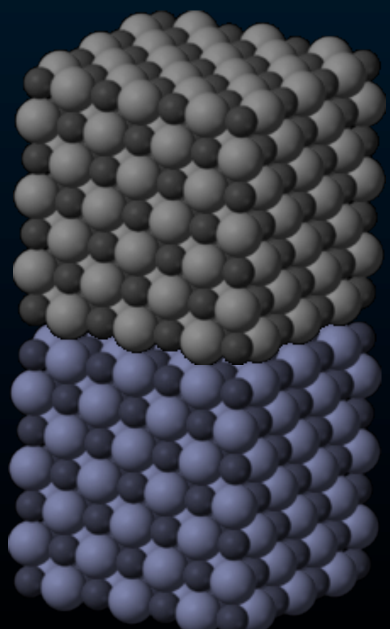
DOPED SEMICONDUCTORS AND CERAMIC MATERIALS: NEW PLATFORM FOR PLASMONICS

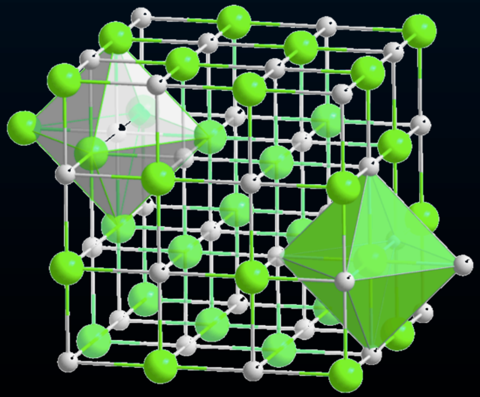


BUILDING NANOSCALE PHOTONIC TECHNOLOGIES OF THE FUTURE

Alexandra Boltasseva
School of Electrical & Computer Engineering
Birck Nanotechnology Center
PURDUE UNIVERSITY

OUTLINE

- Introduction: Plasmonics & Metamaterials
- Material Requirements: Challenges with Gold and Silver
- Alternative Materials?
- Transparent Conducting Oxides
- **Transition Metal Nitrides**
- Figures of Merit and Applications
- CMOS- and Refractory Plasmonics
- Outlook



METALS TO 'LESS-METALS'

- Reduce carrier concentration:
  Mixing them with non-metals ⇒

  Intermetallics

  Ceramics

  - Silicides
  - Germanides
  - Borides
  - Nitrides
  - Oxides
  - Metallic alloys

Wiki: Ceramics = metal + non-metal

TITANIUM NITRIDE

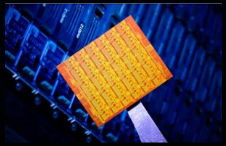
- Metallic: Golden luster
- Hard & tough: high speed drill-bits, coatings

http://www.harborfreight.com

- Mechanically, chemically stable

BIO-COMPATIBLE

CMOS COMPATIBLE

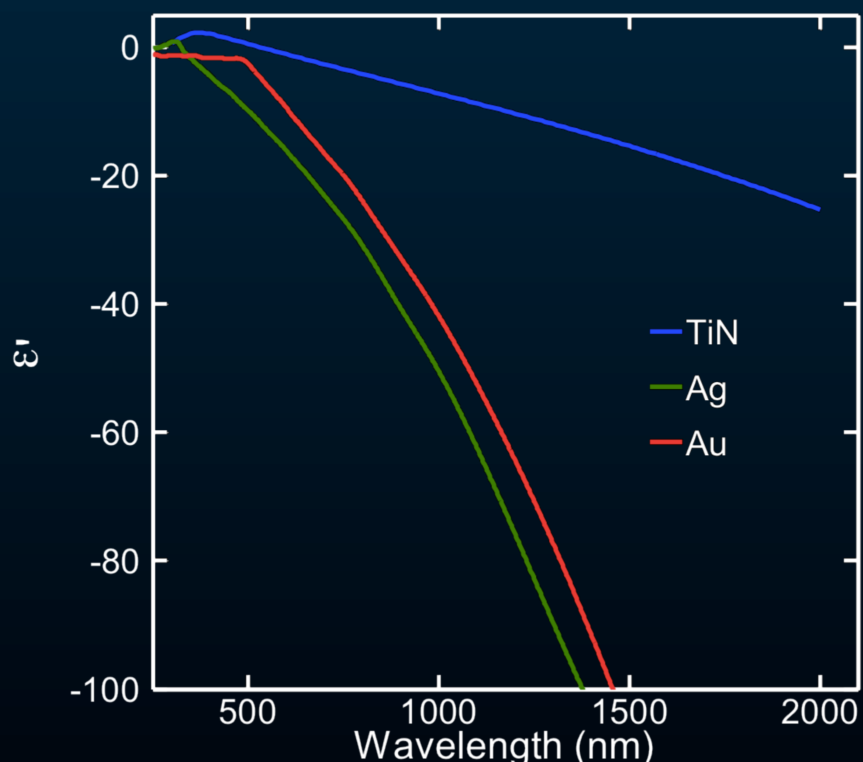


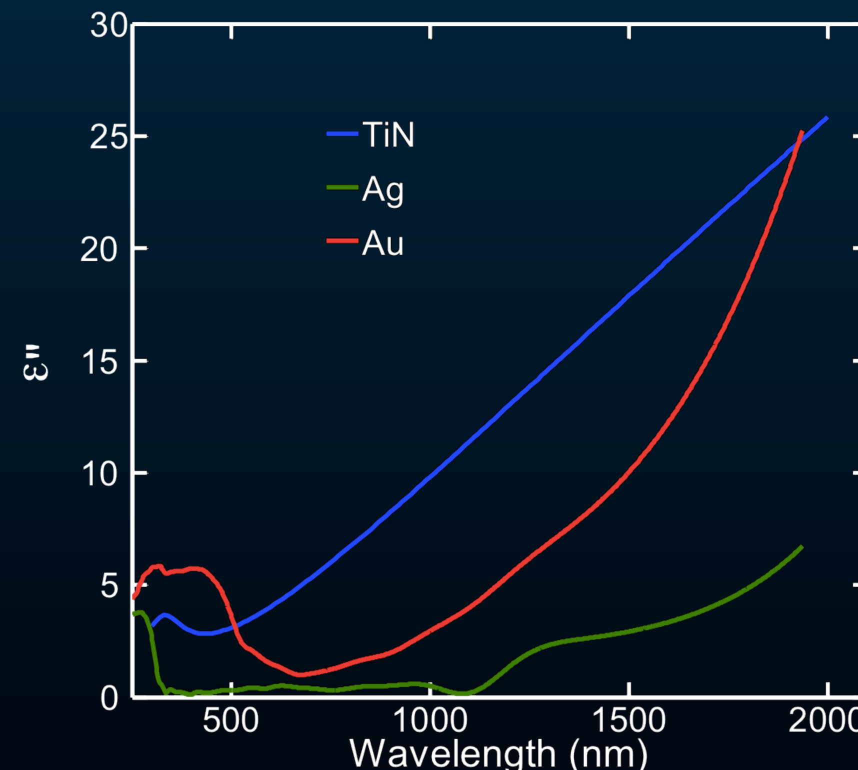
Intel 48 cores cloud processor

FIKO Electron-beam metallurgical plant

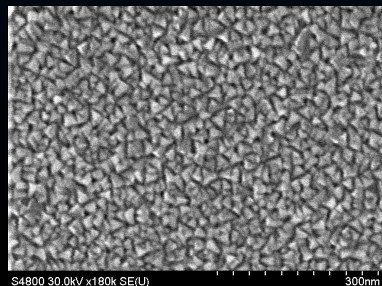
TITANIUM NITRIDE

Plasmonic! With tailorable properties





Ultra-thin
Smooth
Epitaxial growth



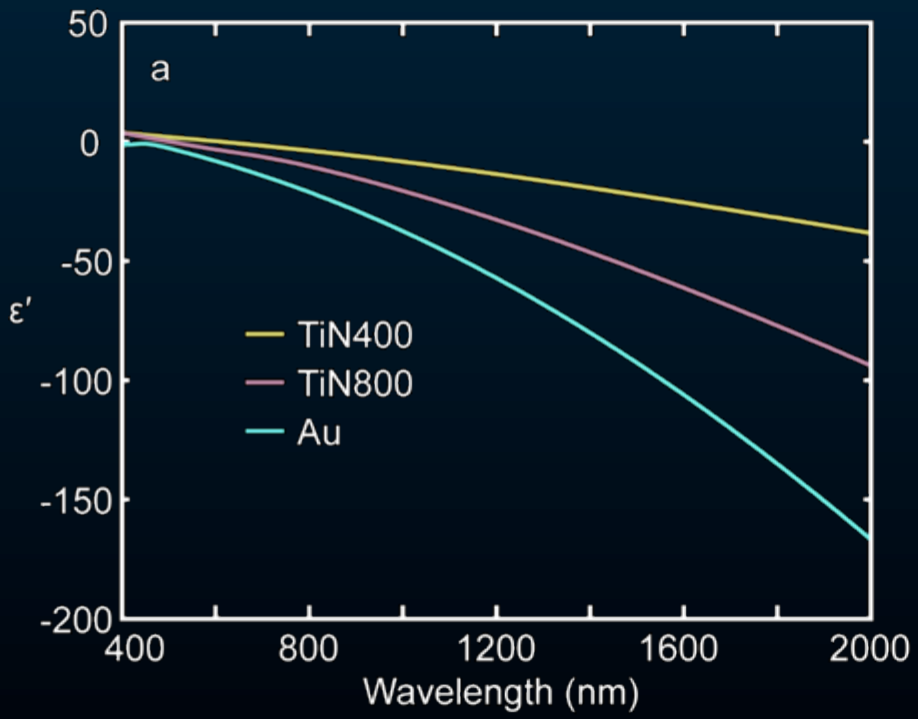
Crystalline TiN on c-Sapphire
(rms roughness 0.5 nm)

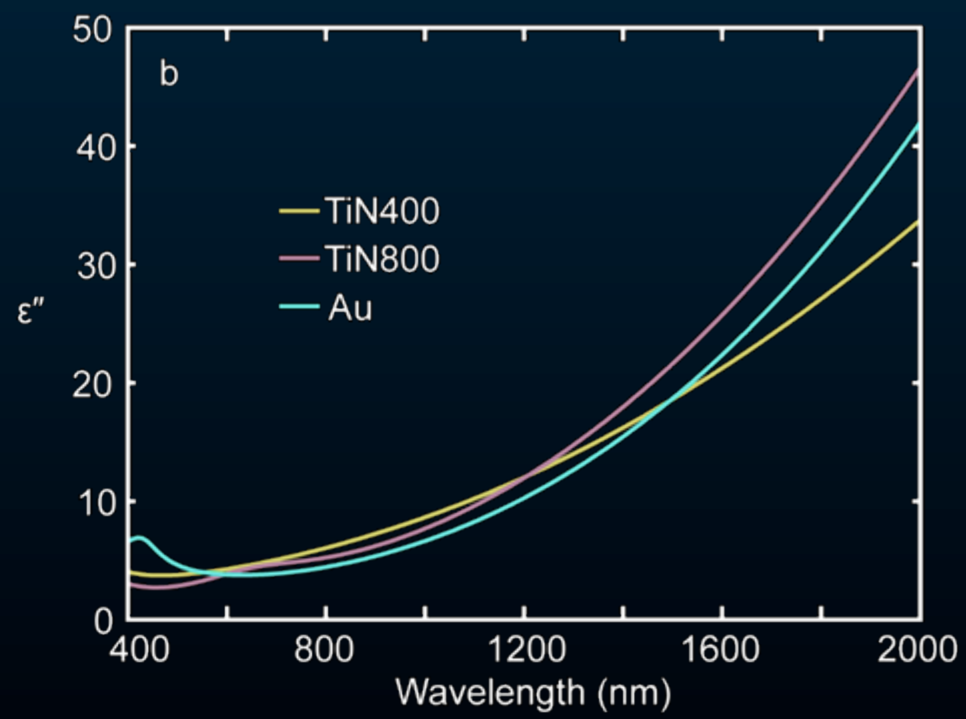
G.V. Naik et al., Optical Materials Express 2, 478 (2012)

