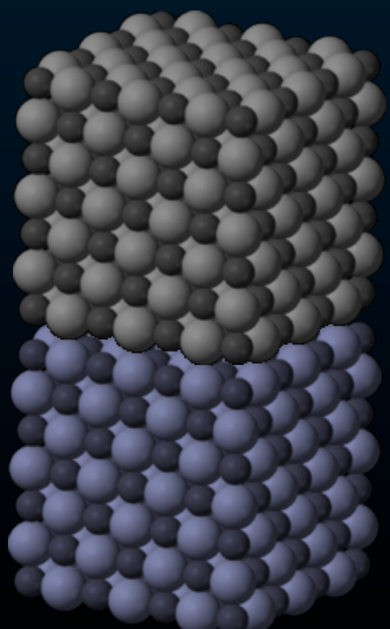
DOPED SEMICONDUCTORS AND CERAMIC MATERIALS: NEW PLATFORM FOR PLASMONICS



BUILDING NANOSCALE PHOTONIC TECHNOLOGIES OF THE FUTURE

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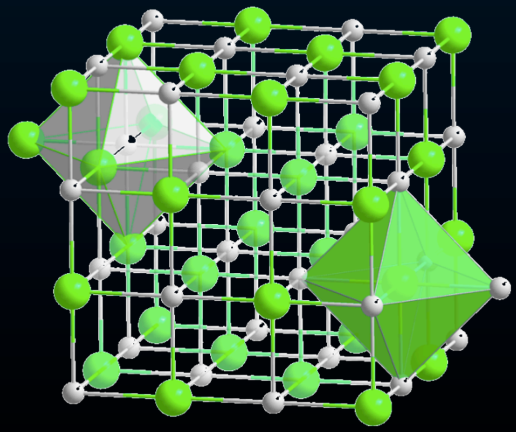
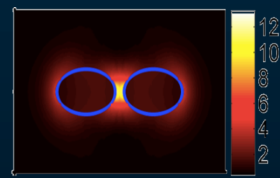
OUTLINE

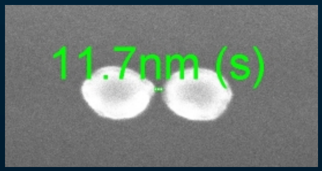
- Introduction: Plasmonics & Metamaterials
- Material Requirements: Challenges with Gold and Silver
- Alternative Materials?
- Transparent Conducting Oxides
- Transition Metal Nitrides
- Figures of Merit and Applications
- CMOS- and Refractory Plasmonics
- Outlook



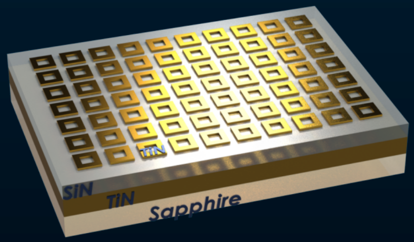
PLASMONICS

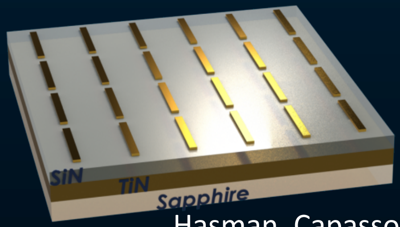
1 Localized SP = Optical Nano-Antenna (imaging, sensing, therapy, energy…)





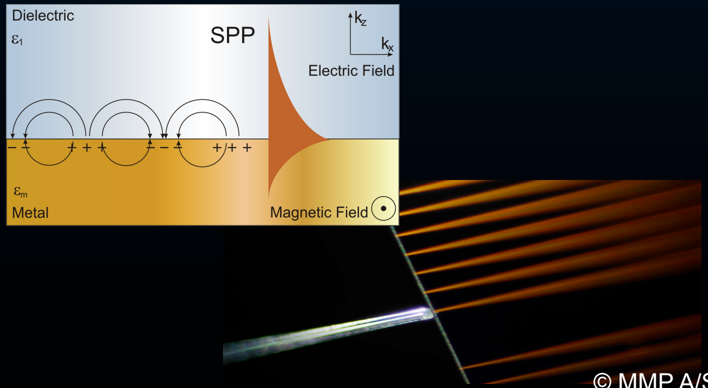
= Optical Metasurfaces (ultra-thin/flat optics, sensors…)





Hasman, Capasso, Zheludev, Alu and others

2 Propagating SP = Nano-Waveguide (integrated photonics, sensors…)



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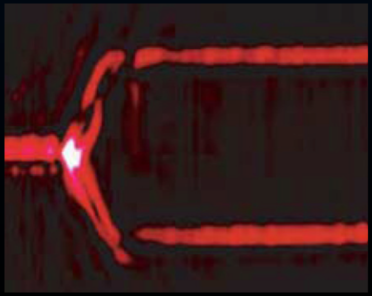
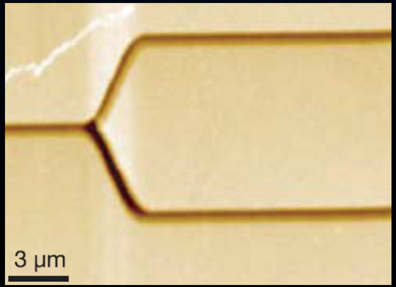
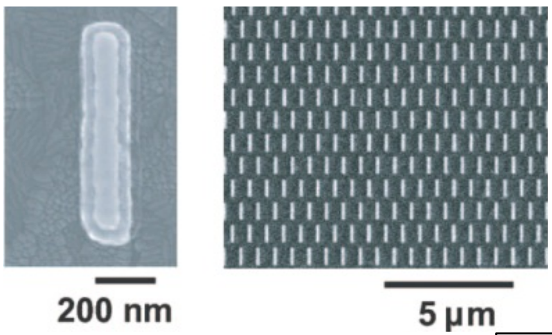
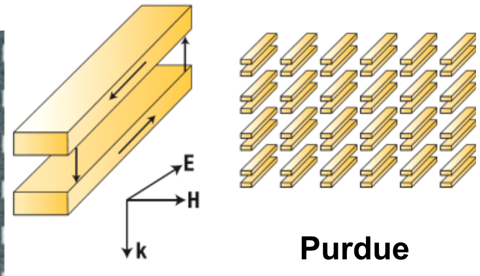




