Near-UV-to-near-IR Hyperbolic Photonic Dispersion in Epitaxial (Hf,Zr)N/ScN Metal/Semiconductor Superlattices

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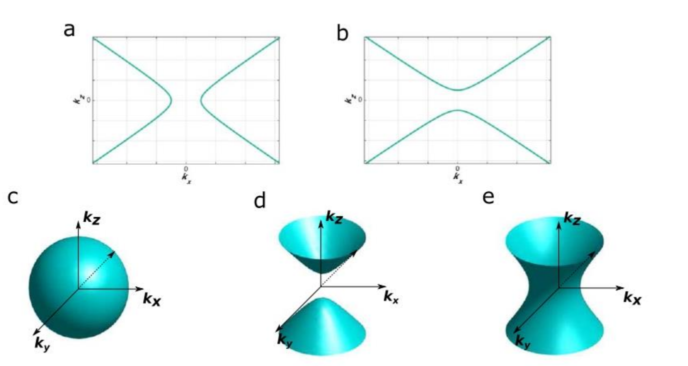
Abstract: Hyperbolic metamaterials have shown great promise in nano-photonic applications due to extreme dielectric anisotropy. Traditionally, noble-metal based metal/dielectric multilayers (Ag/TiO_2, Au/SiO_2) & metallic nano-wires (Ag, Au) embedded in dielectric matrix have been used to demonstrate HMM properties. However, noble-metals are unstable at high temperatures, CMOS incompatible & difficult to deposit in thin film form due to their high surface energies. Transition metal nitride-based TiN/(Al,Sc)N metal/semiconductor superlattices have been developed to exhibit HMM properties but fails to cover full spectral range (near-UV-to-near IR) due to it's longer ENZ wavelength compared to Ag. Here, we demonstrate hyperbolic photonic dispersion in epitaxial (Hf,Zr)N/ScN metal/semiconductor superlattices that covers near-UV to near-IR spectral ranges along with high thermal stability, CMOS compatibility & high figure-of-merit.

Hyperbolic Metamaterials (HMM)

- **Metamaterials** : Artificially designed structure with property that is not found in natural materials.
- **Hyperbolic Metamaterials (HMMs)** :
  - Anisotropic, uniaxial, sub-wavelength metamaterials where principal components of electric permittivity (ε) have different signs.
  - Iso-frequency curve in k-space is hyperboloid following the dispersion relation, $\frac{k_{\parallel}^2}{\varepsilon_{\perp}} + \frac{k_{\perp}^2}{\varepsilon_{\parallel}} = \frac{w^2}{c^2}$
  - Types – (a) Type-I HMM ($\varepsilon_{\parallel} > 0$, $\varepsilon_{\perp} < 0$)
    (b) Type-II HMM ($\varepsilon_{\parallel} < 0$, $\varepsilon_{\perp} > 0$)



(a) Iso-frequency curve in k space for $\varepsilon_{\perp} > 0$, $\varepsilon_{\parallel} < 0$. (b) Iso-frequency curve in k space for $\varepsilon_{\perp} < 0$, $\varepsilon_{\parallel} > 0$. (c) Iso-frequency surface for isotropic media. (d) Iso-frequency surface for $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\parallel} > 0$, $\varepsilon_{zz} = \varepsilon_{\perp} < 0$. (e) Iso-frequency surface for $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\parallel} < 0$, $\varepsilon_{zz} = \varepsilon_{\perp} > 0$

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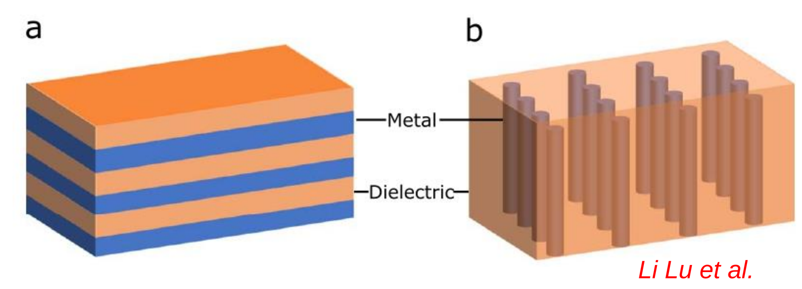
Noble-metal based HMM



Schematic HMM designs: (a) multi-layered HMM, (b) nano-wire HMM

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- **Designs** :
  - Metal/dielectric periodic multilayers (Ag/Al_2O_3, Ag/TiO_2, Au/TiO_2) & Metallic nanowires (Ag, Au) embedded inside dielectric matrix.
  - Exhibit hyperbolic dispersions starting from 390nm covering full visible spectral range.
- **Challenges** :
  - Noble metals are soft.
  - Unstable at high temperatures.
  - CMOS incompatible
  - Difficult to grow in thin film form due to high surface energies.