TITANIUM NITRIDE

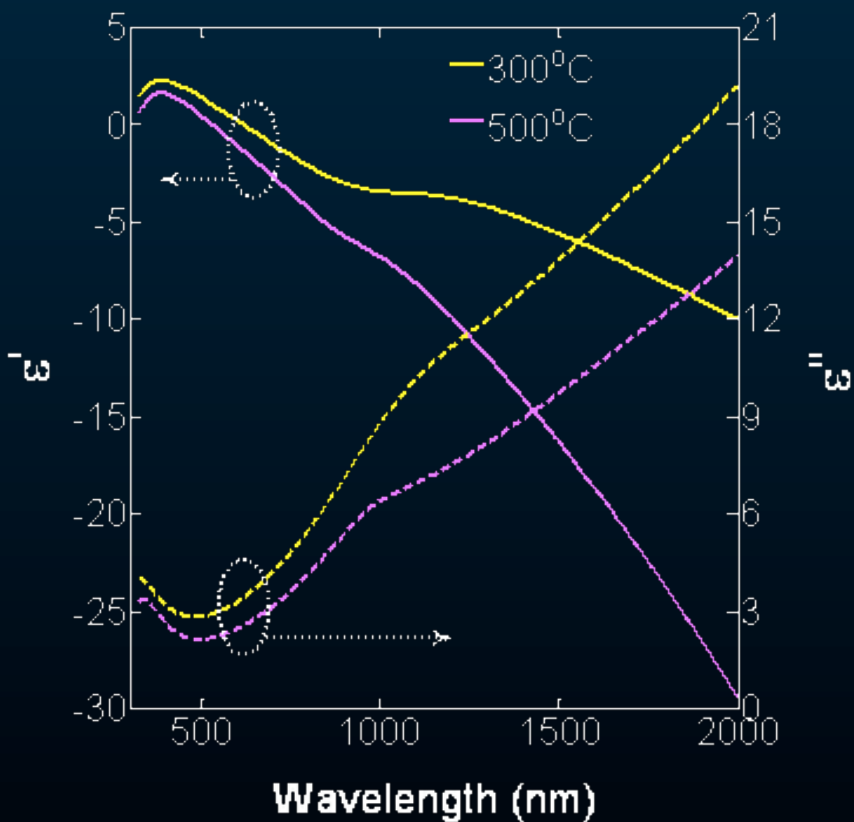
Purdue University

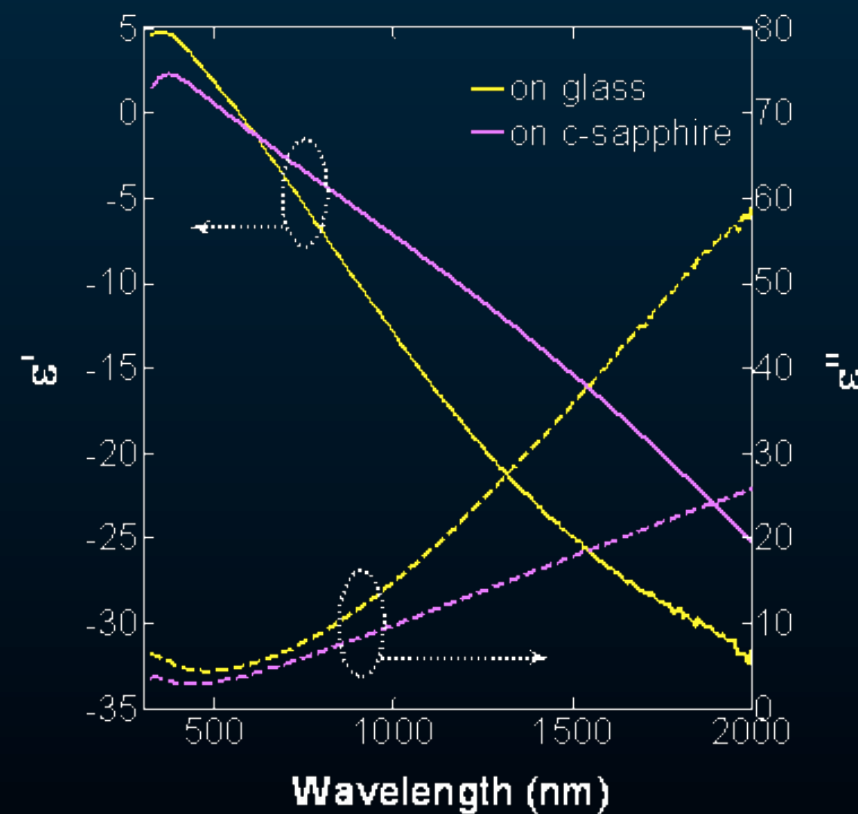
Tailorable properties





TITANIUM NITRIDE: OPTIMIZATION



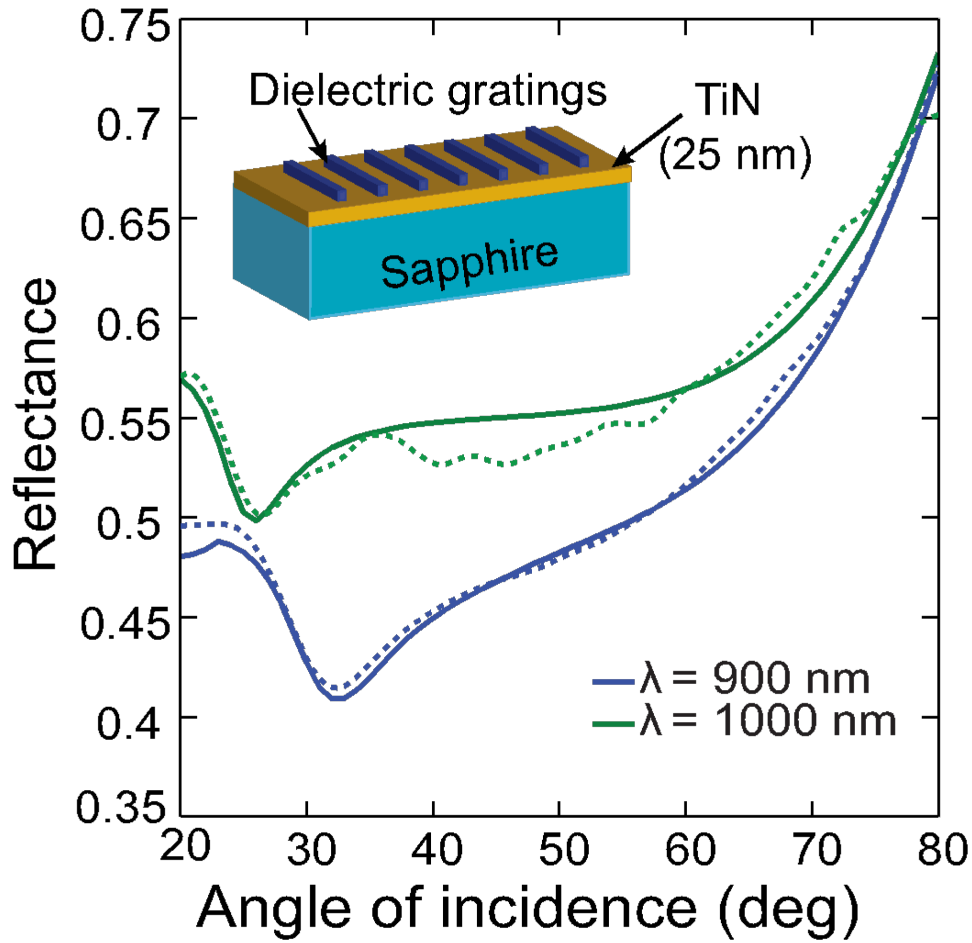


- TiN films deposited at 300^{o}C and 500^{o}C (left)
- TiN films deposited on different substrates (right)
- The films were deposited with the flow ratio of Ar and N set to 4:6

G.V. Naik et al, Optical Materials Express **2** (2012)

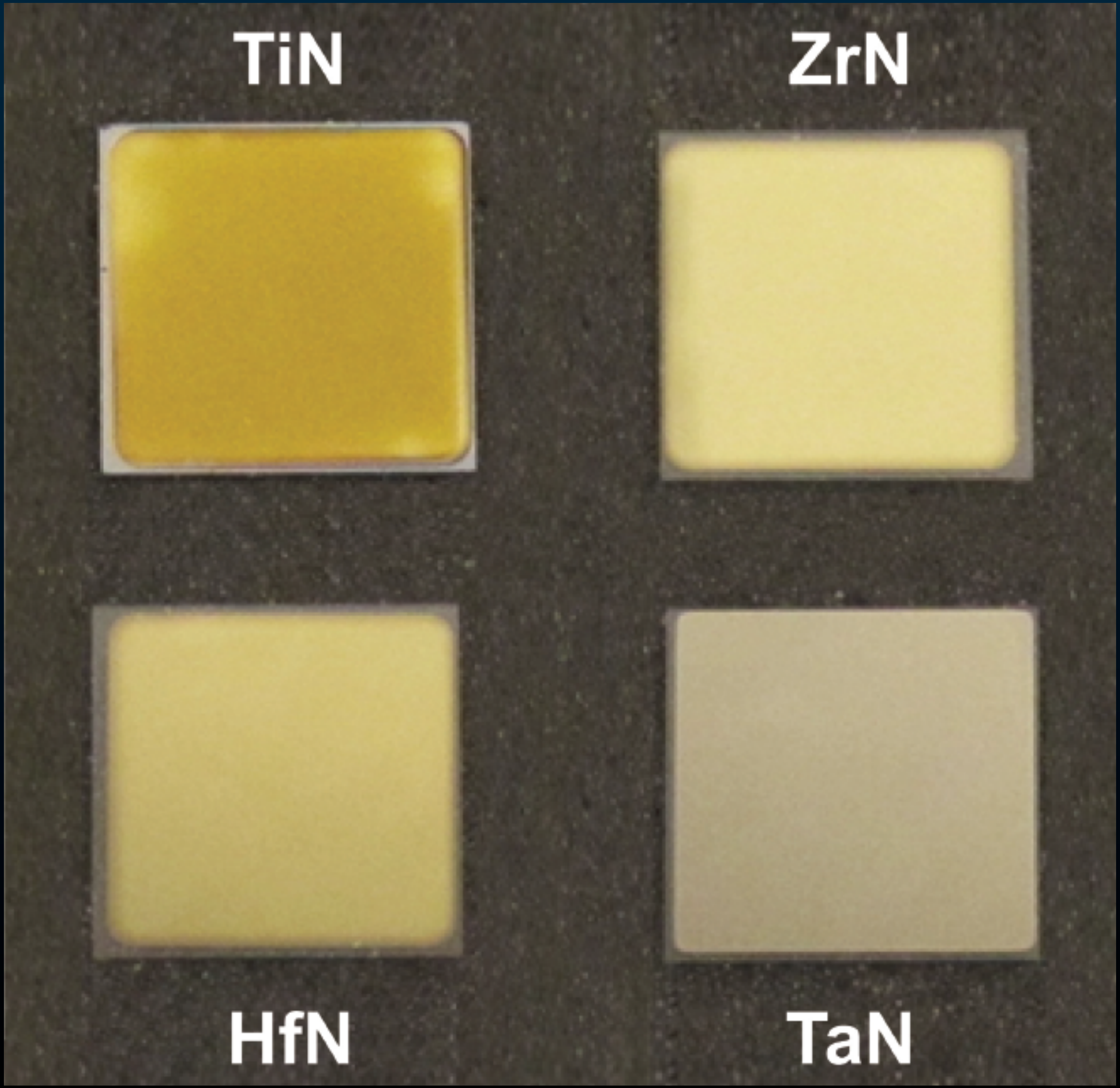
SPP ON TiN FILM

- Dielectric gratings are used to couple SPPs
- Electron-beam resist is patterned into gratings on top of 25 nm thin TiN film
- Angular reflectance shows dip at angles corresponding to excitation of SPPs



G.V. Naik *et al.*, Optical Materials Express 2 (2012) p. 478

TRANSITION METAL NITRIDES



G. Naik, V. Shalaev, A. Boltasseva, Advanced Materials 25 (24), 3264 (2013)

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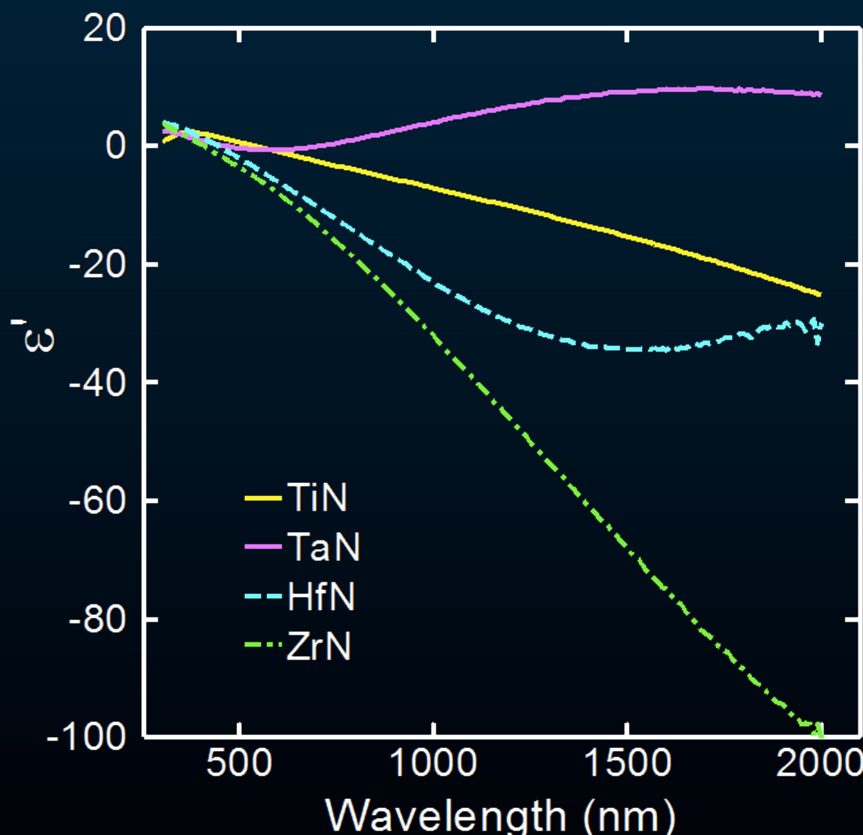
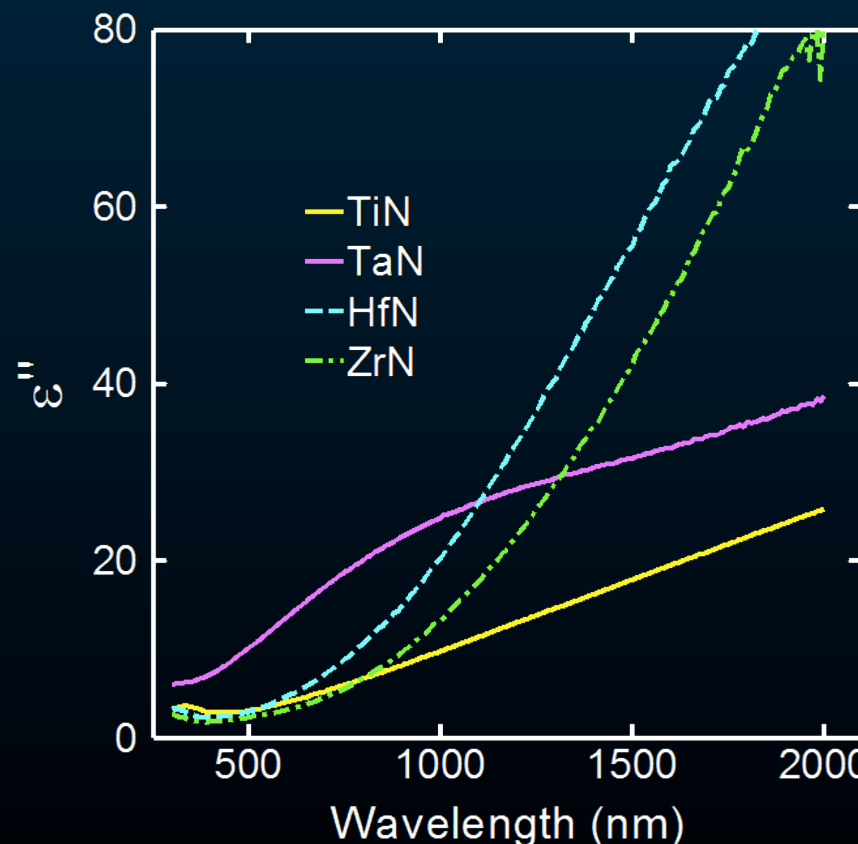
TRANSITION METAL NITRIDES

TaN, HfN, ZrN also exhibit metallic properties in the visible!

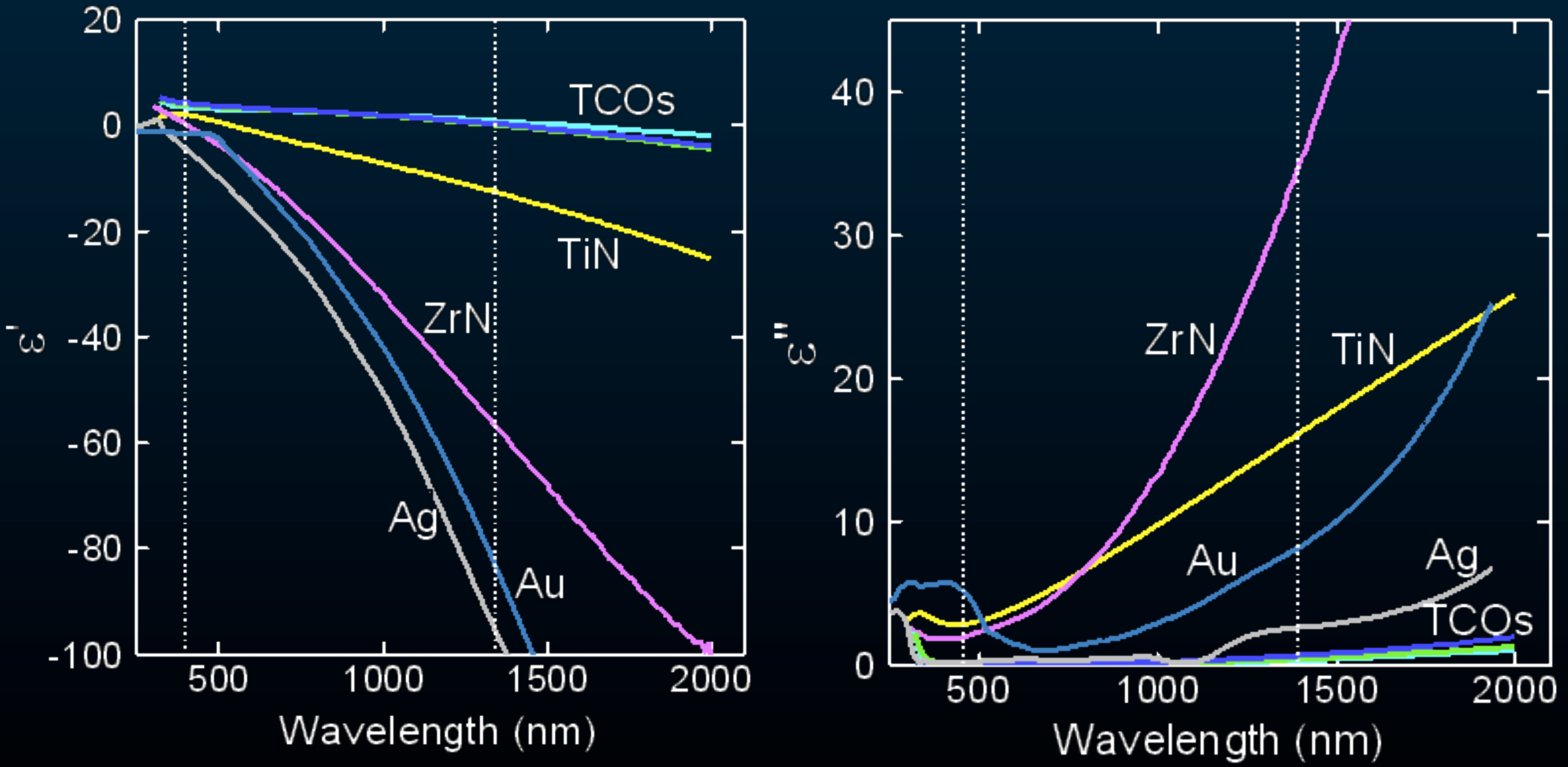




Non stoichiometric!