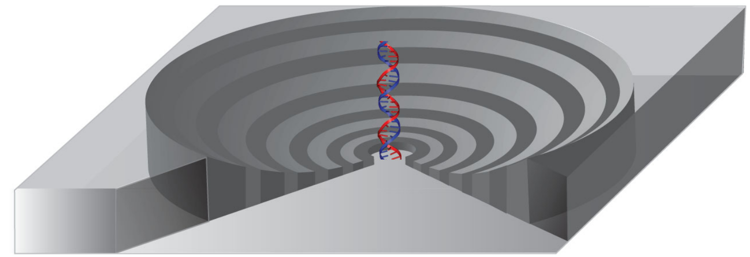
S. I. Bozhevolnyi, et al., Nature 404 (2006)

PLASMONICS/METAMATERIALS/TO



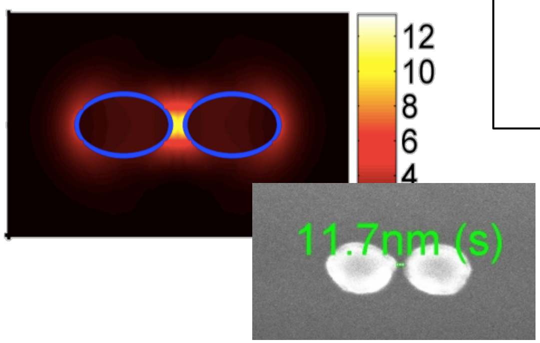


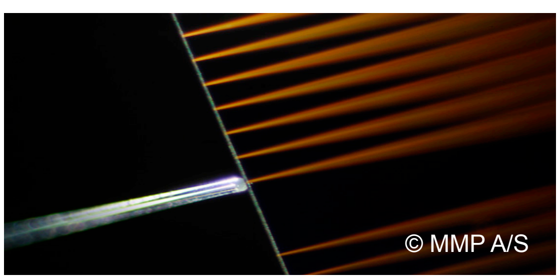
Purdue

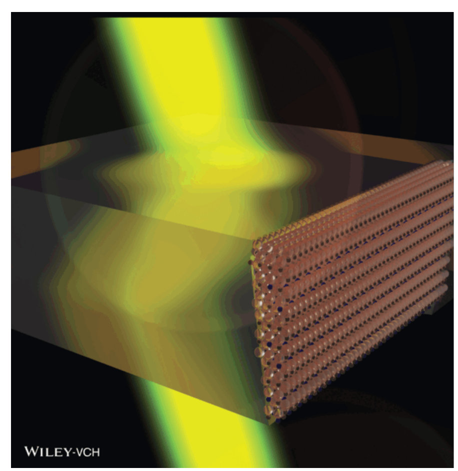


Narimanov, Engheta

Plasmonics and metamaterials offer an unprecedented ability to control light
Numerous examples of extraordinary science







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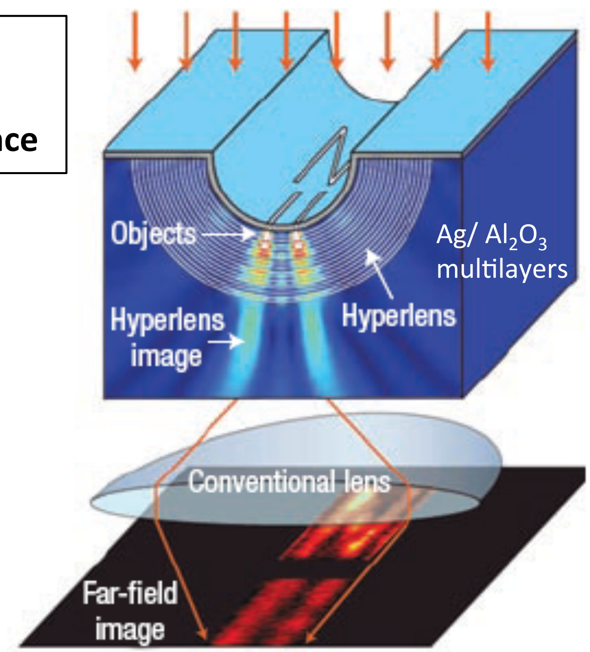


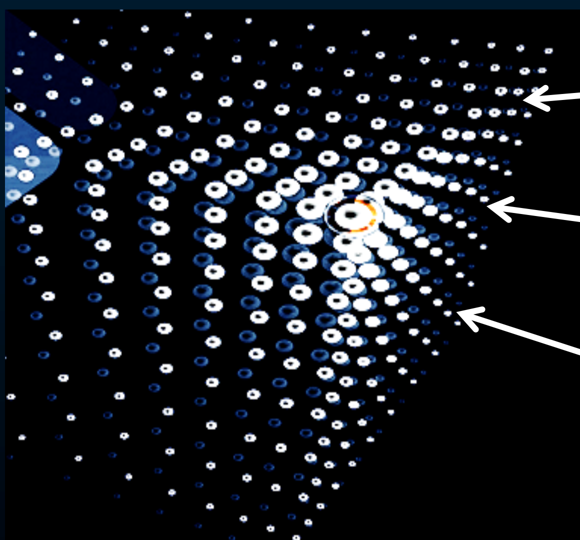
Z. Liu et. al, Science (2007)

METAMATERIALS

size << λ

METAMATERIALS

POSSIBILITIES are VAST!



PERIOD/ARRANGEMENT

GEOMETRY/UNIT CELL DESIGN

MATERIALS

Metamaterial is an arrangement of artificial structural elements, designed to achieve advantageous and/or unusual properties

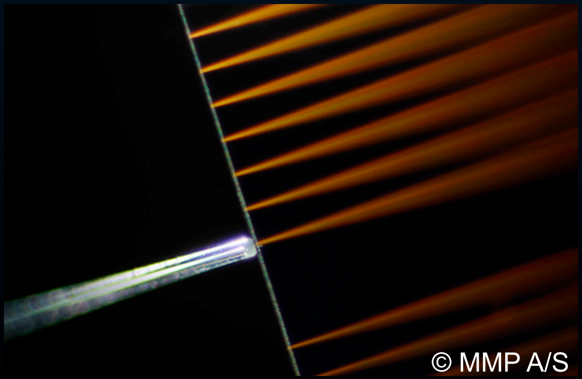
μετα = meta = beyond (Greek)