TMN-based HMM

- **Transition metal nitrides (TMNs)** : TiN, HfN, ZrN, ScN etc.
  - TMNs are corrosion-resistant, hard, stable at high temperatures, CMOS compatible.

HfN	ZrN	ScN
T_m=3578 K	T_m=3253 K	T_m=2873 K
H_v=24.5 GPa	H_v=22.1 GPa	H_v=25.1 GPa

  - Epitaxial TiN/(Al,Sc)N metal/semiconductor superlattices exhibit HMM properties in visible-to-near-IR spectral range as TiN has Epsilon-near-zero (ENZ) wavelength of 500 nm.

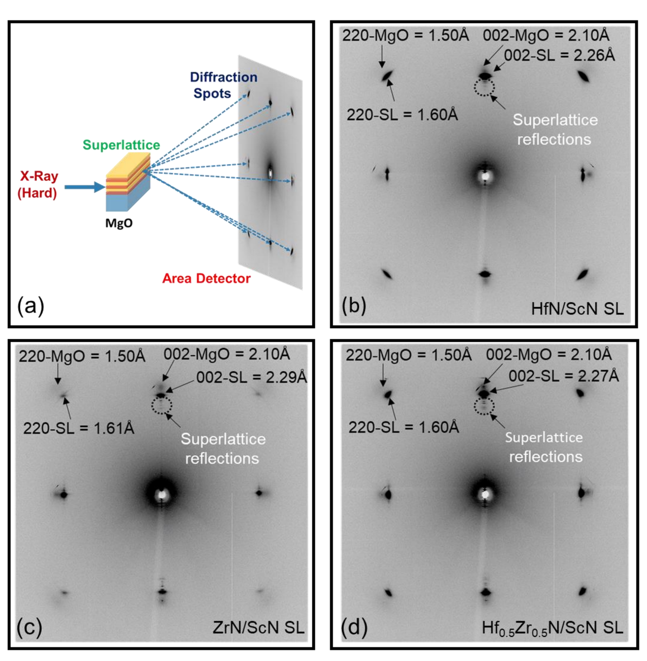
Frequencies	UV	Visible		NIR
Materials	Ag/Al_2O_3	Ag/TiO_2	Ag/Ti_3O_5	TiN/(Al,Sc)N
		Au/TiO_2	Ag/laser dye	Al:ZnO/ZnO
		Ag/MgF_2	TiN/(Al,Sc)N	

?

- **Motivation** :

To show near-UV-to-near-IR hyperbolic dispersion by growing epitaxial (Hf,Zr)N/ScN metal/semiconductor superlattices as ZrN and HfN exhibit ENZ at 340 nm and 370 nm respectively.

