11th International Congress on Engineered Material Platforms for Novel Wave Phenomena – Metamaterials 2017
Marseille, France, Aug. 28th – Sept. 2nd, 2017

Tuneable Epsilon Near-Zero in Chalcogenides

D. Piccinotti[1], B. Gholipour[1, 2], J. Yao[2], K. F. Macdonald[1], B. E. Hayden[2] and N. I. Zheludev[1, 3]

[1] Optoelectronics Research Centre and Centre for Photonic Metamaterials, University of Southampton, Southampton, SO17 1BJ, UK
[2] Department of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK
[3]Centre for Disruptive Photonic Technologies, School of Physical and Mathematical Sciences & The Photonics Institute, Nanyang Technological University, Singapore 637371
b.gholipour@soton.ac.uk

***Abstract* – The enormous potential of chalcogenides as compositionally-tuneable alternatives to noble metals for plasmonics and 'epsilon-near-zero' (ENZ) photonics can be unlocked using high-throughput materials discovery techniques. Taking advantage of the composition-dependent plasmonic properties of binary and ternary telluride alloys, we show the first amorphous ENZ and plasmonic metasurfaces operating across the UV-VIS spectral range.**

I. INTRODUCTION

The chalcogenides are a unique material family, offering high-index dielectric, plasmonic, 'epsilon-near-zero' (ENZ) and topological insulator properties when their constituent elements are combined in the correct proportions. Furthermore, they can be reversibly switched in non-volatile fashion between solid phases with markedly different optical and electronic properties. We report here on the synthesis, characterization and application of plasmonic chalcogenides, including compositions that can be switched between plasmonic and dielectric states, and on the ENZ properties of antimony telluride metasurfaces operating at UV and visible wavelengths.

II. PLASMONIC CHALCOGENIDE ALLOYS

Plasmonic nanostructures, including photonic metamaterials, have conventionally been fabricated from noble metals such as gold and silver, but many of their potential applications are compromised by the metals' high Ohmic losses, especially in the UV-visible spectral range. As elemental platforms with optical properties that are readily degraded by impurities, they also present no possibility for controlled tuning or switching of electromagnetic response parameters. In stark contrast, chalcogenides represent a widely compositionally tuneable alternative material base. Here we show that thin films of chalcogenide alloys including bismuth telluride (Bi:Te), antimony telluride (Sb:Te), bismuth antimony telluride (BST) and germanium antimony telluride (GST) exhibit a plasmonic response in their amorphous and/or crystalline states at UV/VIS frequencies, with the real part of relative permittivity ($\varepsilon 1$) taking negative values over a composition-dependent range of wavelengths extending as low as 250 nm and as high as 980 nm (Fig 1).

Using high-throughput physical vapour deposition and characterization techniques we explore a wide range of alloy compositions (e.g. for the Bi:Te system, at% ratios from 1.6 to 17). Thin film samples are produced, by co-deposition of programmed density gradients of the constituent elements, in which composition varies continuously over the substrate. Optical, electronic, structural and thermal properties can then be positionally mapped to composition. Compositional variation is found to provide an effective means of tuning the spectral band over which a material is plasmonic (has a negative value of ε_1); the corresponding losses (ε_2); and the wavelengths at which it is an ENZ medium.

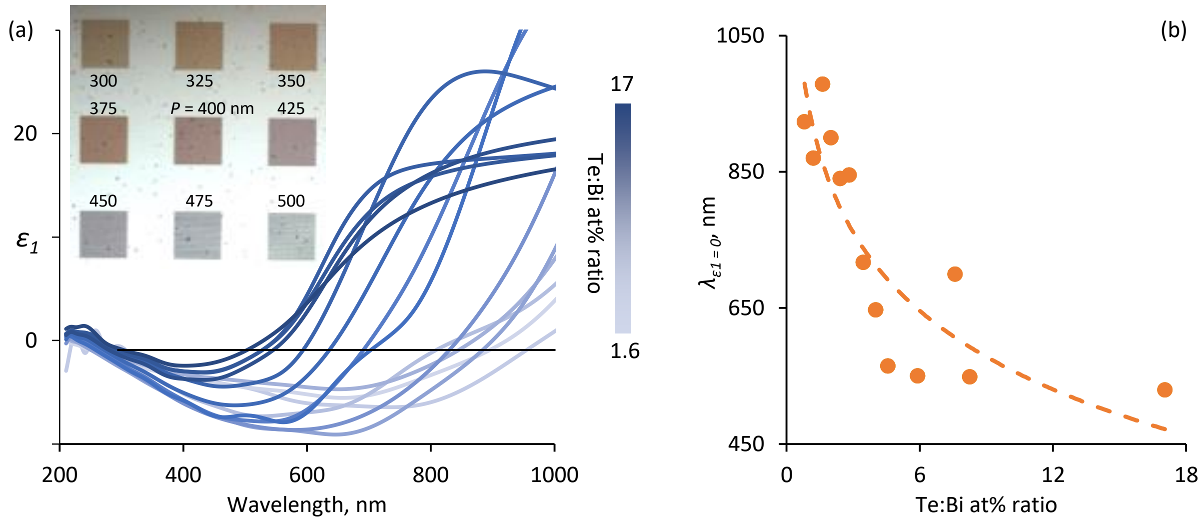

Fig. 1. (a) Real part of the relative permittivity of as-deposited amorphous Bi:Te [from variable angle spectroscopic ellipsometry] for a range of elemental at% ratios over a single compositionally graded thin film sample. The inset shows a TM-polarised optical reflection microscopy image of Bi:Te nano-grating metasurfaces [periods as labelled; surrounding area is unstructured Bi:Te]. (b) Spectral position of the VIS/NIR $\varepsilon 1$ zero-crossing point as a function of Bi:Te compositional ratio.