G.V. Naik, Optical Mater. Exp. 1 , 1090 (2011)

COMPARISON WITH SILVER/GOLD



G.V. Naik, Optical Mater. Exp. 1 , 1090 (2011)

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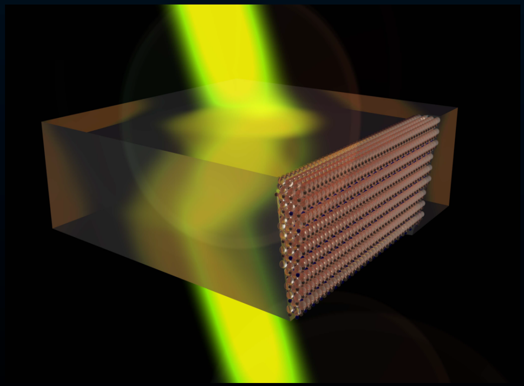


QUALITY FACTORS

- **Im(ε) = ε'' is a necessary indicator of performance *but***
- **Re(ε) = ε' is also important** in quantifying the overall material quality in devices

Metrics/Figures-of-Merit/Quality Factors

are to be estimated for each **APPLICATION**

- Wavelength range
- Materials
- Fabrication...

P. R West et al., Laser & Photonics Reviews (2010)

QUALITY FACTOR FOR SP

LSPR and SPR systems: Local-field enhancement

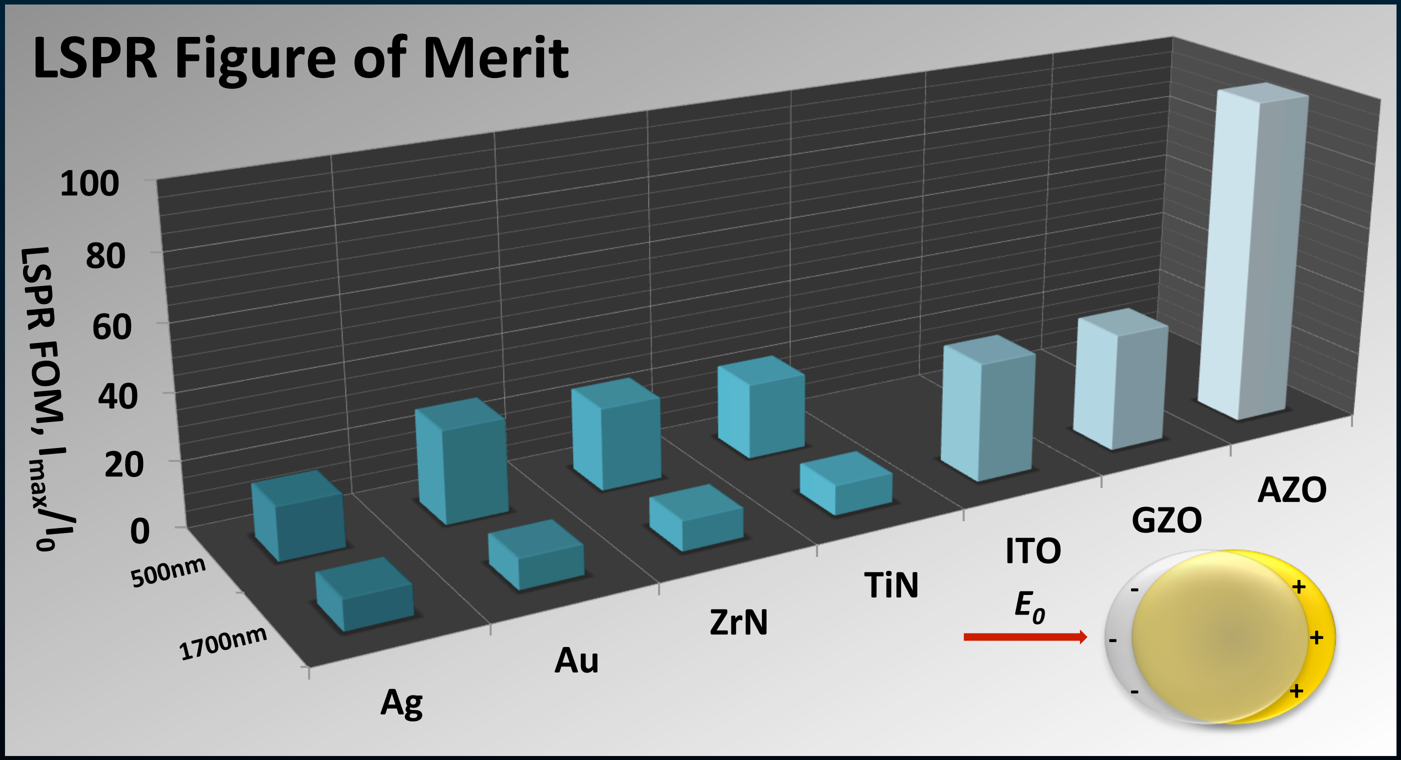
Q_{LSPR} = (Enhanced local-field)/(Incident field)
(depends on the shape)

$$Q_{\mathrm{LSPR}}(\omega) = \frac{-\varepsilon'(\omega)}{\varepsilon''(\omega)}$$ *(sphere)*

P. R West *et al.*, *Laser & Photonics Reviews* 4, 795–808 (2010)

TCOs: LOCALIZED SPR

Max LSPR field intensity enhancement for spherical nanoparticles

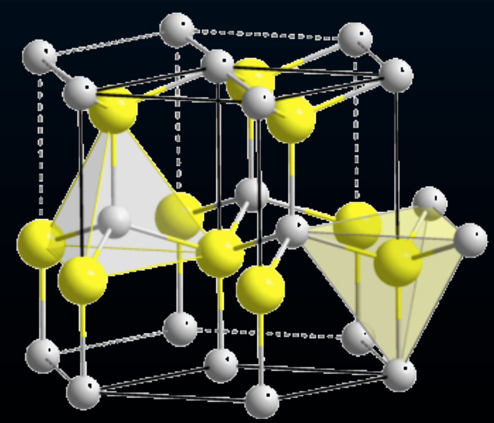


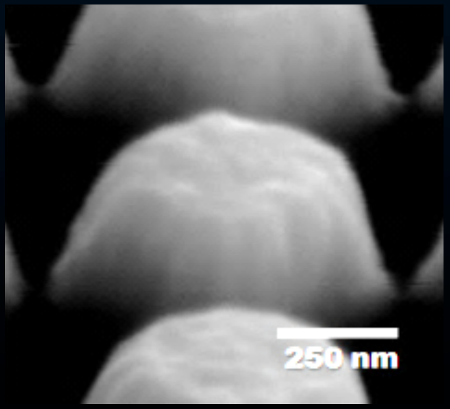
n=1.33
LSPR occurs
$\varepsilon_{metal}' = -2\varepsilon_{diel}$
(dipolar)

- Difficult to obtain for Ag and Au in NIR
- Need other geometries (core-shells): more challenging to fabricate
- TCOs produce strong LSPR in the near and further IR
- TiN broad resonance with higher absorption in biological window

LOCALIZED SPR IN TCOs

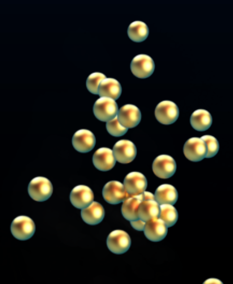
- TCOs could enable LSPR applications in the **NIR** without the need for complex geometries such as core-shell structures (simple spheres)
- Adjustable/Tailorable (while preparing)
- Tunable/Switchable (electrochemical, anneal, electro-, optical means)
- Conventional nanofabrication techniques
- SC-compatible technology



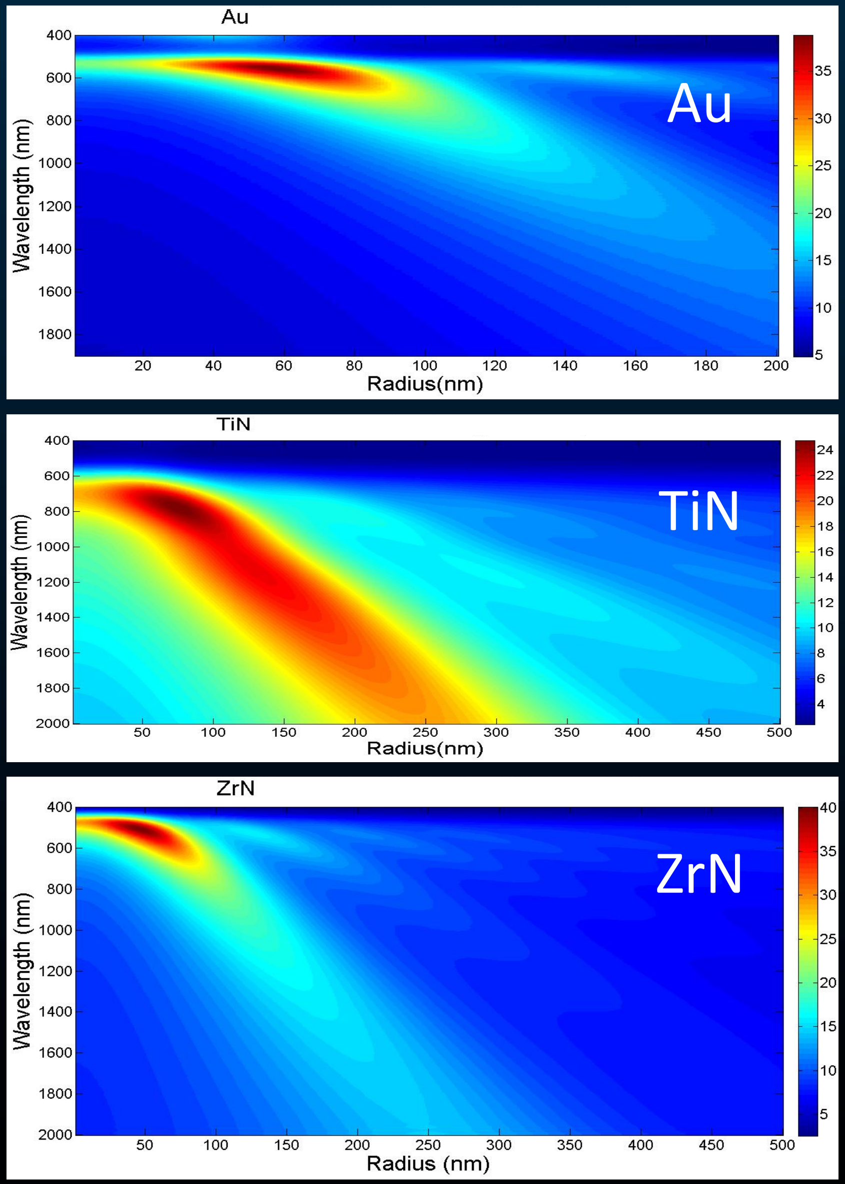


COMPARISON: LSPR

- Field enhancement of metal nanospheres at the surface calculated using Mie theory
- ZrN and TiN nanospheres: Field enhancement comparable to that of Au
- TiN has good broadband performance in the visible and near-IR



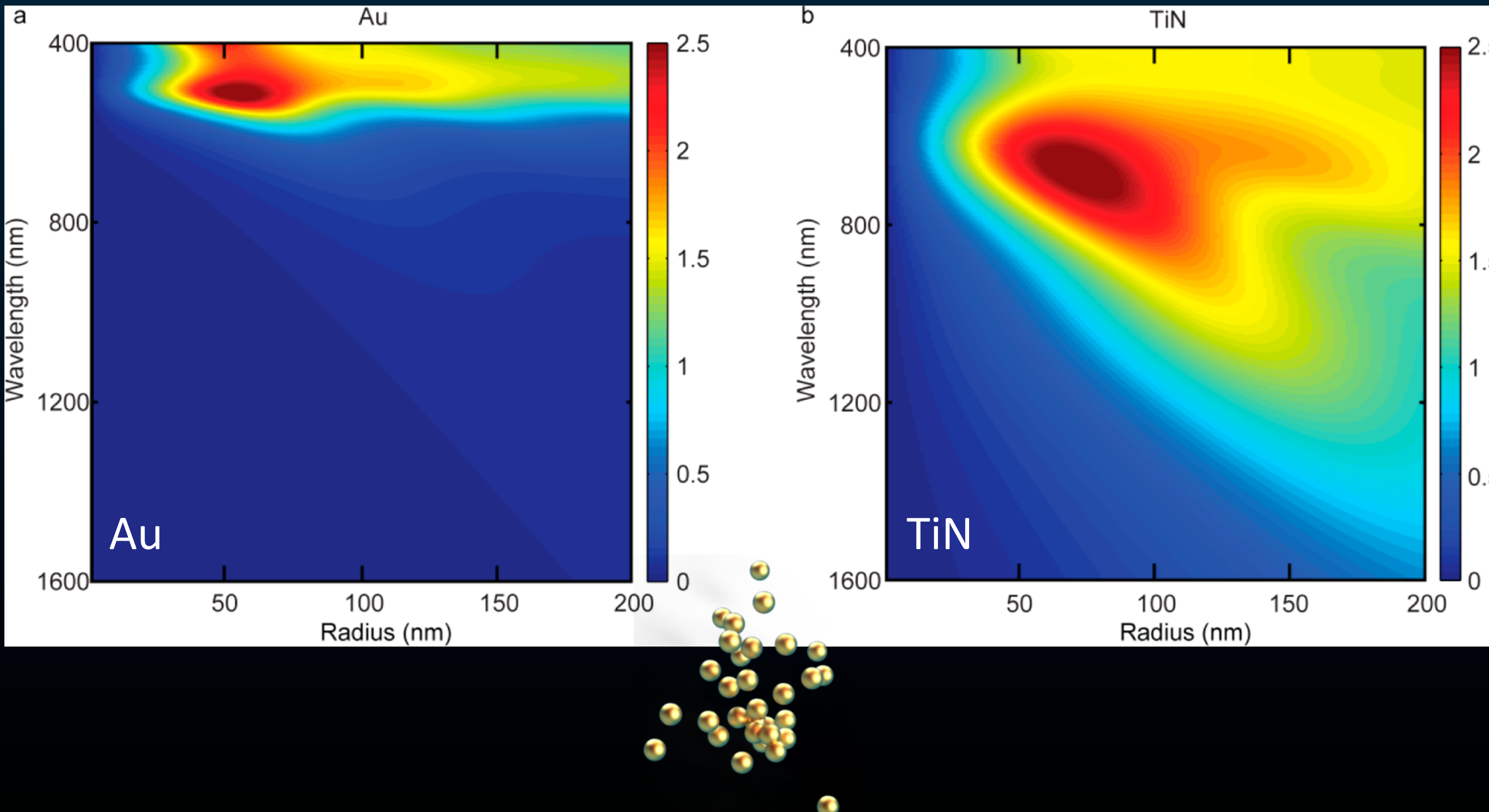
near field intensity enhancement



U. Guler et al., Appl. Phys. B; 107, 285 (2012)

LSPR APPLICATIONS: TiN

Scattering Efficiencies

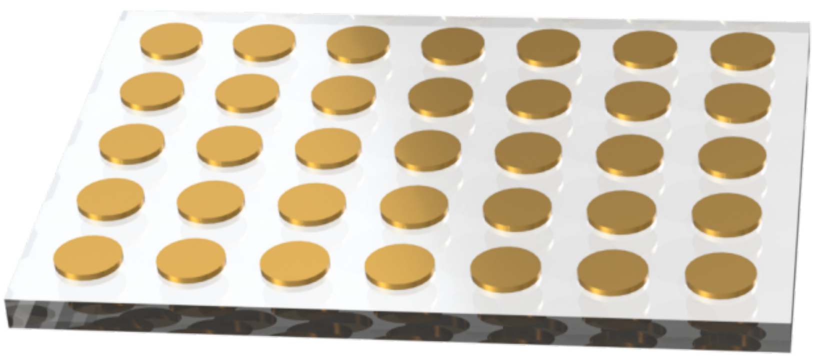


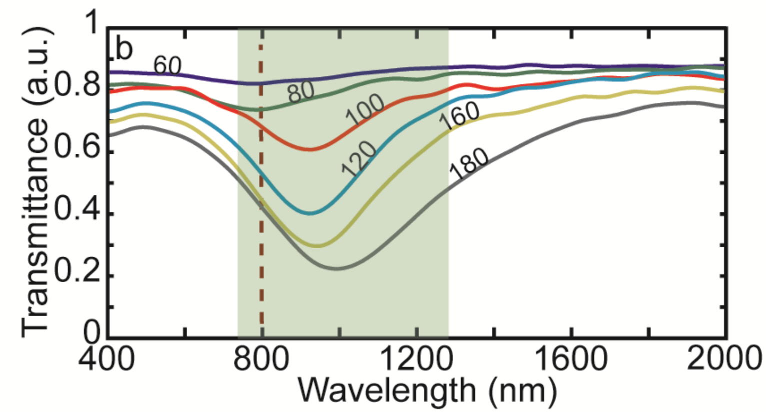
U. Guler et al., Appl. Phys. B; 107, 285 (2012)