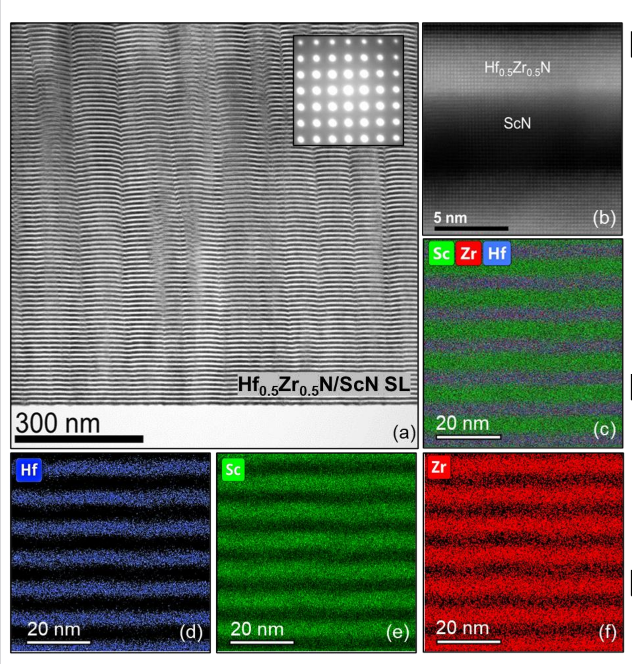
Synchrotron radiation XRD Analysis



(a) Schematic of synchrotron-radiation 2D X-ray diffraction imaging of superlattice in transmission mode. Diffraction patterns of (b) HfN/ScN, (c) ZrN/ScN, and (d) $Hf_{0.5}Zr_{0.5}N$/ScN superlattices.

- HfN/ScN, ZrN/ScN, and $Hf_{0.5}Zr_{0.5}N$/ScN superlattices deposited on (001) MgO substrates show (002) oriented growth as evidenced by the 002 reflections.
- *d*-spacing of 2.26 Å for HfN/ScN, 2.29 Å for ZrN/ScN, and 2.27 Å for $Hf_{0.5}Zr_{0.5}N$/ScN superlattices are measured.

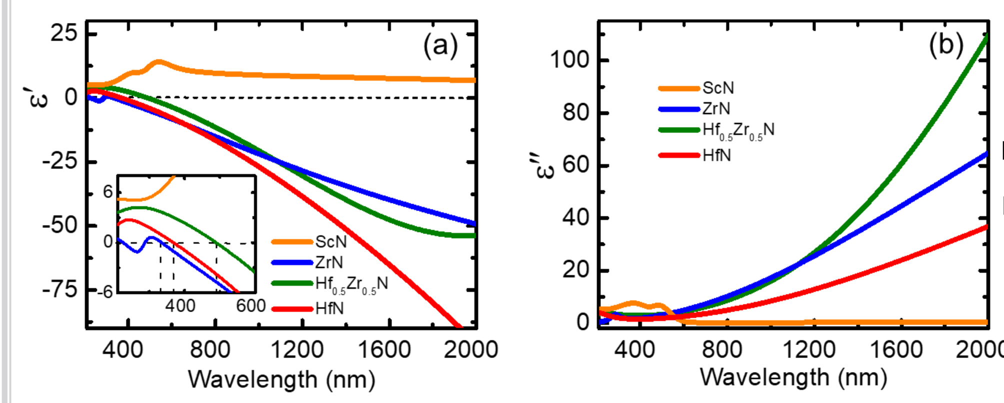
HR(S)/TEM Analyses



(a)(HAADF)-STEM micrograph of a $Hf_{0.5}Zr_{0.5}N$/ScN superlattice. (b) (HR(S)/TEM) image of $Hf_{0.5}Zr_{0.5}N$/ScN superlattice (c) combined STEM-energy-dispersive X-ray spectroscopy (EDS) and (d-f) individual element maps.

- A low-magnification STEM image of an $Hf_{0.5}Zr_{0.5}N$/ScN superlattice shows the superlattice layer growth on the $Hf_{0.5}Zr_{0.5}N$/MgO buffer/substrate layer.
- The interface between the superlattice and bottom metallic buffer layer is sharp.
- Cubic epitaxial growth with an orientation relationship of (001) [001] $Hf_{0.5}Zr_{0.5}N$/ScN || (001) [001] MgO.