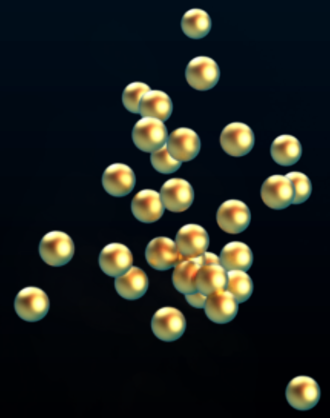
MAKING REAL DEVICES

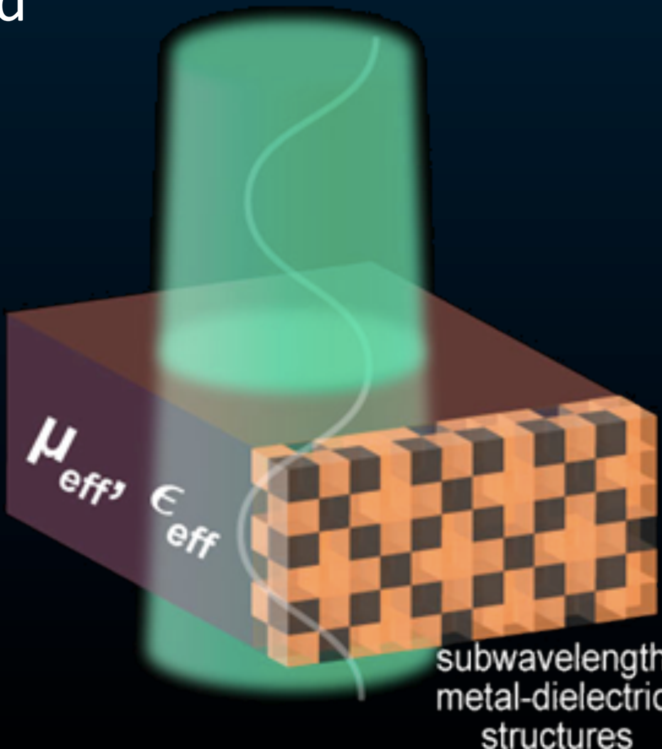
PLASMONICS AND METAMATERIALS: PLENTY OF WONDERFUL DESIGNS AND IDEAS!

We would normally mix metals and dielectrics and arrange in a predesigned fashion

What about constituent materials?







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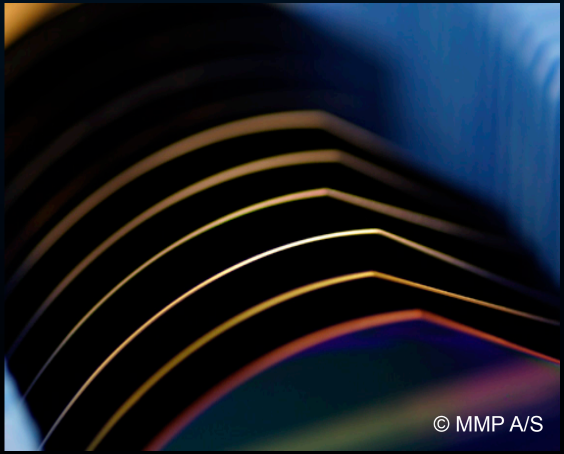


MATERIALS

We want:

- Low loss devices
- Switchable / Tunable devices
- SC-compatible components
- Low cost, robust, stable

- GOLD and SILVER used so far…
  - Large losses in the VIS/NIR
  - Fabrication challenges (continuous thin films)
  - Nanopatterning increases losses
  - Not tunable/adjustable optical properties
  - Not CMOS-compatible
  - High cost
  - Soft, low melting point

CHALLENGES

Conventional materials: Gold and Silver

- Large losses in near-IR and visible ranges

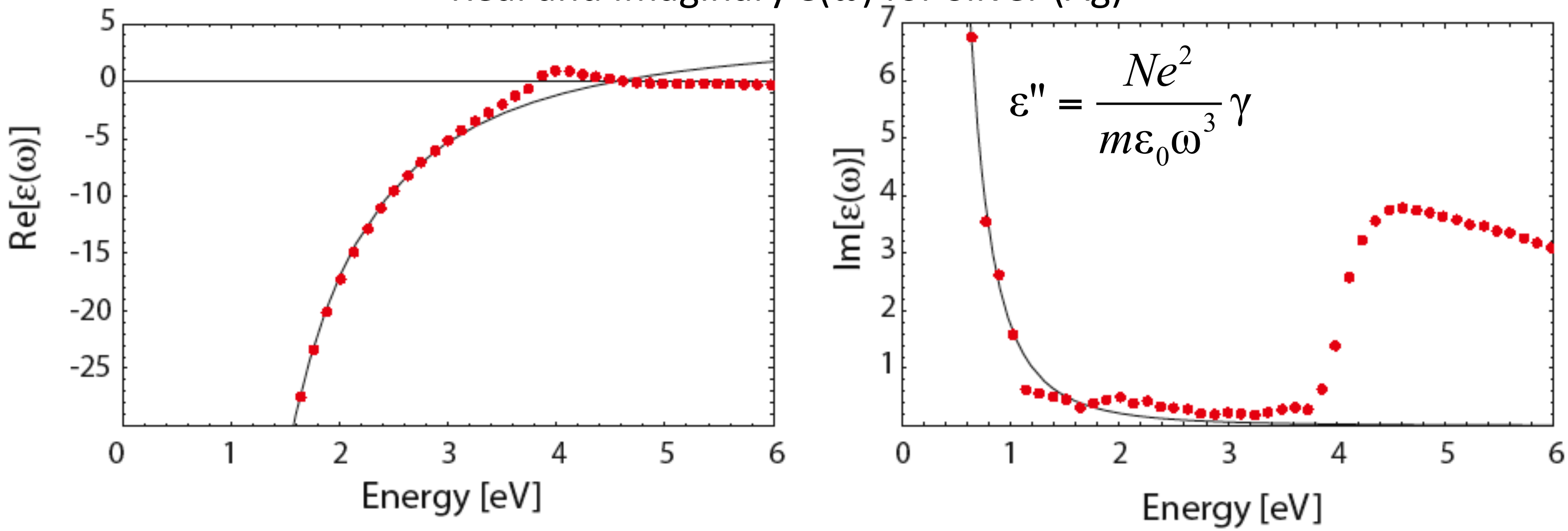
Interband transitions

Surface roughness, grain boundaries, etc…

$$\varepsilon(\omega) = \varepsilon_{ib} - \frac{Ne^2 / m\varepsilon_0}{\omega^2 + i\omega\gamma_m(\omega)}$$

$$\epsilon(\omega) = \epsilon' + i\epsilon'' = \epsilon_b - \frac{\omega_p^2}{(\omega^2 + \gamma^2)} + i\frac{\omega_p^2 \gamma}{(\omega^2 + \gamma^2)\omega}$$

