to-visible spectral range; and that peculiar epsilon-near-zero (ENZ) and sub-unitary index behaviors may be observed at optical frequencies, even in in the presence of realistic losses, in metamaterials combining plasmonic nanostructures with antimony telluride (Sb_2Te_3) inclusions.

II. PHASE-CHANGE-DRIVEN DIELECTRIC-PLASMONIC TRANSITIONS IN CHALCOGENIDE METASURFACES

Amorphous germanium antimony telluride is a transparent dielectric, but in the crystalline phase it presents a negative value of ε_1 (real part of relative permittivity) and supports plasmonic resonances in the ultraviolet-visible spectral range. This change in the character of the chalcogenide is harnessed in metasurface structures comprising a 70 nm layer of GST sandwiched between protective films of ZnS/SiO_2, into which sub-wavelength period slot arrays are etched by focused ion beam milling. Metasurface absorption resonances (dependent on the structural period and on the polarization of incident light) are manifested in the transmitted and reflected colors of metasurface domains. These change markedly when the chalcogenide is switched from its as-deposited amorphous state to the crystalline state (here, by optical excitation using a train of 85 fs laser pulses at 730 nm tailored to achieve temperature in the GST layer between the chalcogenide's glass transition and melting temperatures).

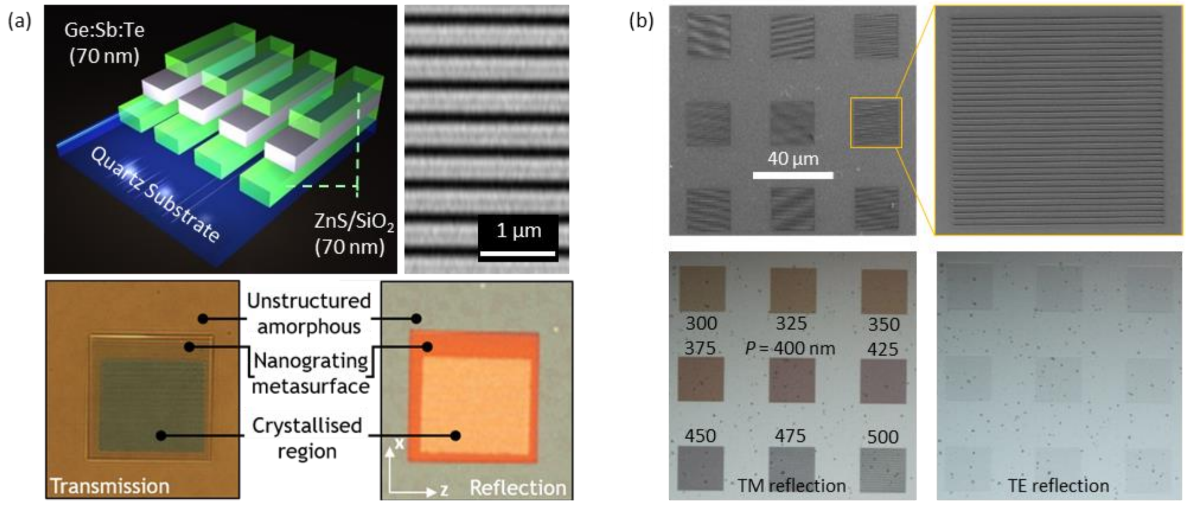

Fig. 1. **All-chalcogenide metasurfaces** (a) Artistic schematic and scanning electron microscope image of a ZnS/SiO_2–GST–ZnS/SiO_2 tri-layer metasurface, above transmission and reflection TM-polarized, normal incidence reflection images of a 20 × 20 µm, 400 nm period, amorphous GST tri-layer metasurface domain, the central part of which has been selectively crystallized by fs-pulsed laser excitation. (b) Scanning electron microscopy images of nano-grating metasurfaces, in a 134 nm thick amorphous film of Bi[34%]:Te[66%] – periods as labelled above corresponding reflection mode optical microscopy images for TM and TE polarized incident light.

III. Compositionally tunable plasmonics in amorphous semiconductor metasurfaces

Many crystalline chalcogenides are metallic (like GST above), and some in bulk monocrystalline form (e.g. Bi:Sb:Te:Se [6]) have been demonstrated recently as topological insulators with low-loss metallic (plasmonic) surface states. We further show here that *amorphous*, vapor-deposited thin films of bismuth telluride are plasmonic at near-ultraviolet to visible frequencies. This plasmonic character is illustrated again via the fabrication of sub-wavelength period nano-grating metasurfaces, which present a highly anisotropic optical response: under TM-polarized illumination (incident electric field perpendicular to the grating lines) plasmonic absorption resonances are manifested as period-dependent variations in the perceived color of the nanostructured domains, while for TE-polarized light the metasurface domains are almost indistinguishable from unstructured Bi:Te. We explore a range of alloy compositions using high-throughput physical vapor deposition and characterization techniques [7] – finding that the real part ε_1 of Bi:Te relative permittivity takes a negative value (i.e. that the alloy is plasmonic) over a composition-dependent range of wavelengths extending from as low as 250 nm to as high as 978 nm.