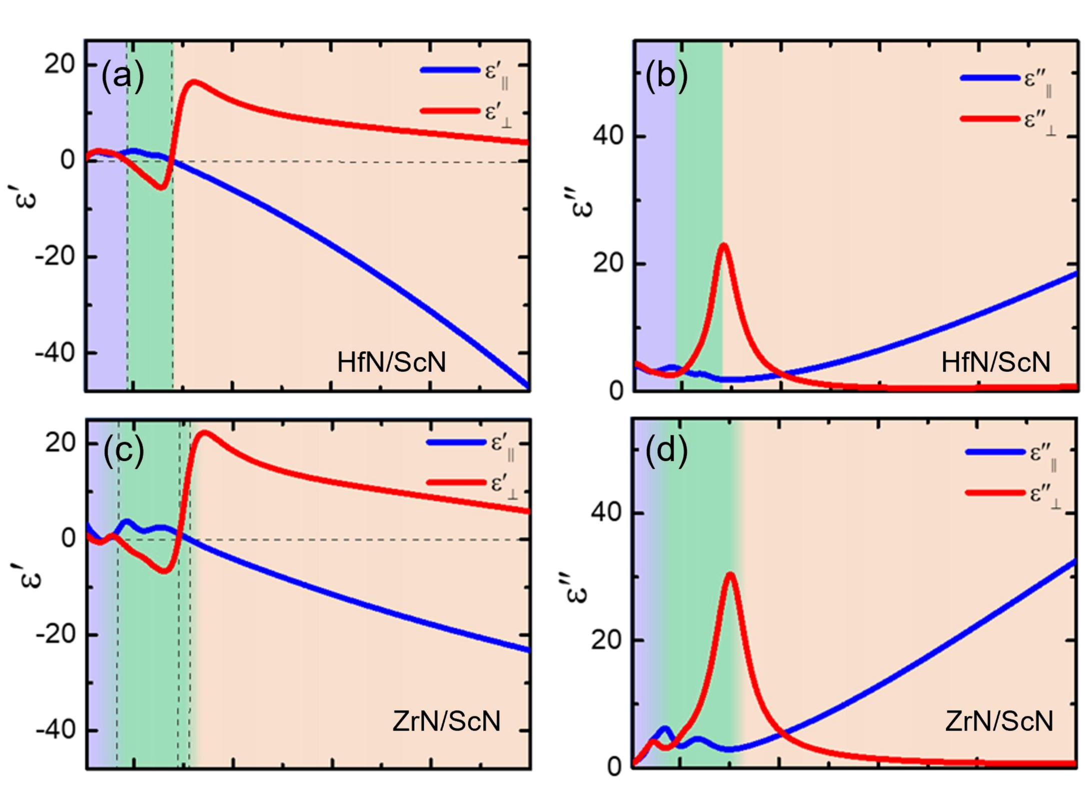
Optical Properties



(a) Real and (b) imaginary parts of dielectric permittivity of the constituent layers (HfN, ZrN, $Hf_{0.5}Zr_{0.5}N$, ScN) of the superlattices

- HfN, ZrN, and $Hf_{0.5}Zr_{0.5}N$ exhibit ϵ' positive-to-negative cross-over at 370 nm, 340 nm, and 490 nm, respectively.
- At the cross-over wavelength, ϵ'' for the HfN, ZrN, and $Hf_{0.5}Zr_{0.5}N$ films is comparable to Au and Ag.
- ScN exhibits a dielectric optical characteristic consistent with its semiconducting nature with a direct bandgap of 2.2 eV.