Real and Imaginary ε(ω) for Silver (Ag)



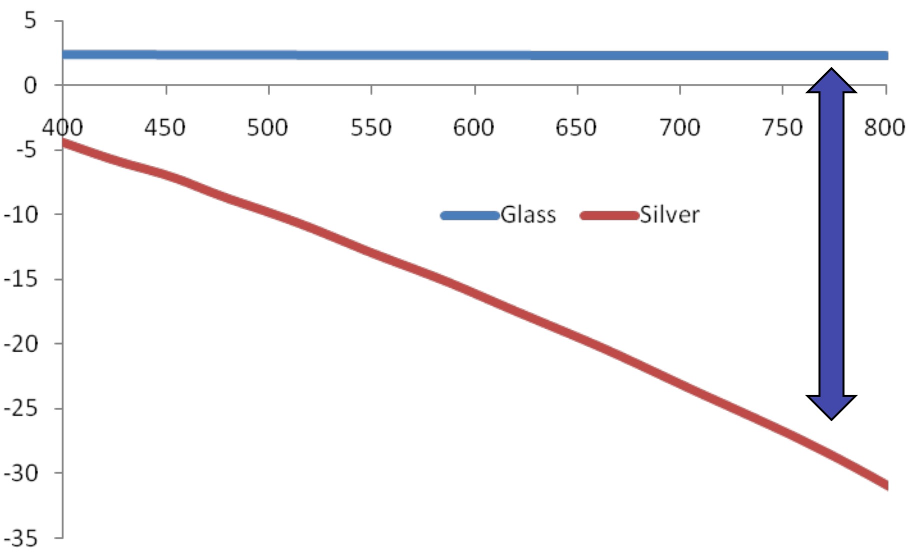
Johnson and Christy (dots) (1972)

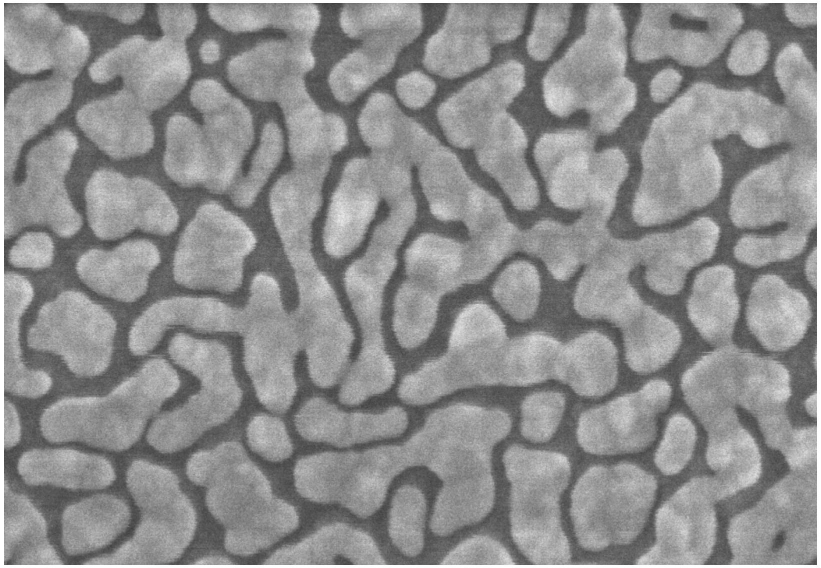
Stefan Maier, Plasmonic Fundamentals and Applications p. 17 (Drude model fit) (2007)

MATERIALS FOR TO / ENZ

- Effective permittivity nearly zero $\varepsilon_{effective} \sim 0$: cloaks, hyperlens etc.
- Real permittivity of metals must be comparable to that of dielectrics

(for example, $\varepsilon_{dielectric} \sim 2$ requires $Re(\varepsilon_{plasmonic\ material}) \sim -2$
while $Re(\varepsilon_{Ag}) << -2$…)





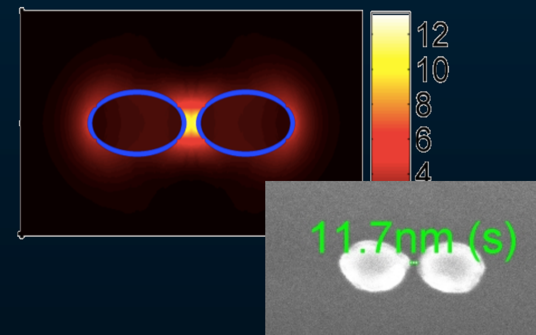
Ag: threshold for uniform continuous films is around 12-23 nm

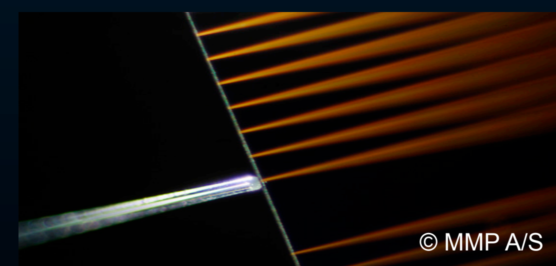
PLASMONICS&MM: BEYOND GOLD AND SILVER

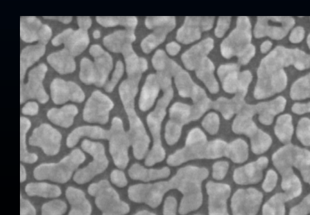
The vast majority of devices use gold & silver

They have many ideal properties, but key drawbacks

- Large losses in the Vis/NIR
- Optical properties are not tunable
- Continuous thin film growth is difficult
- Nanopatterning increases losses, grain boundaries, surface roughness...
- Soft materials
- Low melting point
- Not CMOS-compatible







Au & Ag are **NOT** the ideal material for every application

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

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MATERIAL REQUIREMENTS

- Low loss components
  - Dielectrics can be nearly loss-less
  - Metals have large losses
- Adjustable / Tunable optical properties

  Some Metamaterial + TO designs require comparable magnitudes of ε' of metal and dielectric
    - Epsilon-near-zero (ENZ) materials
    - Effective permittivity nearly zero: e.g. optical cloaks, hyperlens etc.