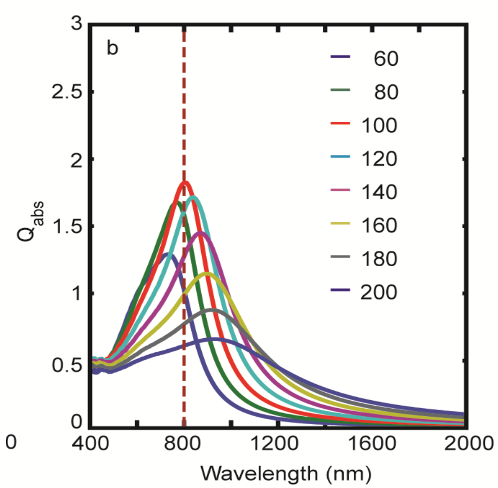
LSPR - TRANSMITTANCE

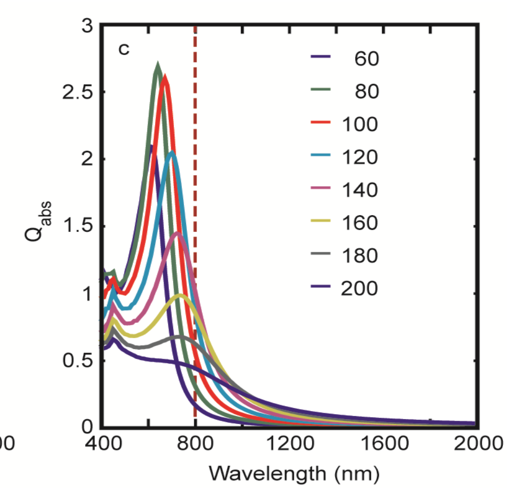
Broad resonance with higher absorption in biological window: Therapeutical applications

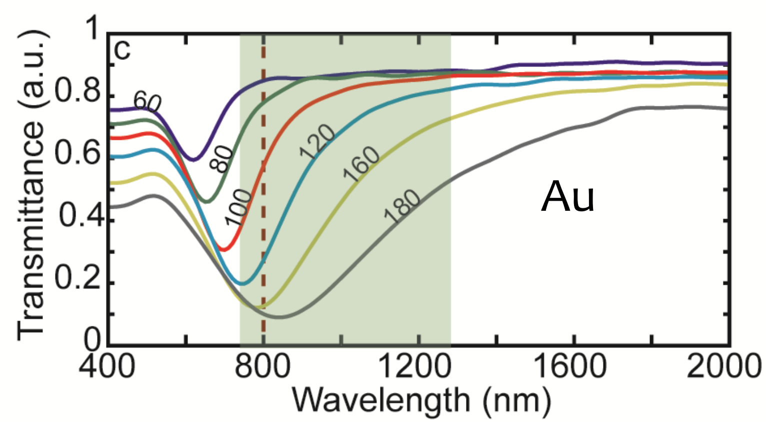
TiN grown @ 800 °C











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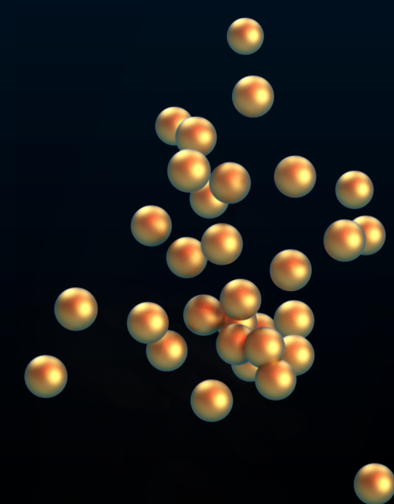
NTT (Nanoparticle Thermal Therapies)

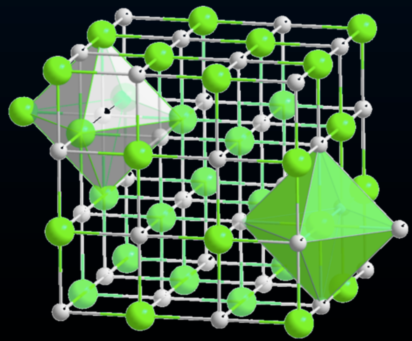
- *Highly targeted cancer therapy without invasive surgery*
- **Problem**: The most recognized biocompatible plasmonic nanoparticle is gold
  - Gold is not naturally resonant in the biological window
  - Requires larger particle sizes and complex shapes
  - Larger sizes & surfactants reduce tumor absorption
- **Solution**: Ceramic plasmonic nanoparticles
  - Made of non-toxic, biocompatible material
  - Naturally resonant in biological window
  - Other apps include drug delivery & imaging



Patent Pending

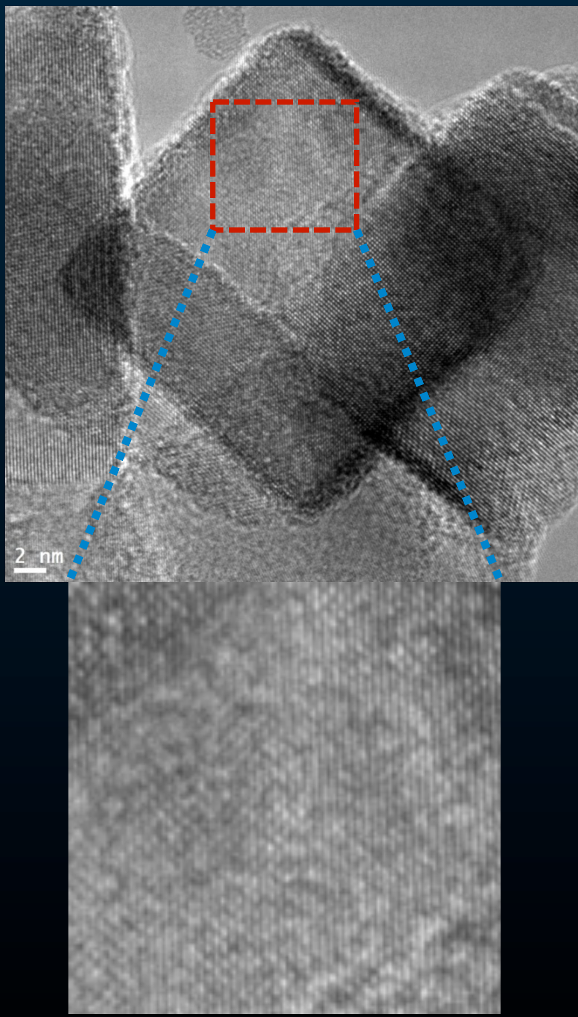
LSPR IN TiN

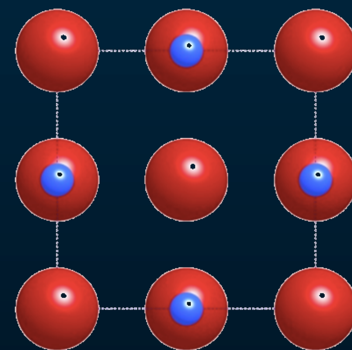
- TiN LSPR cover the entire biological window
- Absorption and heating is higher than Au in this region
- Small, simple TiN nanoparticles can be used for photothermal threatment
  - No need for complex shapes, closely packed assemblies etc.

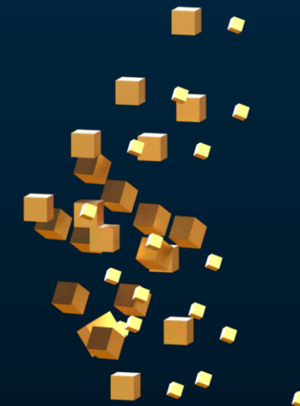


Patent pending

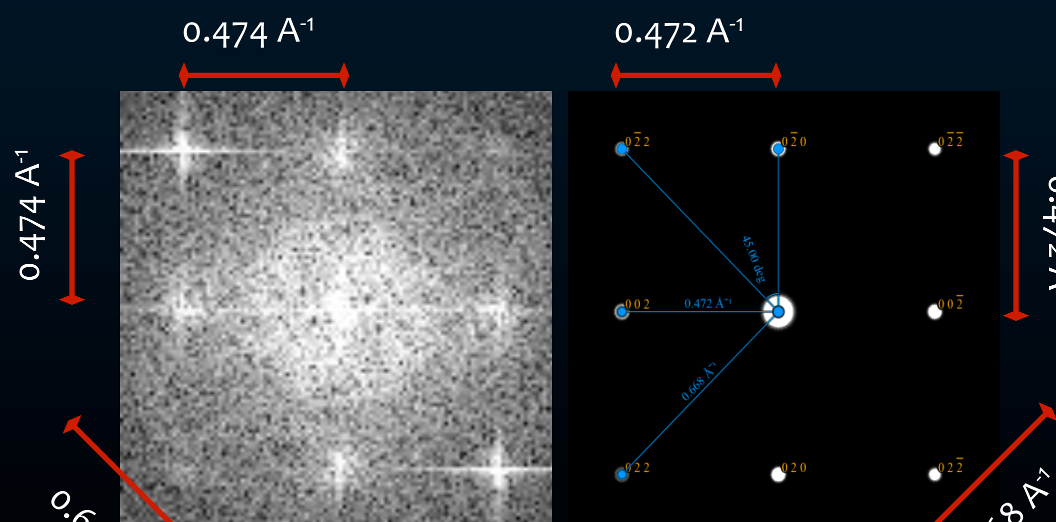
TiN - HRTEM







TiN 100



Measured Simulated

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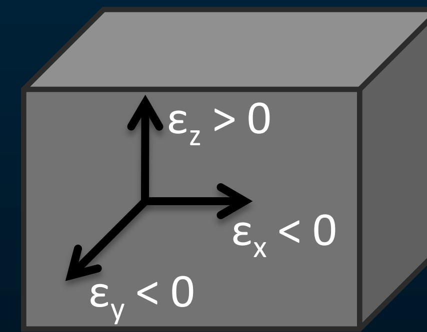
HYPERBOLIC METAMATERIALS

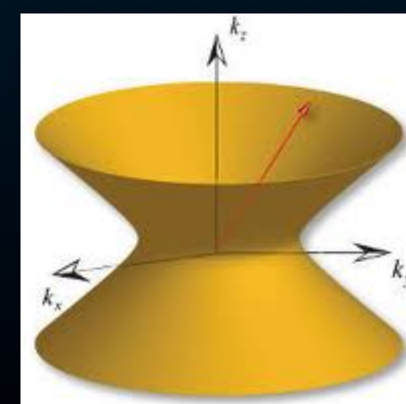
Extremely anisotropic materials

- Extremely large effective index
- Extremely high photonic density of states



Applications

- Quantum optics with metamaterials
- Tailor mechanical, thermal and electromagnetic properties for interesting physics and devices



Designing a material which is metallic in one direction but dielectric in the another

D.R. Smith and D. Schurig, Phys. Rev. Lett. **90** (2003); V.A. Podolskiy and E.E.Narimanov, Phys. Rev. B **71** (2005)
C. L. Cortes et al., arXiv:1204.5529v1 (2012); E.E. Narimanov and I.I. Smolyaninov, arXiv:1109.5444v1 (2011)

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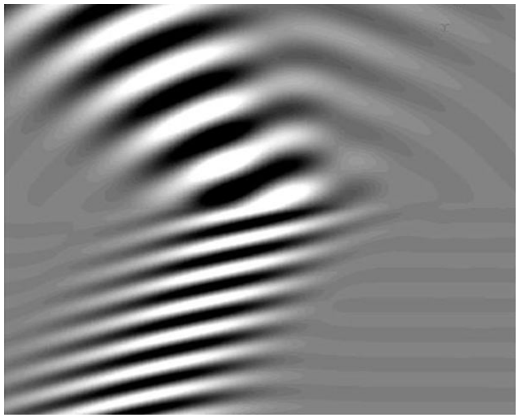
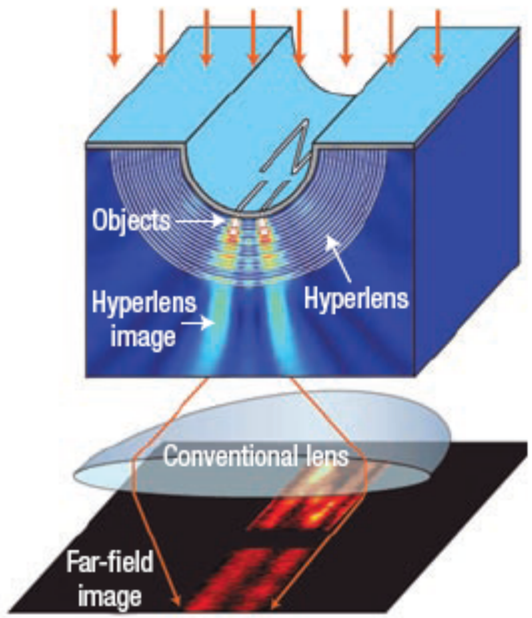
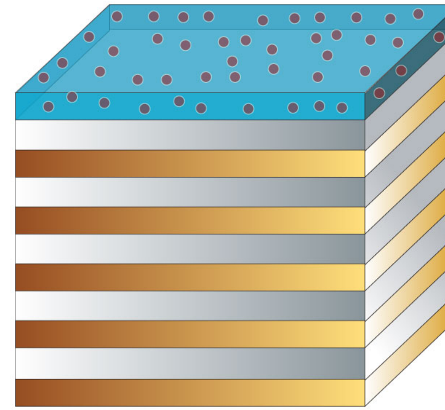
PLANAR HMMs



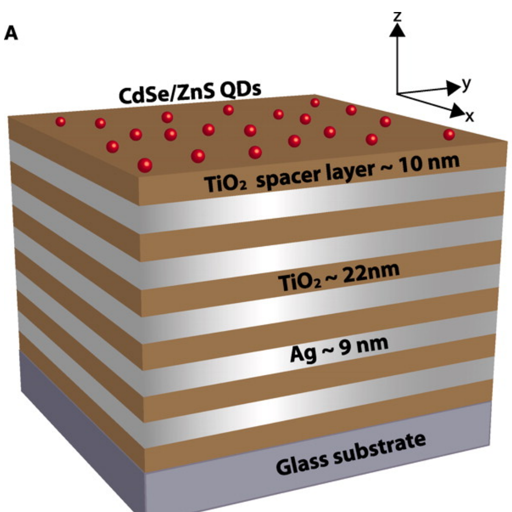
A. Hoffman *et al.*, Nat. Mater. (2007)



Z. Liu et. al, Science (2007)

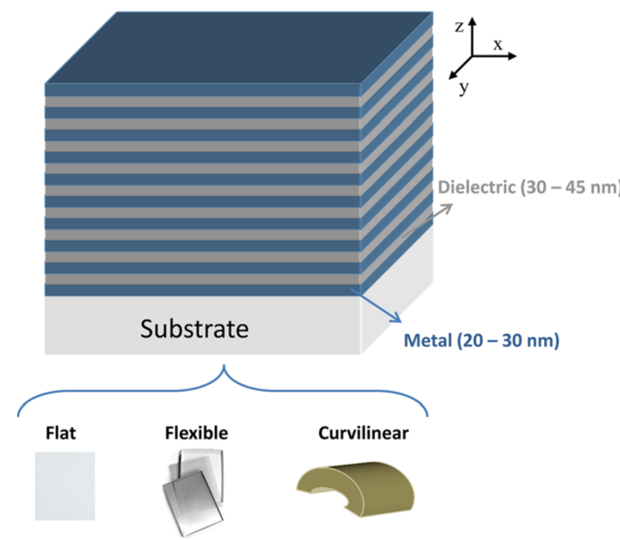


Z. Jacob *et al.*, Appl. Phys. B. (2010)



H.N.S. Krishnamoorthy *et al.*, Science (2012)