IV. Filling Holes in a Metal Film with an ENZ medium

Engheta *et al.* have shown recently that the transmission of sub-wavelength waveguide channels can be enhanced by filling them with zero/low-loss ENZ media [8], whereby these channels can act as 'wires' for light, and a range of exciting phenomena affecting the quantum properties of emitters in ENZ materials has been predicted [9]. Although some proof-of principle experiments in the microwave parts of the spectrum have confirmed predictions of unusual ENZ properties, studies in the optical part of the spectrum are generally precluded by intrinsic losses. We show here, however, that there are circumstances - nanostructural geometries - in which materials with sufficiently low values of epsilon can manifest ENZ behaviors at optical frequencies.

We find that low-epsilon chalcogenide inclusions can serve as conduits for the 'laminar flow' of light through deeply sub-wavelength slots in a plasmonic metal screen: around empty slots, 'whirlpools' of optical energy are formed, characteristically rotating (as around plasmonic nanoparticles) in opposite directions at wavelengths either side of a plasmonic resonance; Sb_2Te_3 inclusions funnel light through the nanoscale apertures, suppressing the turbulent powerflow whirlpools and associated local field enhancement, resulting in a broadband

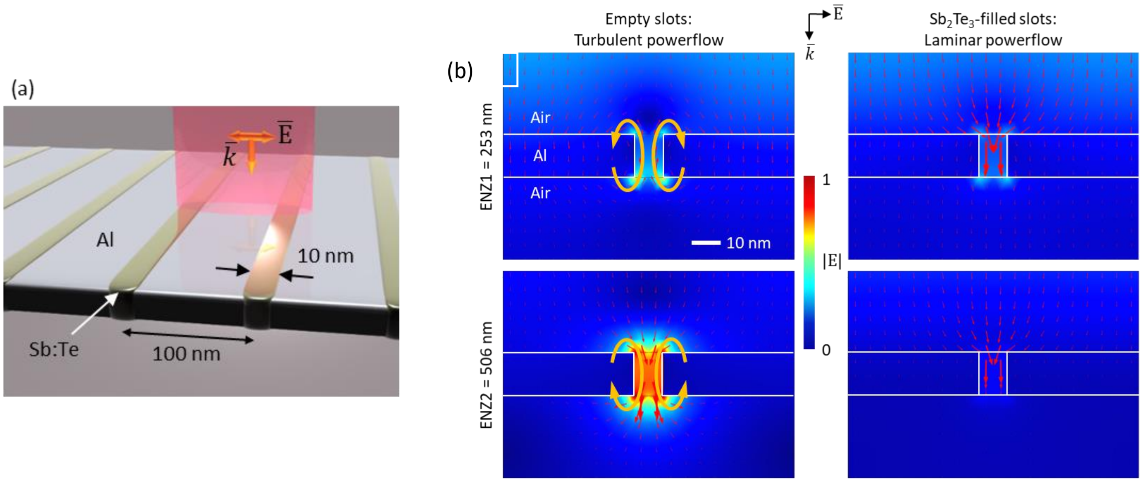

Fig. 2. **Laminar vs. turbulent light flow through an Al nano-slot metasurface** (a) Schematic illustration of the numerically simulated metasurface, comprising a periodic array of linear slots (width << illumination wavelength λ, period <λ) in a 15 nm thick Al film. (b) Cross-sectional distributions of electric field, overlaid with arrows showing time-averaged powerflow, for Al metasurfaces (of the geometry shown in Fig. 2a) with empty (left) and Sb2Te3-filled (right) slots at the chalcogenide's two ε1 zero-crossing wavelengths, ENZ1, 2 = 253 and 506 nm (upper and lower rows respectively).

enhancement of transmission. Intriguingly though, transmission is not strongly enhanced at the low-loss epsilon-nearest-zero wavelength. Indeed a reduction of losses in the chalcogenide is found to suppress transmission at this point and can increase, rather than decrease, metasurface absorption depending on the magnitude of refractive index and the extent of index matching to the surroundings.

VI. Conclusion

Using the examples of Ge:Sb:Te (switchable between dielectric and plasmonic states), Bi:Te (plasmonic in the as-deposited amorphous state) and Sb:Te (low-index/epsilon properties), chalcogenides are demonstrated as a uniquely compositionally adaptable, CMOS-compatible material base for photonic metamaterial applications.

Acknowledgement

This work was supported by the EPSRC, UK [grant numbers EP/M009122/1 and EP/N00762X/1].

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