  Engheta, Narimanov, Alu groups
- Switchable devices

  M. Ren *et al.*, *Adv. Mater.* 23 (2011) 5540; J.Y. Ou *et al.*, *Nano Lett.* 11 (2011) 2142 – Zheludev group
  E. Feigenbaium *et* al., *Nano Lett.* 10 (2010) 2111 – Atwater group
- SC-compatible components

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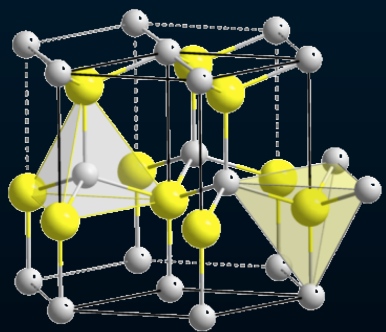
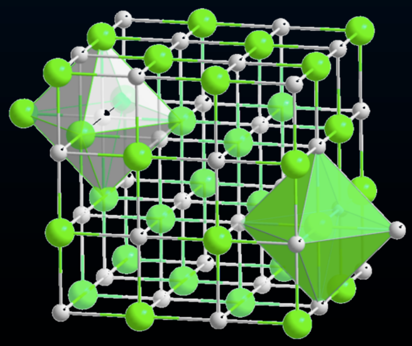