Fabrication and integration are easier



T. Tumkur *et al.*, Appl. Phys. Lett. (2011)

HMM PERFORMANCE: TCOs / NITRIDES

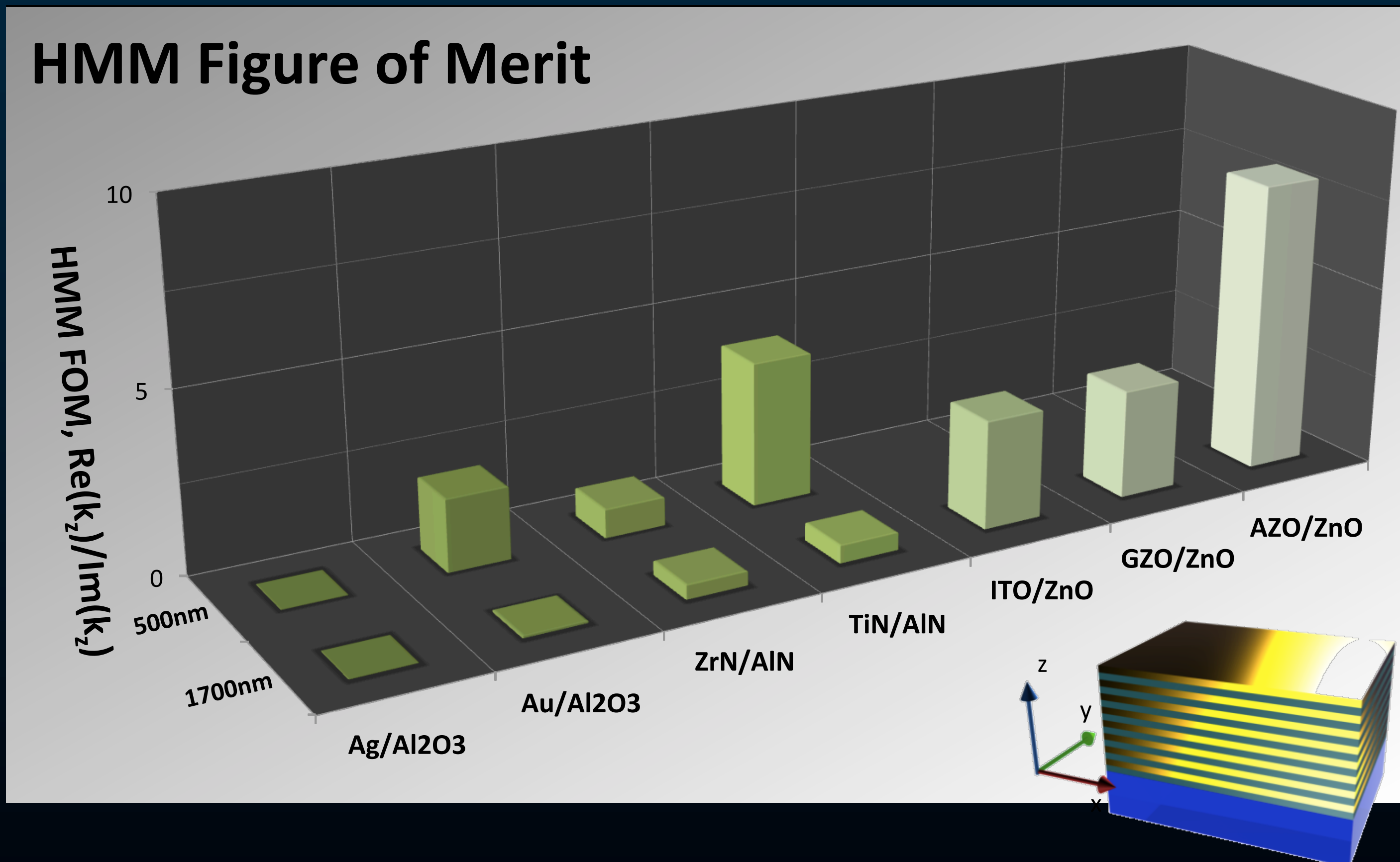


Figure-of-Merit = Re($\beta_\perp$)/Im($\beta_\perp$)

- **HMMs have extremely large photonic density of states**
- **Can tailor mechanical, thermal, and electromagnetic properties**

AZO-BASED HMM

Negative refraction in all-semiconductor optical metamaterial

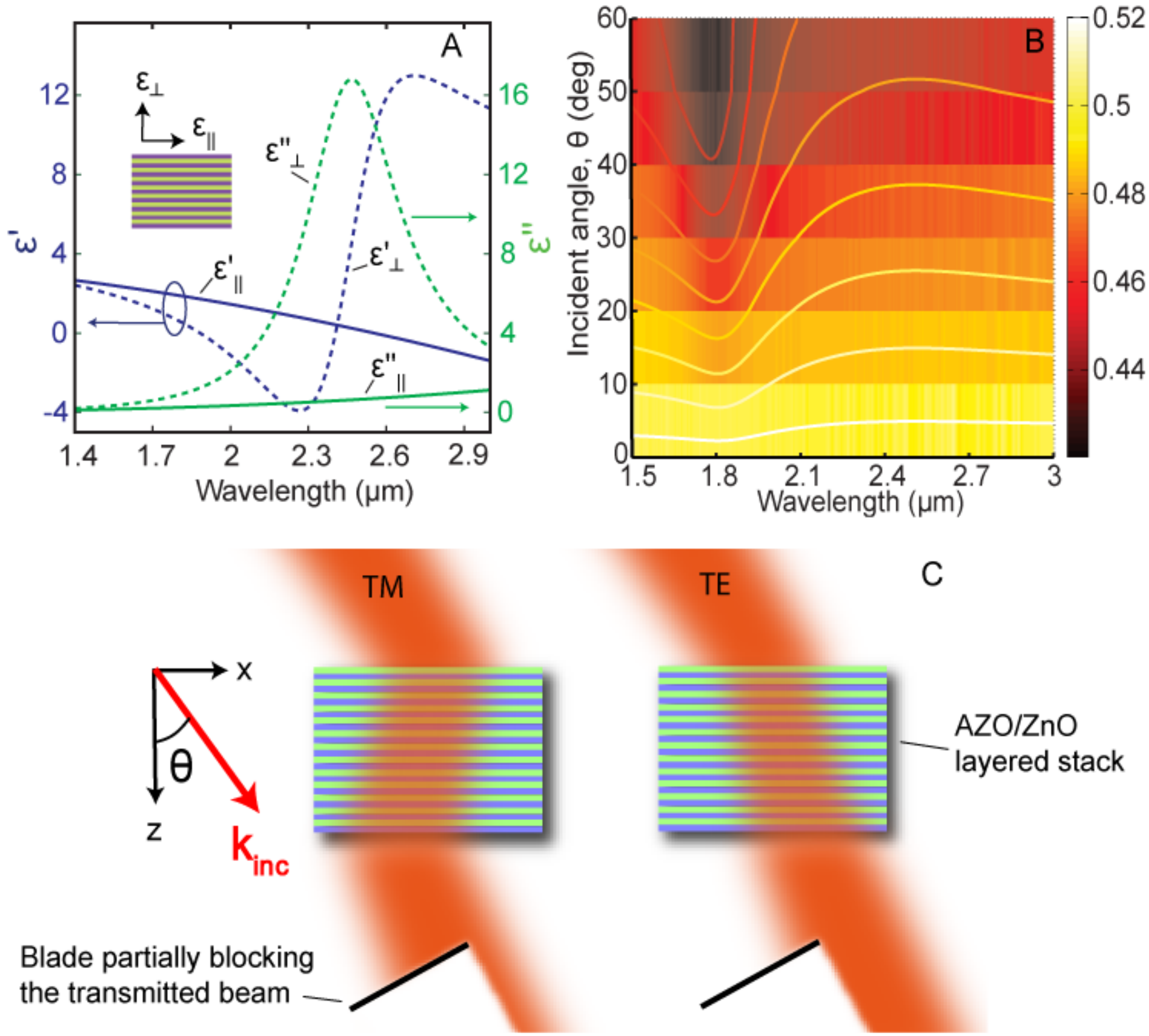
16 alternating layers of AZO and ZnO, each 60 nm thick, on a silicon substrate

Low-loss

Large scale

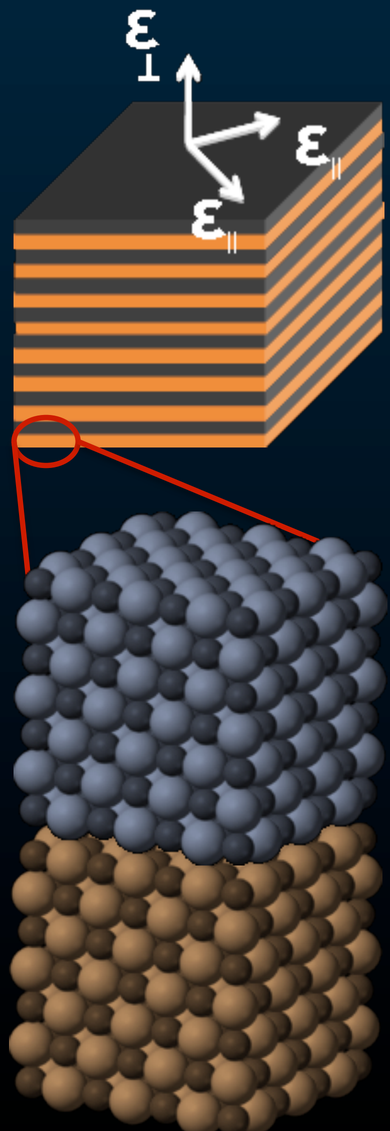
Negative refraction 1.8-2.4 µm

FOM 11



G.V. Naik, J. Liu, A.V. Kildishev, V.M. Shalaev and A. Boltasseva, PNAS (2012)

HMMs WITH TiN



- HMMs: metallic (TiN) and dielectric (AlN) alternating layers
- Nitrides: AlN is a dielectric
- Both nitride ceramics: Low surface energy
- Dielectric: deposited in the same chamber as that of TiN
- AlN + Sc: the same lattice structure and lattice constant
- For the first time MMs can be grown epitaxially as a superlattice!

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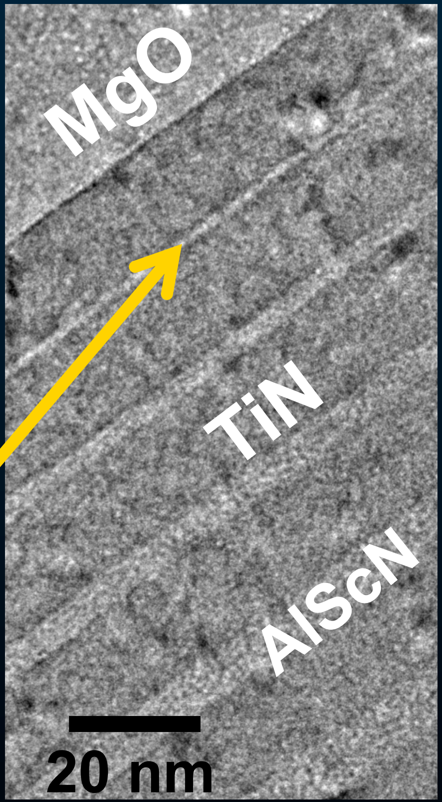
ADVANTAGES OF SUPERLATTICE SYSTEM

- Reactive DC magnetron sputtering on [001] MgO substrates
- Lattice matched:
  - Rocksalt / 4.24 Å
  - $Al_{0.72}Sc_{0.28}N$
  - Perfect interfaces
  - Possible to make ultra-thin continuous layers
  - Small surface roughness
- Other functionalities:
  - Thermoelectric
  - Plasmoelectric



2 nm Al(Sc)N interlayer is clearly visible

Test sample:
- Ultra-thin layers
- Interfaces are very sharp!

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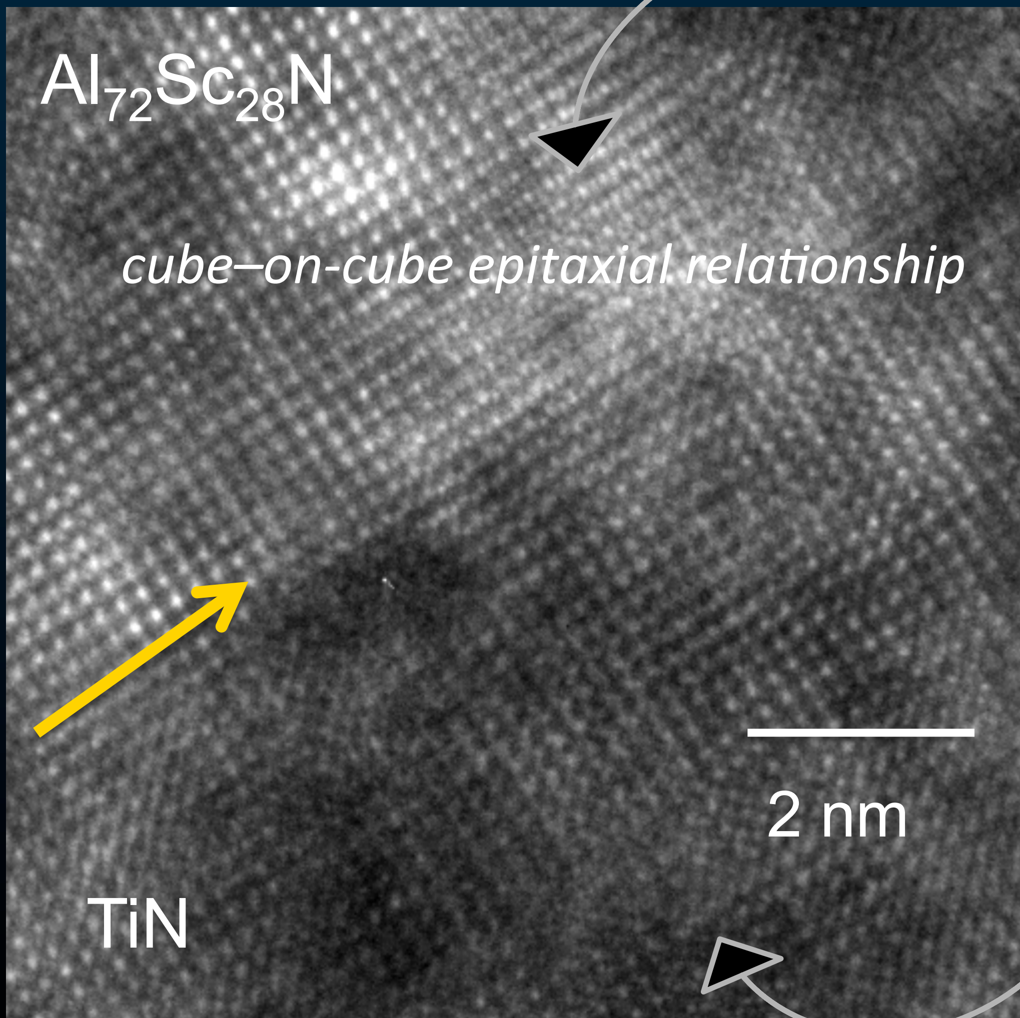
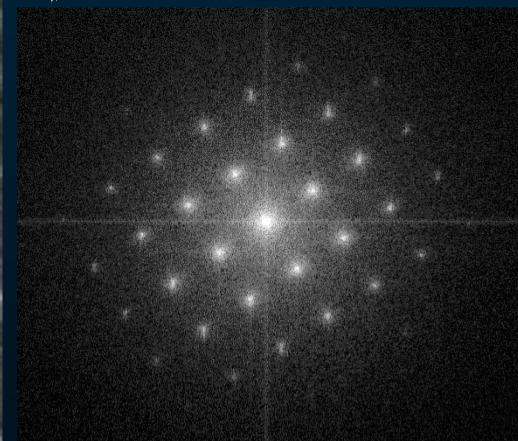
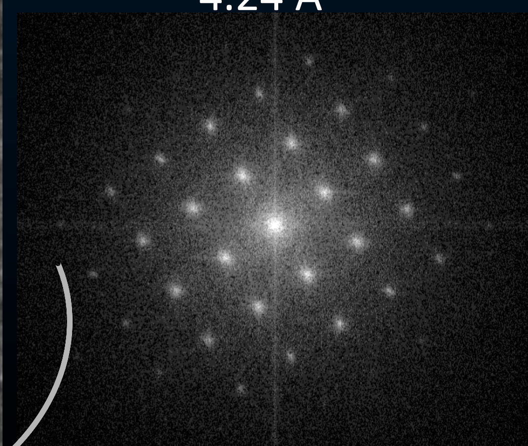
TEM OF TiN/Al(Sc)N SUPERLATTICE