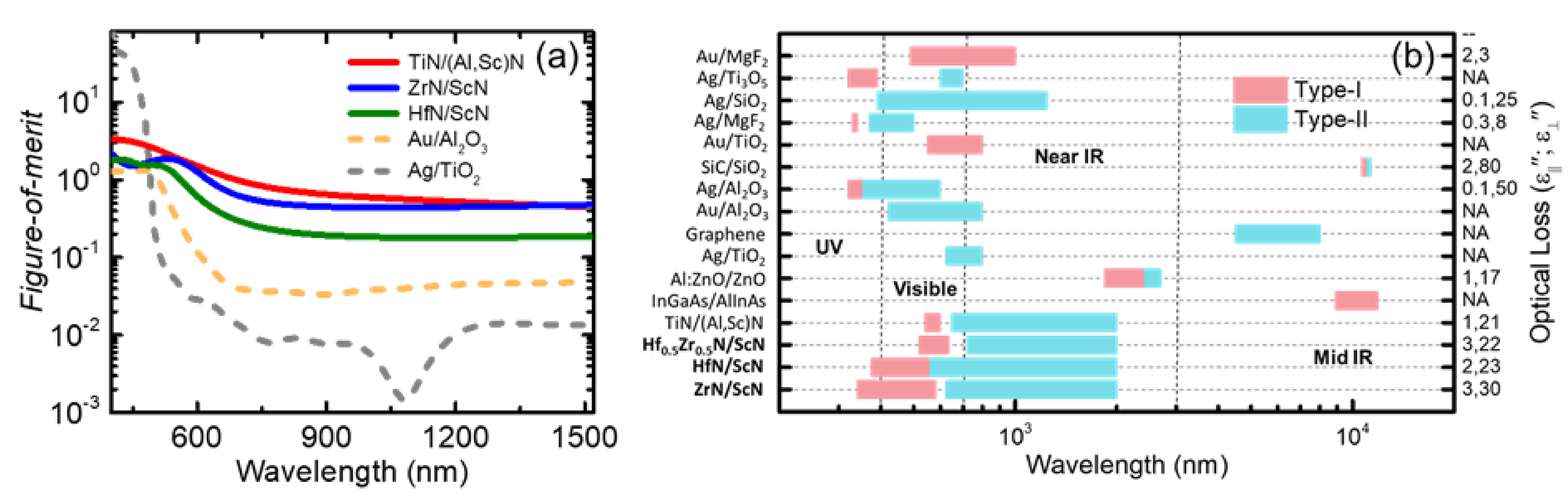
Hyperbolic Dispersion



Real and imaginary components of the effective permittivity for the HfN/ScN (a and b), ZrN/ScN (c and d) superlattices

- HfN/ScN superlattices exhibit type-I hyperbolic dispersion from 375 nm to 560 nm and type-II hyperbolic dispersion from 560 nm to 2000 nm.
- ZrN/ScN superlattices exhibit type-I hyperbolic dispersion from 340 nm to 580 nm and type-II hyperbolic dispersion from 625 nm to 2000 nm.
- $\epsilon_{\perp}''$ of both superlattices exhibits a Gaussian-like sharp peak centered at the type-I to type-II cross-over wavelength.

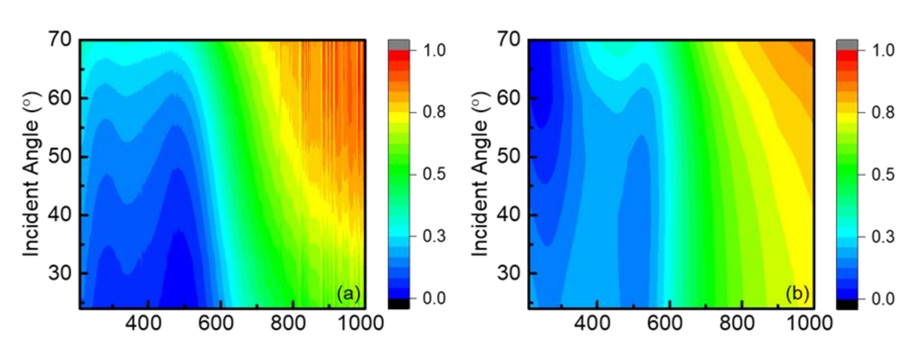
Figure-of-merit



(a) Figure-of-merit (FOM) of HfN/ScN and ZrN/ScN superlattices (b) Hyperbolic wavelength bands for various metal/dielectric multilayers

- Compared to the Ag/TiO_2 and Au/Al_2O_3 HMMs, HfN/ScN and ZrN/ScN superlattices exhibit about 10 times higher FOM ($\frac{Re(k_{\perp})}{Im(k_{\perp})}$) in the long-wavelength spectral range.
- With the development of (Hf,Zr)N/ScN superlattice HMMs, the entire near-UV-to-visible-to-near-IR region of the spectrum can be covered with TMN-based materials.

Angle-dependent Reflection



(a) Experimental and (b) Theoretically calculated reflection spectra of the HfN/ScN superlattice as a function of incident angles.

- At longer wavelengths, high reflectivity is observed in both experiment as well as in the modelling.
- As the wavelength is reduced, two dips in the reflection spectra at ~290 nm and ~ 485 nm are observed.

Conclusions

- We extend the spectral operation range of the TMN-based HMMs by developing epitaxial (Hf,Zr)N/ScN metal/semiconductor superlattice.
- Synchrotron-radiation XRD and HR(S)/TEM analyses are performed to demonstrate cubic epitaxial crystal growth on (001) MgO substrates.
- The figure-of-merit (FOM) of these HMMs is found to be high.

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