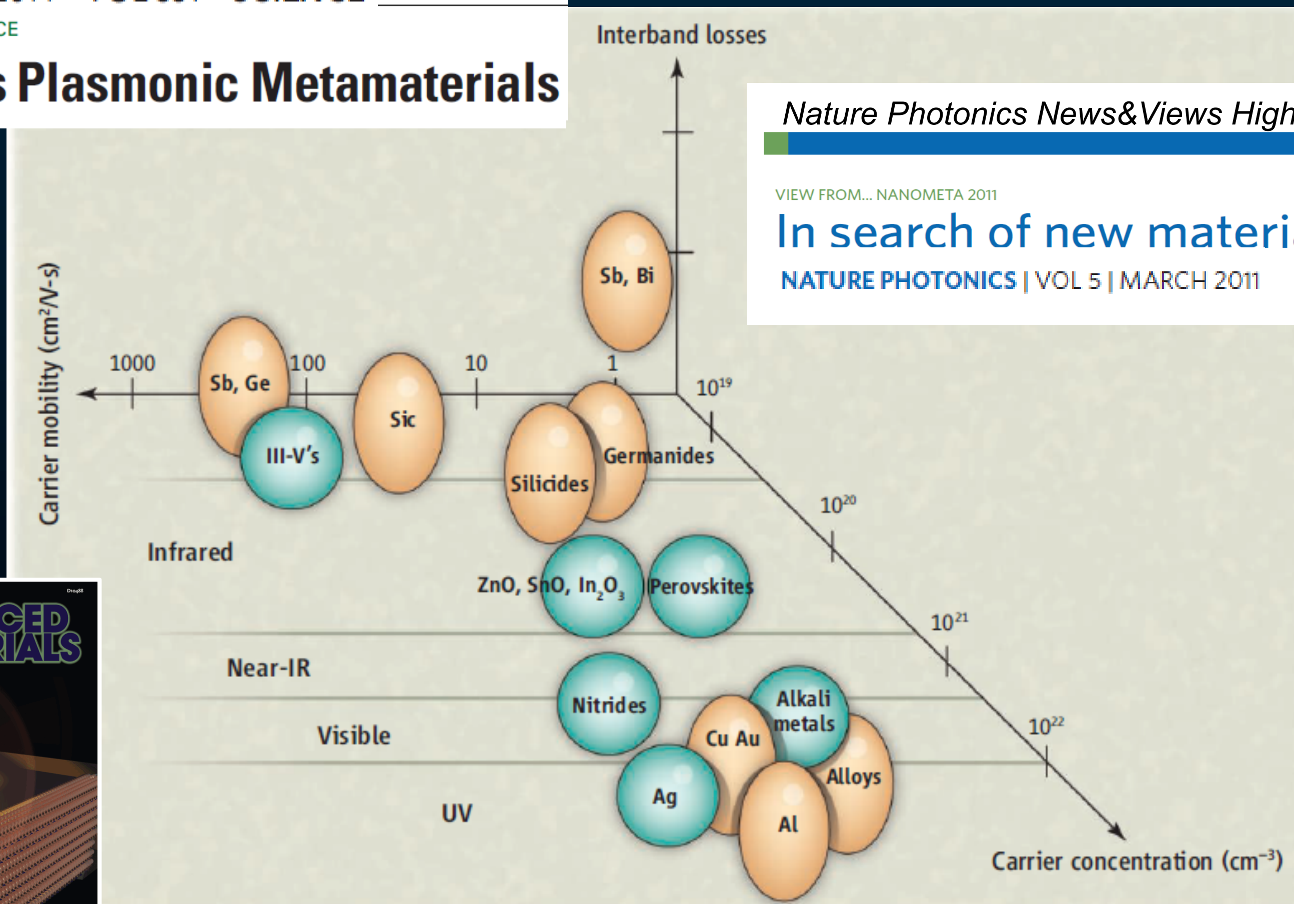


ALTERNATIVE MATERIALS

21 JANUARY 2011 VOL 331 SCIENCE

MATERIALS SCIENCE

Low-Loss Plasmonic Metamaterials



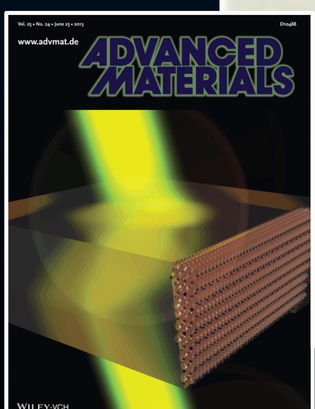
Nature Photonics News&Views Highlight

news & views

VIEW FROM... NANOMETA 2011

In search of new materials

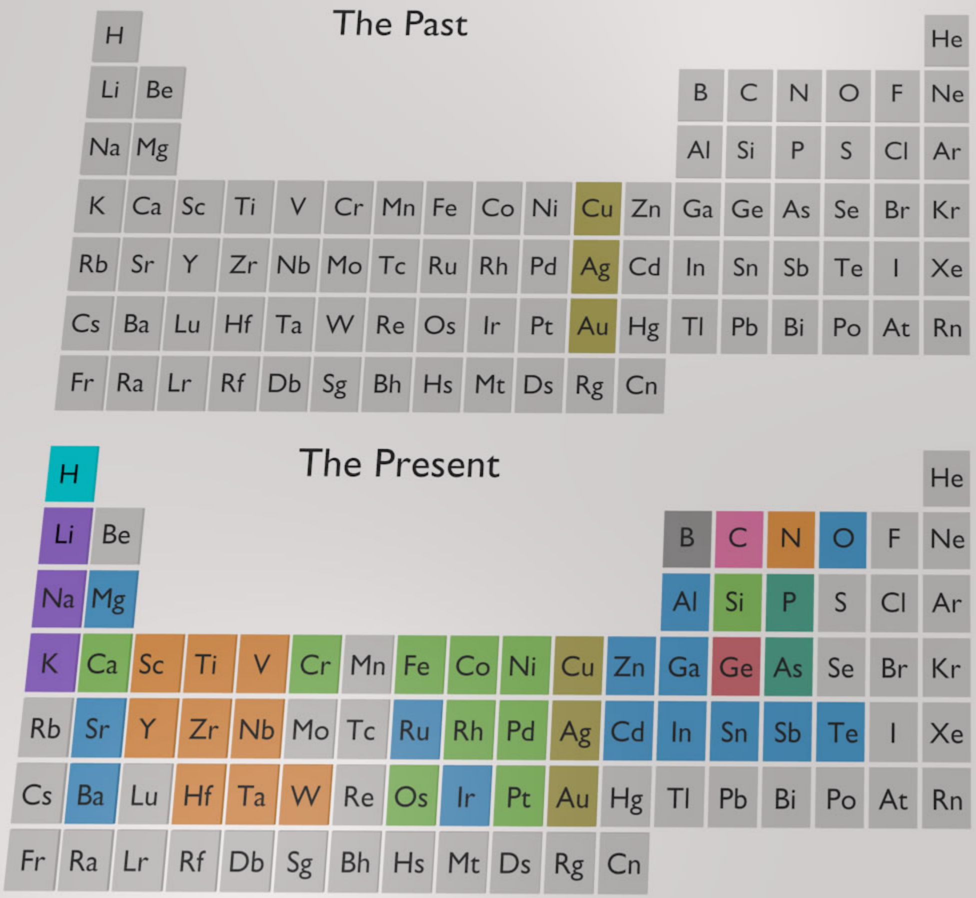
NATURE PHOTONICS | VOL 5 | MARCH 2011



A. Boltasseva and H.A Atwater, Science **331**, 290 (2011) G. Naik, V. Shalaev, A. Boltasseva, Advanced Materials 25 (24), 3264 (2013)

THE PAST AND PRESENT

Looking for intermediate carrier density materials



Au, Ag, Cu

TiN, TiAlN, ZrN, HfN, ScN, TaN, YN, VN, NbN, CuN, WN

ITO, Ga:ZnO, Al:ZnO, CdO, CdSbO, GaInO, MgInO, SrTiO, SrSnO, CdTeO, BaSnO, SrGeO, InO, TiO, IrO, VO, RuO

CoSi, CrSi, FeSi, HfSi, IrSi, NbSi, NiSi, OsSi, PtSi, PdSi, ReSi, RhSi, RuSi, TaSi, TiSi, VSi, WSi, ZrSi, CaSi, MgSi

RuGe, OsGe, BaGe, SrGe, CaGe, MgGe, CrGe

GaAs, AlGaAs, InGaAs, InP, AlInAs

Li, Na, K   YH

Graphene   MgB

Au, Ag, Cu

A. Boltasseva and H.A Atwater, Science **331**, 290 (2011)
G. Naik, V. Shalaev, A. Boltasseva, Advanced Materials 25 (24), 3264 (2013) + REFS THEREIN
A. Boltasseva, MRS Bulletin (2014)

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PLASMONIC MATERIALS

- Metals (Ag, Au, Cu, Al, Alkali)
- Alloys (Noble-Alkali[1], alloys of noble/transition metals Cadmium/Zinc[2])
- Doped Semiconductors: Highly doped SCs[3], doped conducting oxides (ITO[4], Al:ZnO and Ga:ZnO[5], ICO)
- Intermetallics (nitrides, germanides, oxides, hydrides[6]…)
- Graphene and other 2D systems (MoS_2 and other)
- Dielectrics!

1: M. G. Blaber et al., J.Phys. Cond. Matter. 21, 144211 (2009), 2: D. A. Bobb et al., Appl. Phys. Lett. 95, 151102 (2009); 3: A. J .Hoffman et al., Nature Mater. 6, 946 (2007); 4: C. Rhodes et al., J. Appl. Phys. 100, 54905 (2008); M.A. Noginov et al., Appl. Phys. Lett. 99, 021101 (2011); 5: LPR 4, 795 (2010), Phys. Status Solidi RRL 4, 295 (2010), Metamaterials 5, 1 (2011), OMEx (2011), Advanced Materials 25 (24), 3264 (2013); 6: Nano Lett., 2014, 14 (3), p 1140, H. Giessen group

also work by groups of N. Halas, H. Atwater, N. Zheludev, D. Basov, J. Garcia de Abajo, H. Giessen, C. Murray, O. Muskens

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METALS

Ag – Conventional Plasmonics, usual choice

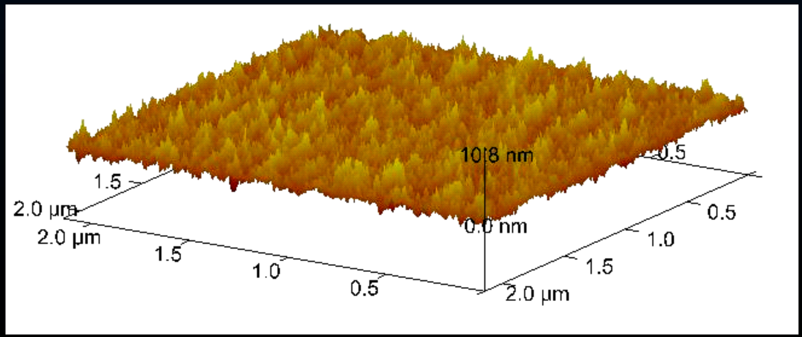
- Low loss
- Standard physical vapor deposition (PVD) methods + chemical methods
- But *degrades* in air