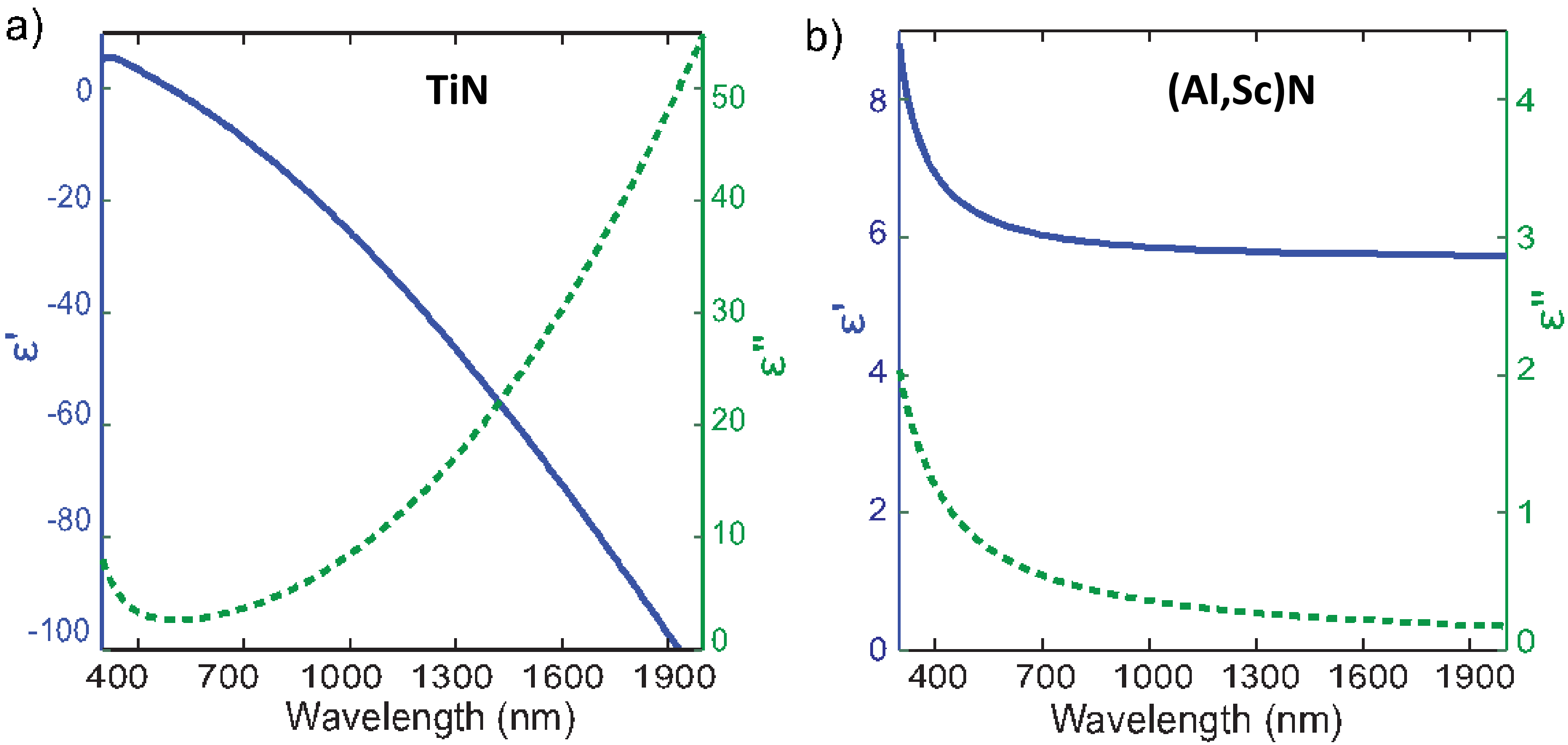
4.24 Å



fast Fourier transforms: diffractograms on the either sides of the interface

OPTICAL PROPERTIES

Measured Using Spectroscopic Ellipsometer

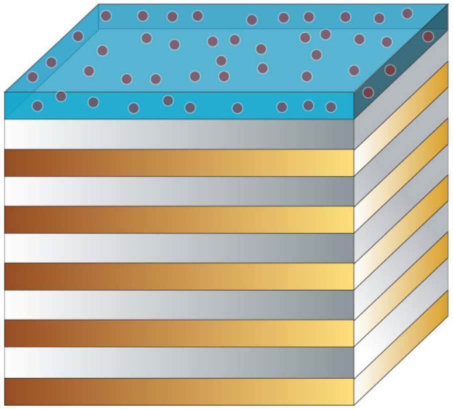


Approximation for superlattice: uniaxial anisotropic effective medium

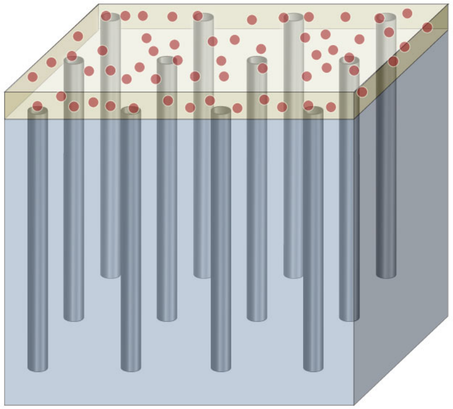
$Al_xSc_{1-x}N$ is a direct bandgap semiconductor (in rocksalt lattice) with band-edge in blue

G. Naik, et al, PNAS (2014)

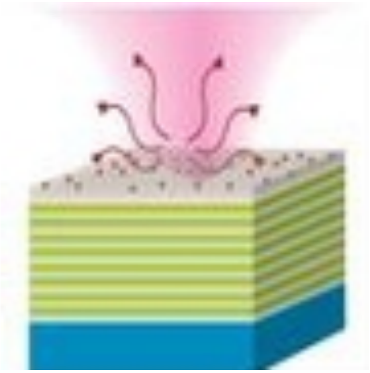
PROBING PHOTONIC DENSITY OF STATES



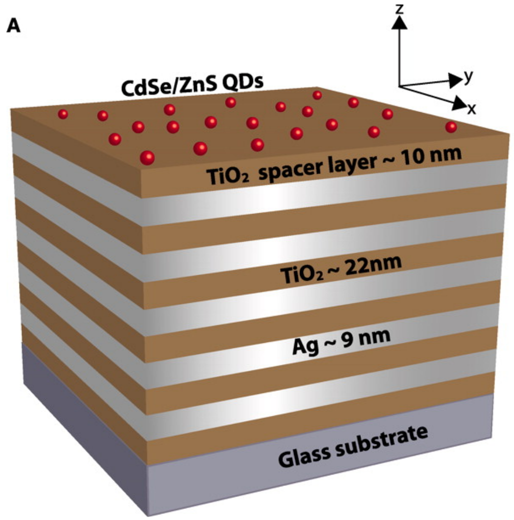
Z. Jacob *et al.*, Appl. Phys. B. (2010)



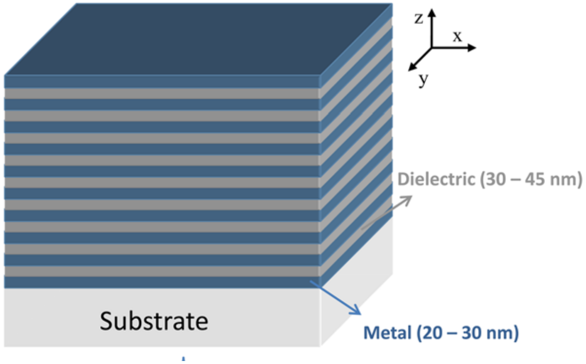
M.A. Noginov et al., Opt. Lett. (2010).



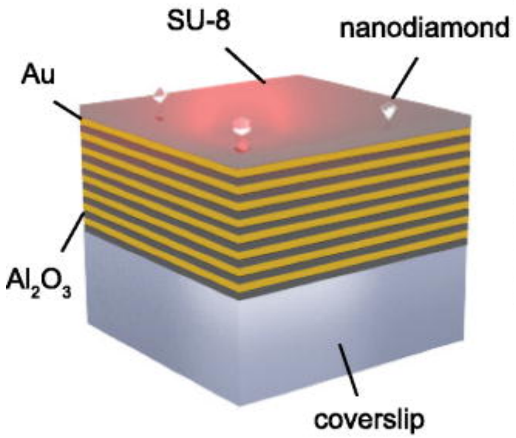
J. Kim *et al.*, Opt. Exp. (2012).



H.N.S. Krishnamoorthy *et al.*, Science (2012)



T. Tumkur *et al.*, Appl. Phys. Lett. (2011)



M.Y. Shalaginov et al., Appl. Phys. Lett. (2013).

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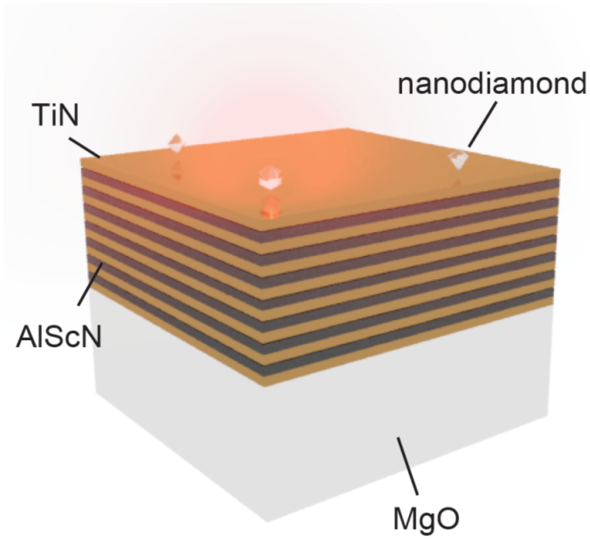
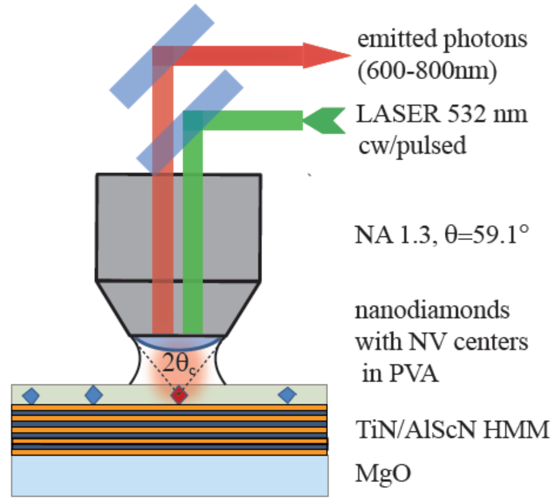
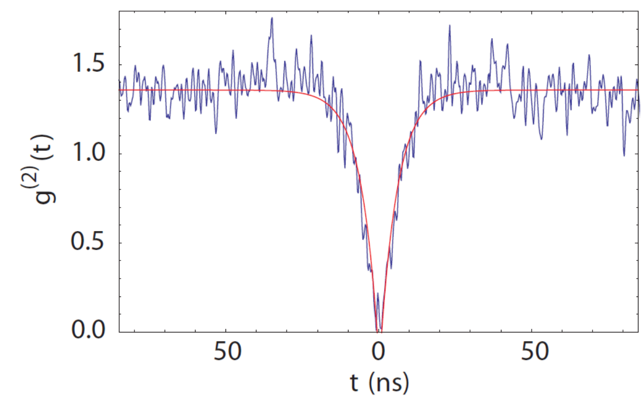
NV CENTERS COUPLED TO TiN HMM

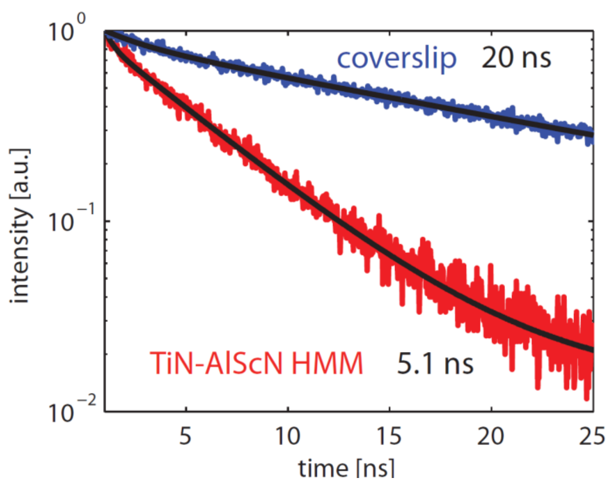




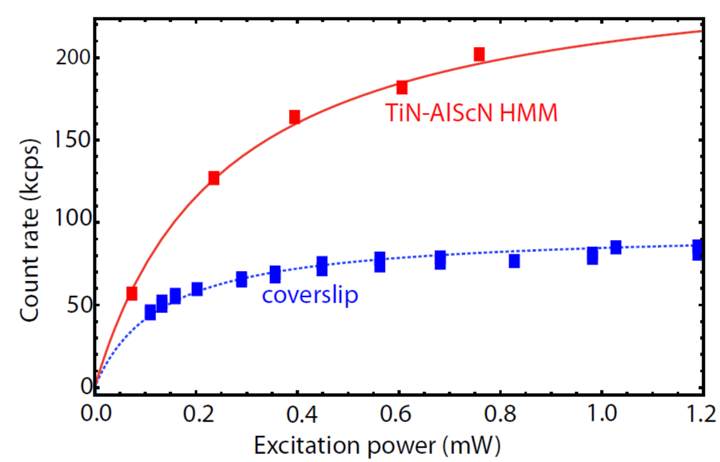
Photon anti-bunching statistics



Fluorescence lifetime

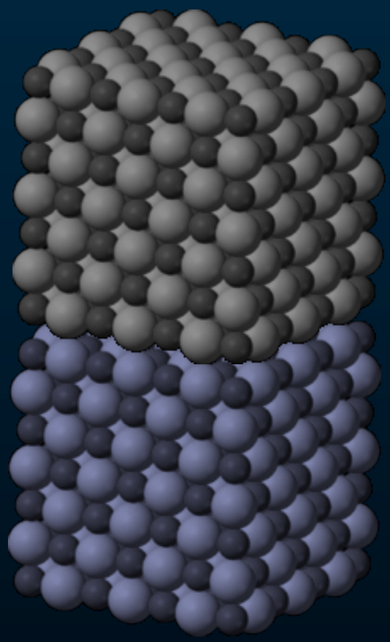


Collected emission rate



SUPERLATTICE HMM

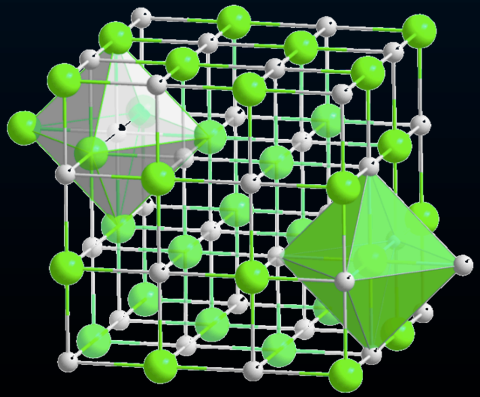
- NITRIDE SUPERLATTICE
- ULTRA-THIN LAYERS
- HIGH QUALITY
- LOW-LOSS
- THERMALLY STABLE
- BIO and CMOS-COMPATIBLE



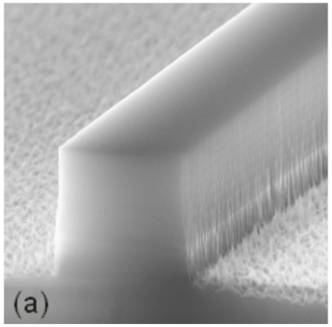
- High photonic density of states
- Ultra-thin metal films: strong quantum effects, plasmonics at ultra-small gaps – quantum plasmonics
- Tailor mechanical, thermal and electromagnetic properties for interesting physics and devices

OUTLINE

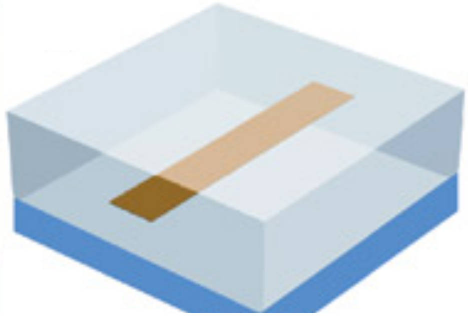
- Introduction: Plasmonics & Metamaterials
- Material Requirements: Challenges with Gold and Silver
- Alternative Materials?
- Transparent Conducting Oxides
- Transition Metal Nitrides
- Figures of Merit and Applications
- CMOS-Compatible Plasmonics
- Outlook