The chalcogenide's plasmonic character is demonstrated via the fabrication of subwavelength period 'nano-grating' metasurfaces, which under TM-polarized illumination (incident electric field perpendicular to the grating lines) present strong period-dependent plasmonic absorption resonances in the visible range, manifested in the perceived colour of the nanostructured domains in reflection [see inset to Fig. 1a], while for TE-polarized light the metasurface domains are almost indistinguishable from unstructured Bi:Te.

III. Epsilon-Near-Zero Properties of Chalcogenide Metasurfaces

Epsilon-near-zero (ENZ) materials have attracted enormous interest in recent years [1-4] for their potential to enable extraordinary phenomena such as light 'squeezing' or tunnelling without change in optical phase, and they have been studied extensively in the microwave spectral range (both theoretically and experimentally using conventional noble metal plasmonic media). Here, we consider amorphous antimony telluride (Sb:Te) as a material platform for ENZ metamaterials in the UV-VIS spectral range.

Figure 2 presents the optical response of a metasurface based on an array of sub-wavelength holes in an amorphous Sb:Te film. The (finite-difference time-domain) model assumes normally incident narrowband plane wave illumination and (by virtue of periodic boundary conditions) an infinite planar metamaterial array, employing ellipsometrically evaluated optical constants for Sb:Te. A transmission peak is observed at a wavelength of ~250 nm that is independent of the size and period of the holes and the thickness of the Sb:Te film. This is a manifestation of the ENZ-nature of the chalcogenide in this spectral band, illustrated further by the distribution of electric field in the sample plane, which shows light transmitted through the holes with no local enhancement of the field (relative to the incident field) or coupling among neighbouring unit cells of the metamaterial array.

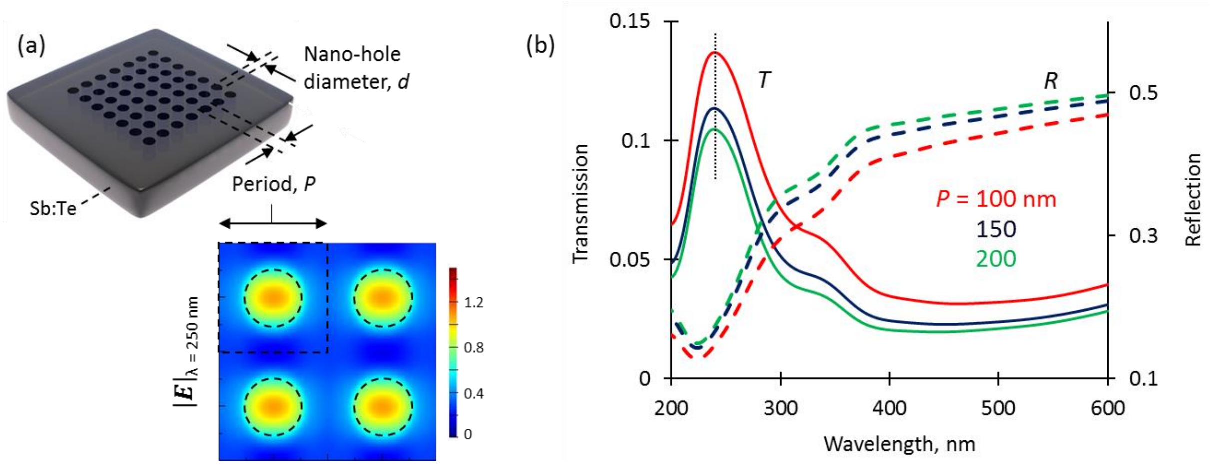

Fig. 2. (a) Sb:Te nano-hole array metasurface schematic and numerically simulated distribution of electric field magnitude [relative to incident field] at the amorphous chalcogenide's UV $\varepsilon_1 = 0$ point. (b) Numerically simulated spectral dispersion of Sb:Te nano-hole metasurface transmission [solid lines] and reflection [dashed] for a selection of different array periods [$d = 40$ nm].

IV. CONCLUSION

In summary, we present the first demonstration of compositionally-tuneable all-chalcogenide material platforms for plasmonic and ENZ metadevices in the UV-VIS spectral range. The chalcogenide family includes numerous binary, ternary and quaternary sulphides, selenides and tellurides, offering a uniquely adaptable, CMOS-compatible material base for plasmonics with compositionally-controlled, and electrically-/optically-switchable, optical properties.

ACKNOWLEDGEMENT

This work was supported by the Engineering and Physical Sciences Research Council (EPSRC), UK [grant no. EP/M009122/1].

REFERENCES

[1] M. Silveirinha and N. Engheta, "Tunneling of Electromagnetic Energy through Subwavelength Channels and Bends using " ε-Near-Zero Materials," *Physical Review Letters,* vol. 97, p. 157403, 2006.

[2] R. Maas, J. Parsons, N. Engheta, and A. Polman, "Experimental realization of an epsilon-near-zero metamaterial at visible wavelengths," *Nature Photonics,* vol. 7, pp. 907-912, 2013.

[3] N. Kinsey, C. DeVault, J. Kim, M. Ferrera, V. M. Shalaev, and A. Boltasseva, "Epsilon-near-zero Al-doped ZnO for ultrafast switching at telecom wavelengths," *Optica,* vol. 2, pp. 616-622, 2015.

[4] M. Z. Alam, I. De Leon, and R. W. Boyd, "Large optical nonlinearity of indium tin oxide in its epsilon-near-zero region," *Science,* vol. 352, pp. 795-797, 2016.