Au – Second Best for VIS, NIR

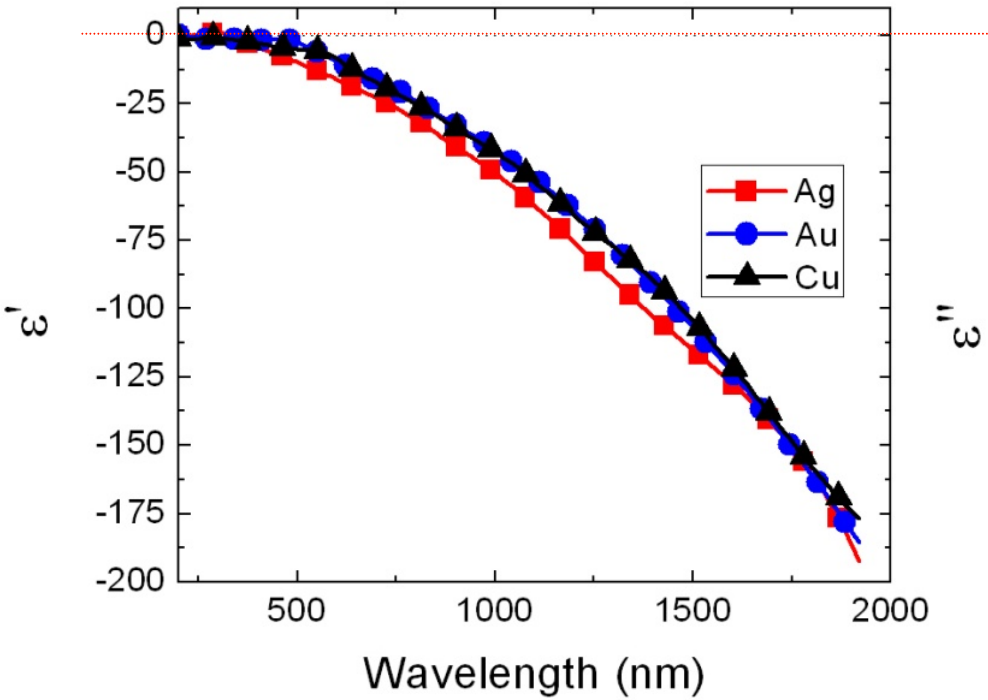
- Acceptable loss but *interband transition* (5d-6p) within VIS range
- Standard PVD methods + chemical methods: Chemically stable
- Continuous film at thickness of 2-7nm

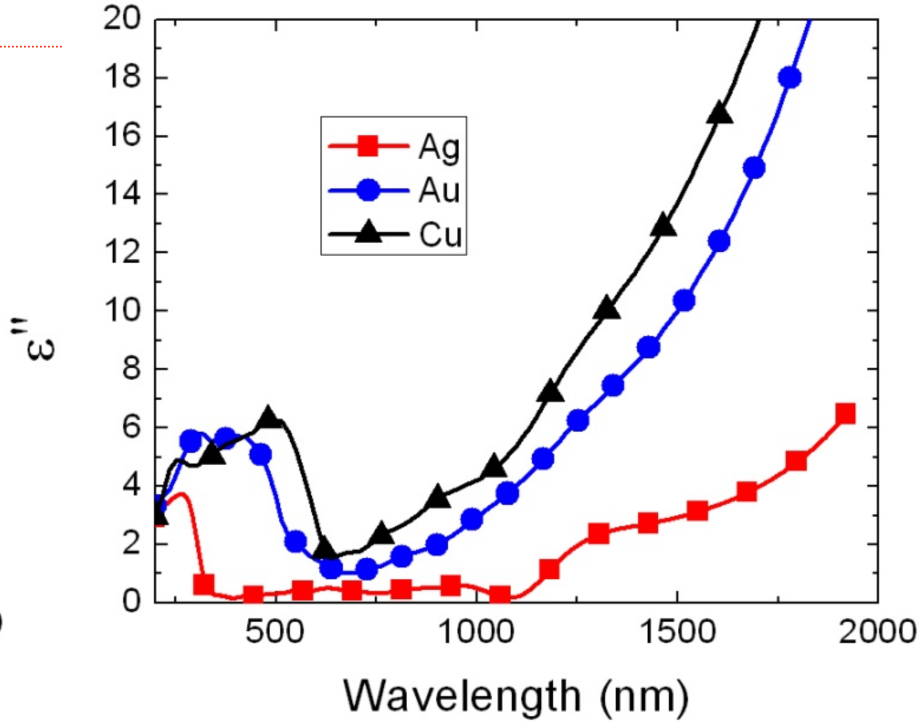
Cu – Ok for VIS (similar to Au)