INTERCONNECTS: PLASMONICS VS PHOTONICS



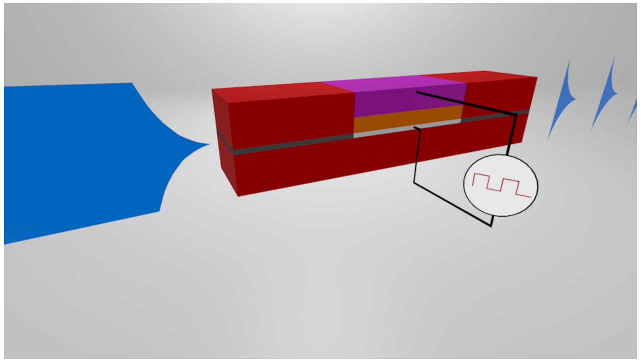
Silicon ridge waveguides:
- **Propagation loss: 0.1 dB/mm**
- **Mode size: 1 µm**



Plasmonic strip WGs (LR-SPP):
- **Propagation loss: 0.5 dB/mm**
- **Mode size: 7 µm**

Plasmonic interconnects offer key advantages over photonic interconnects

1) Active devices compact in length
2) Coupling to nanoscale plasmonic devices
3) Metal serves dual purpose electro-optic devices
4) Enormous sensitivity to surface
5) Reduced fabrication complexity
6) Polarization purity



V. Babicheva et al, Opt. Express 21(22), 2013. (Boltasseva Group)

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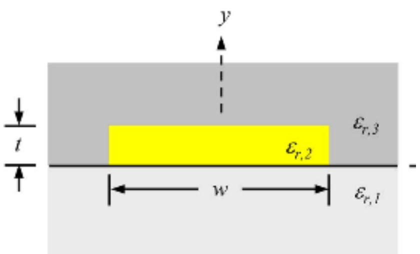
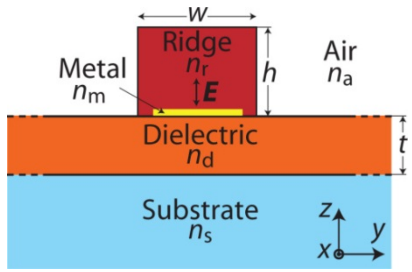
CONVENTIONAL PLASMONICS

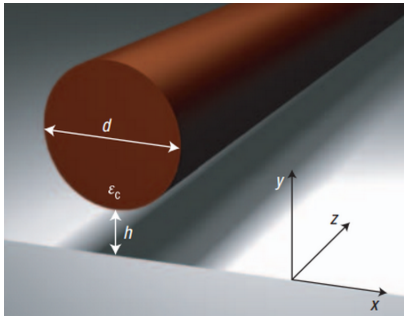
- Many wonderful examples have been demonstrated using noble metals



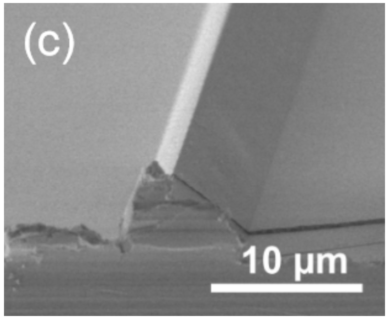
P. Berini, Adv. Opt. Photon. 1, 2009.



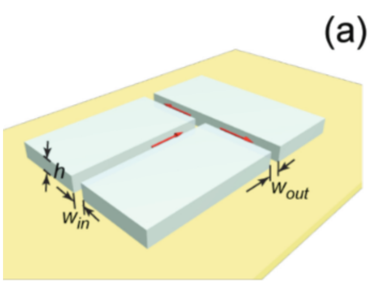
V. Volkov, et al, Opt. Lett. 36(21), 2011. (Bozhevolnyi Group)



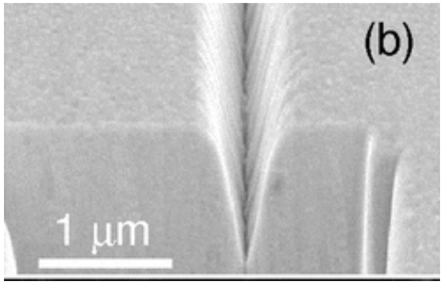
R. Oulton, et al, Nat. Photon. 2, 2008. (Zhang Group)



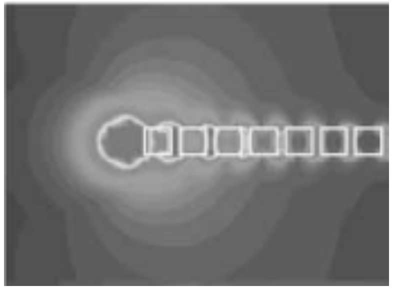
A. Boltasseva, et al., Opt. Express. 16(8), 2008. (Bozhevolnyi Group)



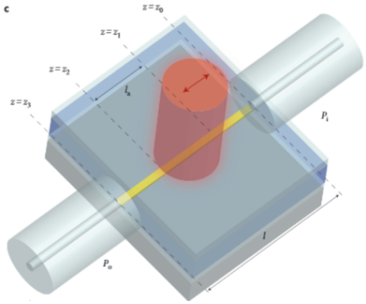
W. Cai, et al., Adv. Mat. 22(45), 2010. (Brongersma Group)



S. Bozhevolnyi, et al., Phys. Rev. Lett. 95, 2005. (Ebessen Group)



S. Maier, IEEE J. Sel. Topics Quant. Electron. 12(6), 2006.



I. De Leon, et al., Nat. Photon. 4, 2010. (Berini Group)

- However, these are **not** CMOS compatible!

QUALITY FACTORS FOR SP

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The performance of many 2D plasmonic waveguides, non-spherical LSPR structures, resonant metamaterial devices such as negative-index-metamaterials depend on the quantity

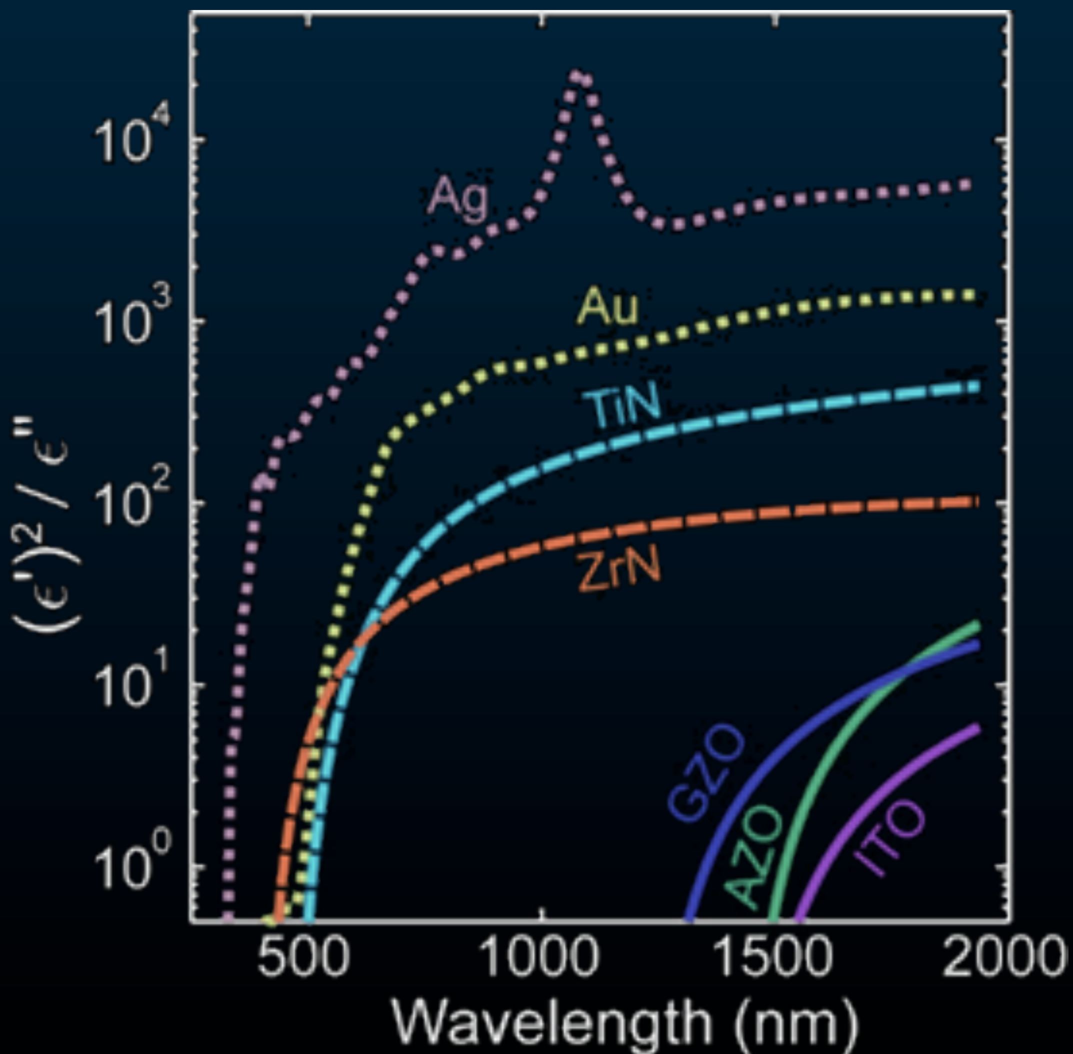
$Q_{SPP} = k'_{SPP} / k''_{SPP}$

$$Q'_{\mathrm{SPP}}(\omega) = \frac{k'_{\mathrm{x}}(\omega)}{k''_{\mathrm{x}}(\omega)} = \frac{\varepsilon'_{\mathrm{m}}(\omega) + \varepsilon_{\mathrm{d}}(\omega)}{\varepsilon'_{\mathrm{m}}(\omega)\varepsilon_{\mathrm{d}}(\omega)} \frac{\varepsilon'_{\mathrm{m}}(\omega)^2}{\varepsilon''_{\mathrm{m}}(\omega)}$$

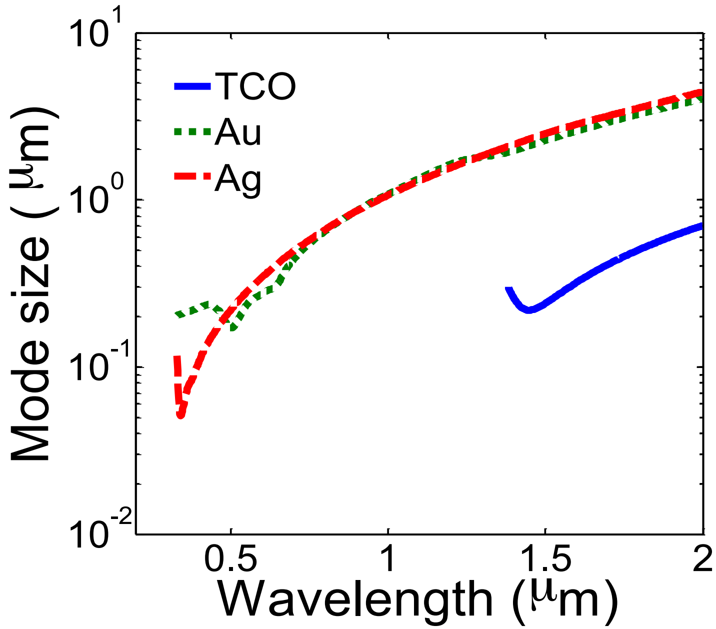
$$Q_{\mathrm{SPP}}(\omega) = \frac{\varepsilon'_{\mathrm{m}}(\omega)^2}{\varepsilon''_{\mathrm{m}}(\omega)}$$

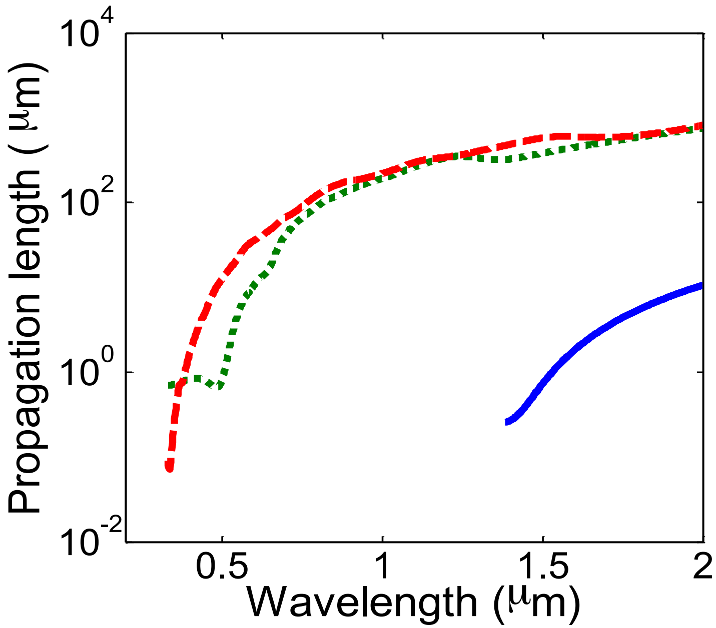
P. R West *et* al., *Laser & Photonics Reviews* 4, 795–808 (2010)

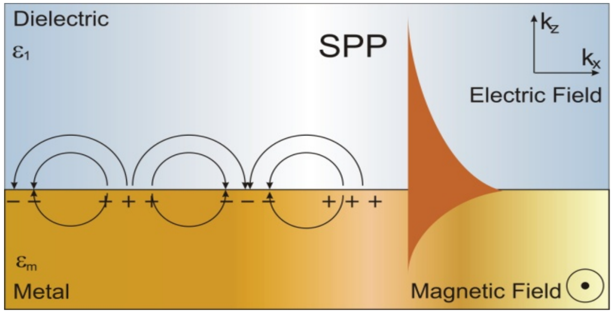
QUALITY FACTORS FOR SP



QUALITY FACTORS FOR SPP: TCOs





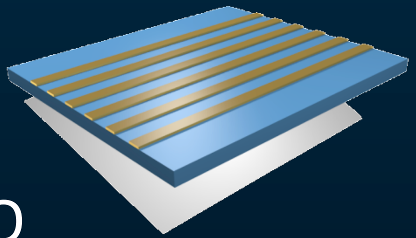


Good confinement but, poor propagation length!

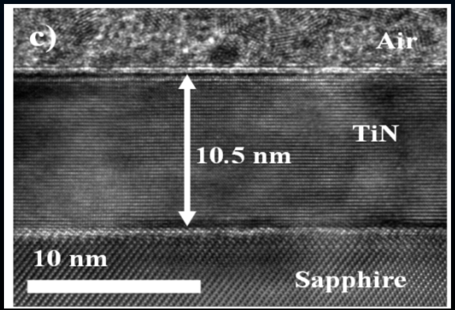
G. V. Naik, *et. al.*, Metamaterials **5, 1-7** (2011)

ADVANTAGES OF TiN

TiN offers additional advantages for plasmonics:



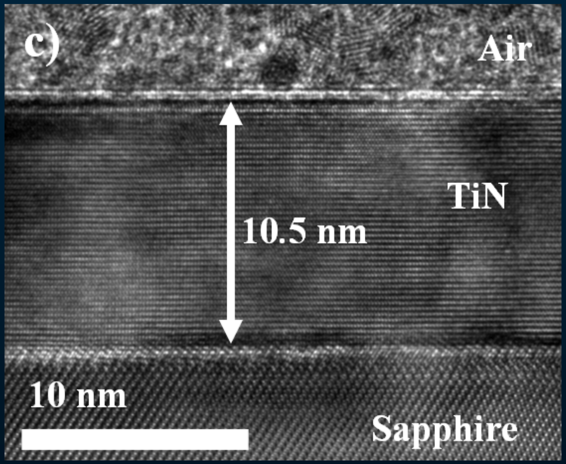
- Grows epitaxial on silicon, sapphire, and MgO
- Ultra-thin films
- Nonstoichiometric = tunable properties
- Chemically stable
- High temperature stability
- Copper/aluminum require a TiN diffusion barrier
- Biocompatibility
- CMOS-compatibility

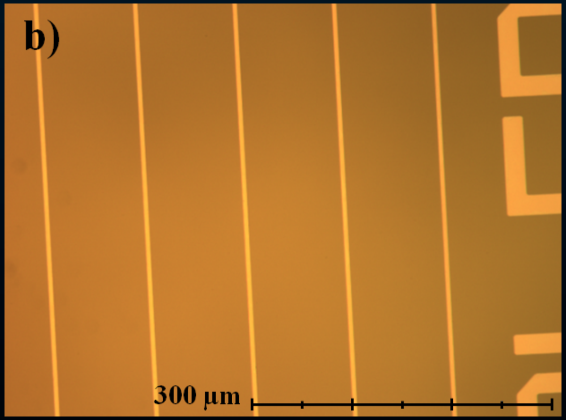


G. Naik, et al., Adv. Mater. 25, 2013 (Boltasseva Group)

CMOS-Compatible Waveguides

- Utilize the strip geometry
  - Supports long range SPP mode
  - 8 µm wide, 10 nm thick
  - Fabricated on c-sapphire
- TiN deposited using reactive magnetron sputtering in N_2 + Ar environment
- Pattered using standard photolithography techniques and reactive ion etching
- Measured using end-fire coupling and cut-back technique



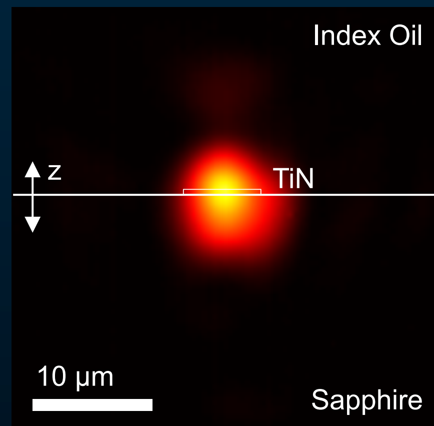


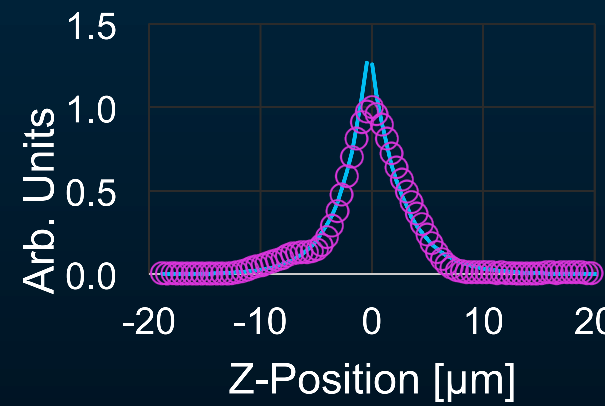
N. Kinsey et al, Opt. Express **22**(10), 2014

CMOS-Compatible Waveguides

Experiment

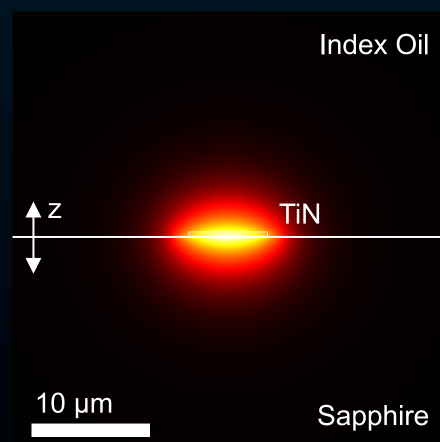
- L_{prop} = 5.5 mm
- δ_z = 9.8 µm

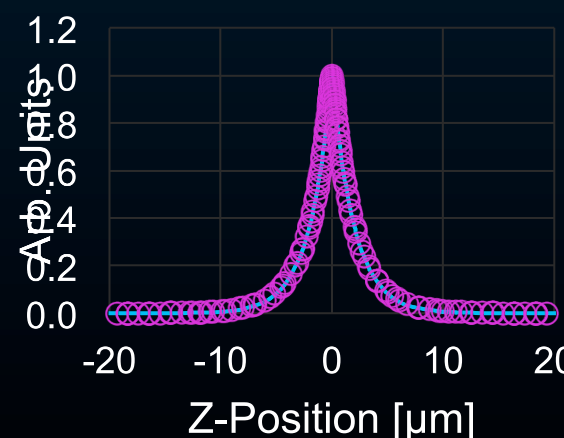




Simulation

- L_{prop} = 5.7 mm
- δ_z = 8.0 µm





N. Kinsey et al, Opt. Express **22**(10), 2014

Purdue University

COMPARISON TO Au

Material	Metal Permittivity	Cladding Index	Strip Thickness [nm]	Strip Width [μm]	L_{prop} [mm]	α [dB/mm]	δ_z [μm]	$FoM_1 = \varepsilon'/\varepsilon''$	$FoM_2 = L_{prop}/n\delta_z$
TiN on Sapphire	-75 + 23i	1.75	10	9.38	5.5	0.79	9.8	**3**	**321**
Gold on Polymer	-132 + 13i	1.535	10	8.0	7	0.6	20	10	229

L_{prop} is the propagation length (defined as the 1/e decay of the power)
δ_z is the mode size (1/e^2 decay of the power) in the vertical direction
n is the cladding refractive index

- Despite lower material FoM, TiN-based waveguides outperform those made using gold
- Gold's difficulty in forming high quality thin films limits the performance

N. Kinsey et al, Opt. Express **22**(10), 2014
P. Berini, Opt. Express, **14**(26), 2006
A. Boltasseva et al, J. Lightw. Technol. **23**(1), 2005

TiN: OUTLOOK

- Plasmonic in the Visible:
  - Intermetallics: Silicides, Germanides, Nitrides, Oxides, Hydrides…
  - Titanium nitride, Tantalum nitride, Ruthenium oxide

  - *Comparable to Au*
  - *Bio-compatible*
  - *CMOS-compatible*
  - *Stable, robust*
  - *New physics (HMM, ultra-thin layers, quantum effects)*
  - *Refractory (HIGH T) plasmonics*

OUTLINE

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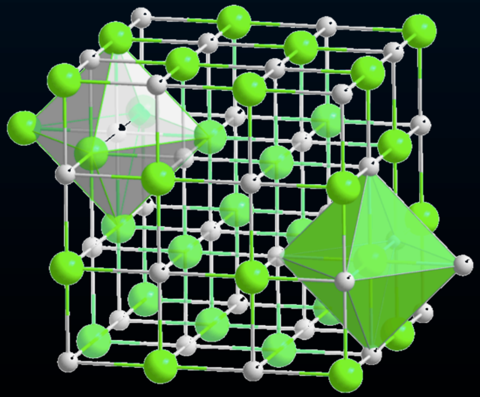
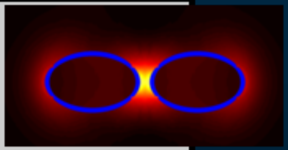
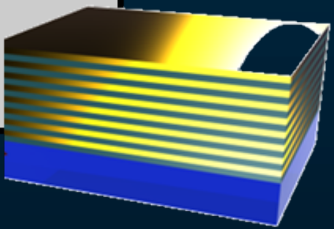
- Material Requirements: Challenges with Gold and Silver
- Alternative Materials?
- Transparent Conducting Oxides
- Transition Metal Nitrides
- Figures of Merit and Applications
- CMOS- and Refractory Plasmonics
- **Outlook**

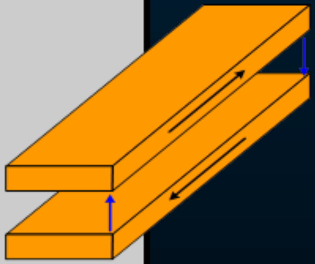


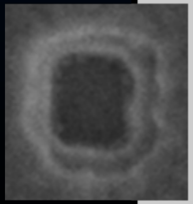
Nanophotonic Devices:
Nanoantennas
Plasmonic Waveguides
Optical Metamaterial Devices



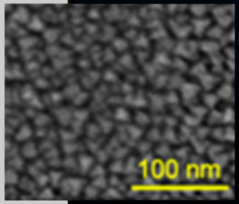


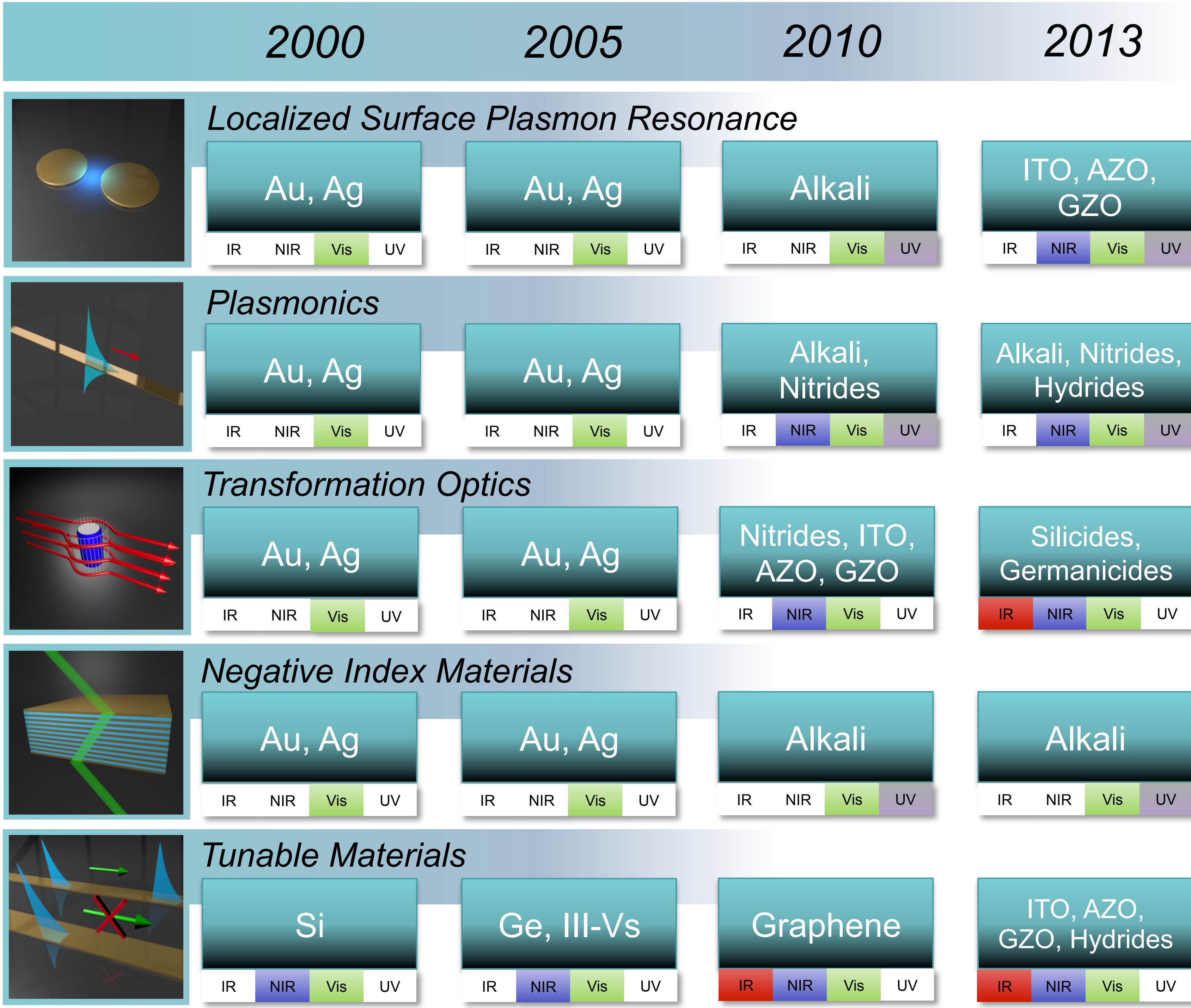
Design of
Nanosized Building Blocks:
Nanometer-Thin Films
Nanoparticles





Constituent Materials:
Metals ***(lossy, not tunable challenging fabrication and integration)***
NEW PLASMONIC MATERIALS




2000
2005
2010
2013
Localized Surface Plasmon Resonance
Au, Ag
IR NIR Vis UV
Au, Ag
IR NIR Vis UV
Alkali
IR NIR Vis UV
ITO, AZO, GZO
IR NIR Vis UV
Plasmonics
Au, Ag
IR NIR Vis UV
Au, Ag
IR NIR Vis UV
Alkali, Nitrides
IR NIR Vis UV
Alkali, Nitrides, Hydrides
IR NIR Vis UV
Transformation Optics
Au, Ag
IR NIR Vis UV
Au, Ag
IR NIR Vis UV
Nitrides, ITO, AZO, GZO
IR NIR Vis UV
Silicides, Germanicides
IR NIR Vis UV
Negative Index Materials
Au, Ag
IR NIR Vis UV
Au, Ag
IR NIR Vis UV
Alkali
IR NIR Vis UV
Alkali
IR NIR Vis UV
Tunable Materials
Si
IR NIR Vis UV
Ge, III-Vs
IR NIR Vis UV
Graphene
IR NIR Vis UV
ITO, AZO, GZO, Hydrides
IR NIR Vis UV

MATERIAL CHOICES: OUTLOOK

- Infrared:
  - Silicides, Germanides, GaAs, SiC, Si, Ge, InAs
- Near-infrared:
  - Perovskites: Heavily doped barium tin oxide, strontium titanate, cadmium tellurium oxide, calcium titanate, strontium tin oxide
  - TCOs: AZO, GZO, ITO
  - *Tune plasma frequency by doping*
  - *Great switching opportunities (TCOs, Graphene, YH2)*
  - *Low loss, small real part of permittivity*
- Visible:
  - Intermetallics: Silicides, Germanides, Nitrides, Oxides…
  - Titanium nitride, Tantalum nitride, Ruthenium oxide
  - *Comparable to Au, Bio- and CMOS-compatibility*
  - *New physics (HMM), Refractory (HIGH T) plasmonics*

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TEAM AND SUPPORT

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- **Nathaniel Kinsey**
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- Aveek Dutta
- Sajid Choudhury
- Krishnakali Chaudhuri

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- Prof. A. Kildishev (Purdue)
- Prof. N. Engheta (UPenn)
- Prof. A. Alu (UTexas Austin)
- Prof. Mossalei (Northeast.)

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- Dr. Urcan Guler
- **Dr. Marcello Ferrera**
- Dr. Simeon Bogdanov

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- Dr. N. Emani (DSI)
- Dr. P. West (Intel)

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- Air Force Office of Scientific Research (FA9550-14-1-0138)
- Army Research Office (57981-PH, 56154-PH-MUR)
- Office of Naval Research (ONR-MURI N00014-10-1-0942)
- National Science Foundation (C-PHOM, NSF MRSEC 3002095871)

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PLASMONIC MATERIALS RESEARCH

- Laser & Photonics Reviews 4, 795–808 (2010)
- Phys. Status Solidi RRL 4, 295–297 (2010)
- Metamaterials 5, 1–7 (2011)
- Science 331, 290 (2011)
- Optical Materials Express 1 (6), 1090–1099 (2011)
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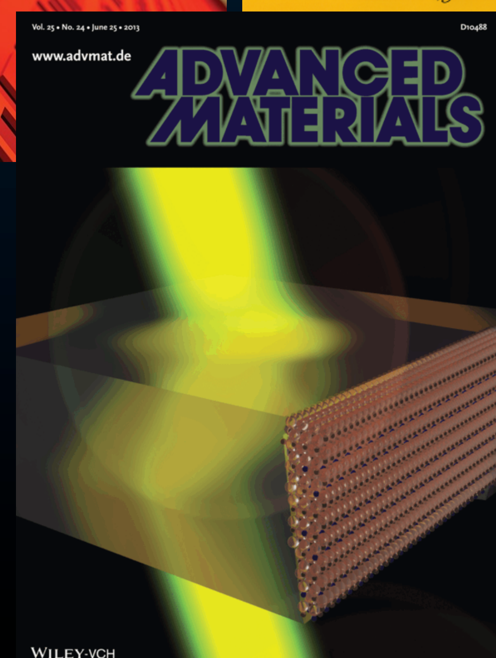
- Appl. Phys. B 107, 285-291 (2012)
- MRS Bulletin 37 (8), 768 (2012)
- Proc. Natl. Acad. Sci. 109 (23), 8834 (2012)
- IEEE JSTQE 19, 4601907 (2013)
- Phys. Rev. X 3, 041037 (2013)
- Advanced Materials 25 (24), 3264 (2013)
- Nano Letters, 13 (12), 6078-6083 (2013)
- Optics Express 21(22), 2013.
- Optics Express 22 (10), 12238 (2014)
- Science 344, 263 (2014)
- Proc. Natl. Acad. Sci. (2014)
- Advanced Materials, 26(47), 2014
- Nano Letters, 15(1), 2014
- Materials Today 18(4) 227, 2014
- ACS Nano 8(9), 9035, 2014
- JOSA B 32(1), 2015
- Science 347, 1308, 2015

THANK YOU!



Nature Photonics News&Views Highlight

news & views

VIEW FROM... NANOMETA 2011

In search of new materials

MATERIALS SCIENCE

Low-Loss Plasmonic Metamaterials

21 JANUARY 2011 VOL 331 SCIENCE