- High conductivity + low cost
- But prone to surface *oxidation*



Ag, Au, Cu



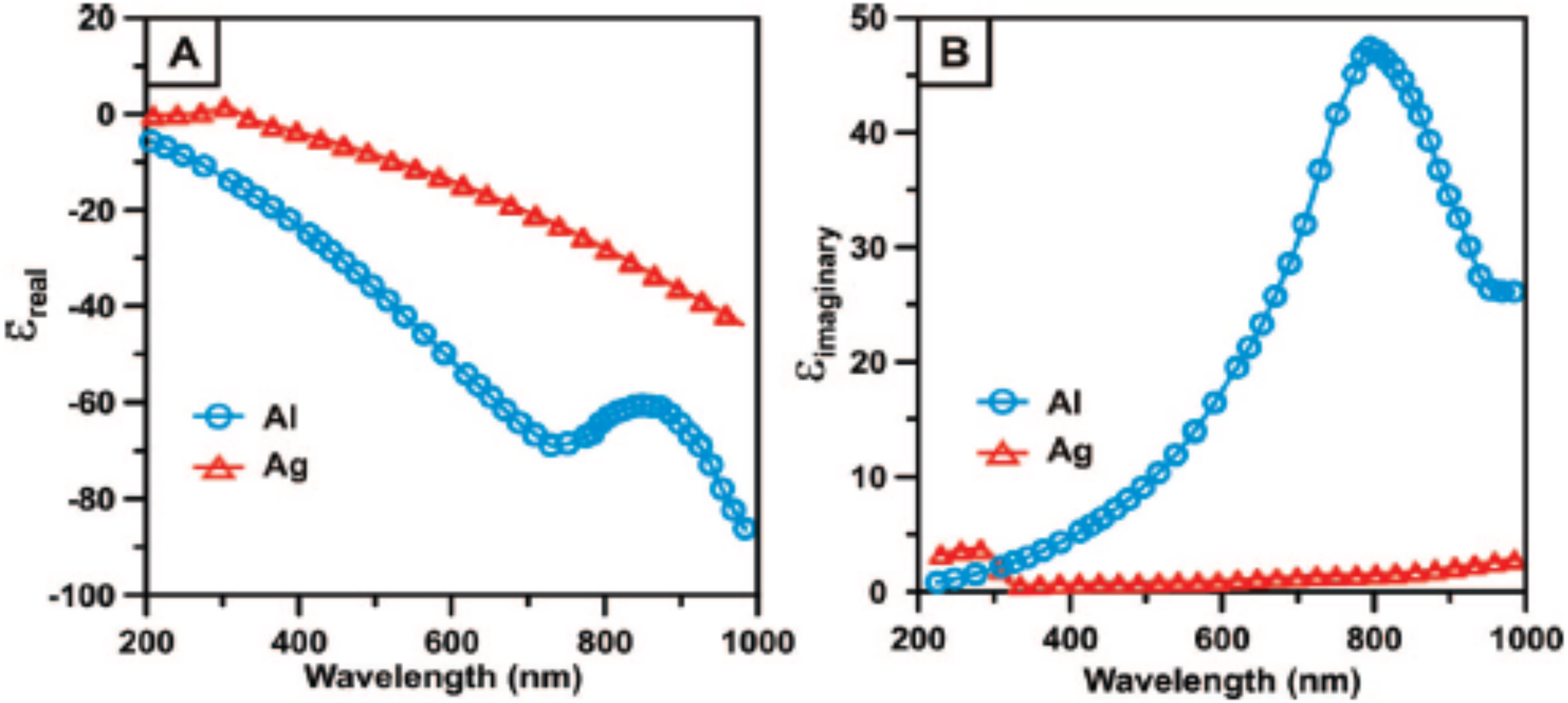


Cu – similar to Au 600-750 nm **CMOS compatible!**
fabrication is challenging (easily oxidizes)

ALUMINUM

Al – Higher loss in VIS + NIR

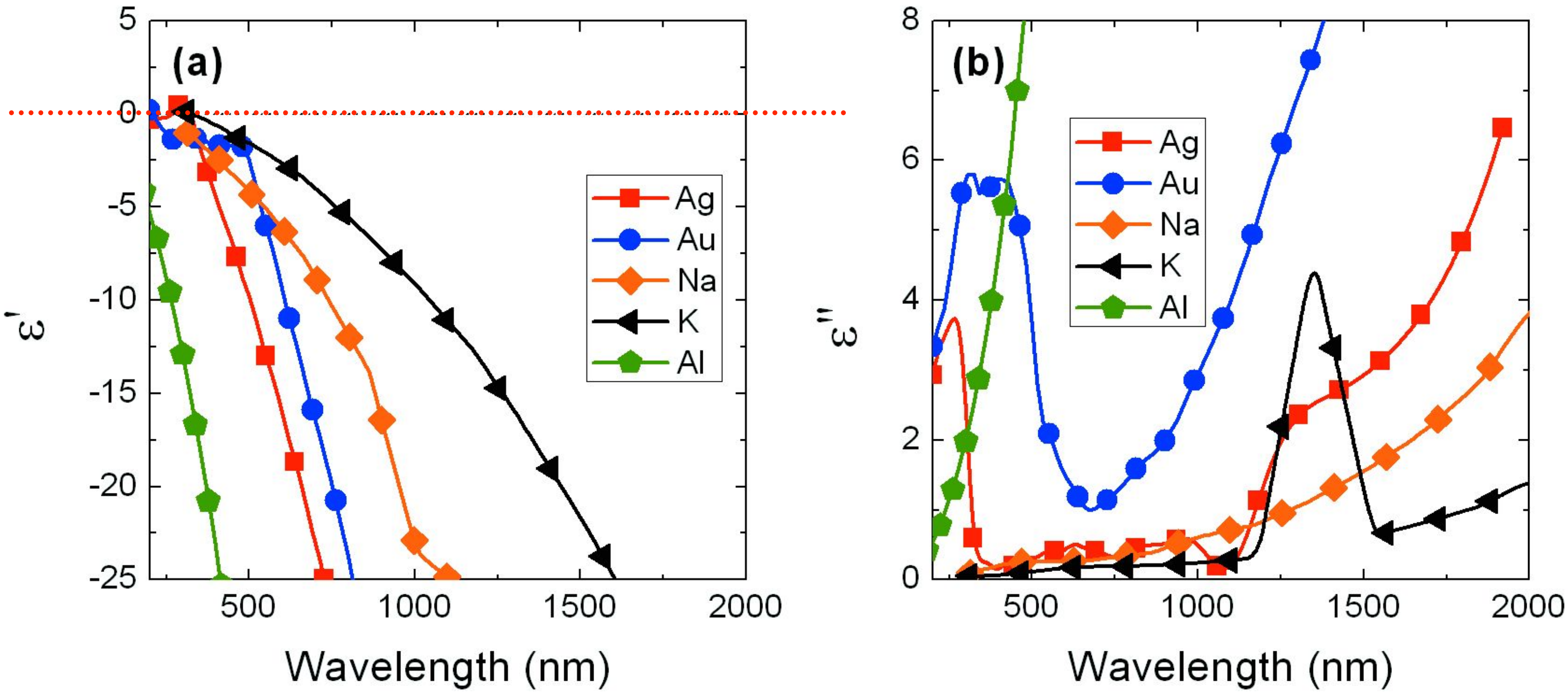
- Best for short wavelengths **(still plasmonic below 200 nm!)**
- Prone to surface *oxidation* (Al_2O_3 2.5~3nm)



G. Chan, et al, J. Phys. Chem. C, 112, 13958 (2008)
C. Langhammer, et al, Nano Letter, 8, 1461 (2008)

ALKALI

Alkali (Sodium, Potassium) – Lowest losses, closest to free-electron gas
- Very *reactive* (ultra-high vacuum 10^{-19} Torr reqiurement, passivation)



Ag, Au: P. B. Johnson and R. W. Christy, Phys. Rev. B 6, 4370-4379 (1972)
Al, Na, K: E. D. Palik, Handbook of Optical Constants of Solids

ALLOYS: IMPROVING METALS

Improving Noble Metals:

- To shift interband transitions to another (unimportant) part of the spectrum
-By alloying two or more elements to create unique band structures that can be fine-tuned by adjusting the proportion of each alloyed material

Noble-Transition Metal Alloys

Bivalent transition metals (Cadmium and Zinc) contribute one extra electron to the free-electron plasma n-type doping ⇒
- Increasing of ω_p
- Shifting the threshold for interband transitions
- Reducing the absorption at a specific wavelength

"Band Engineering"

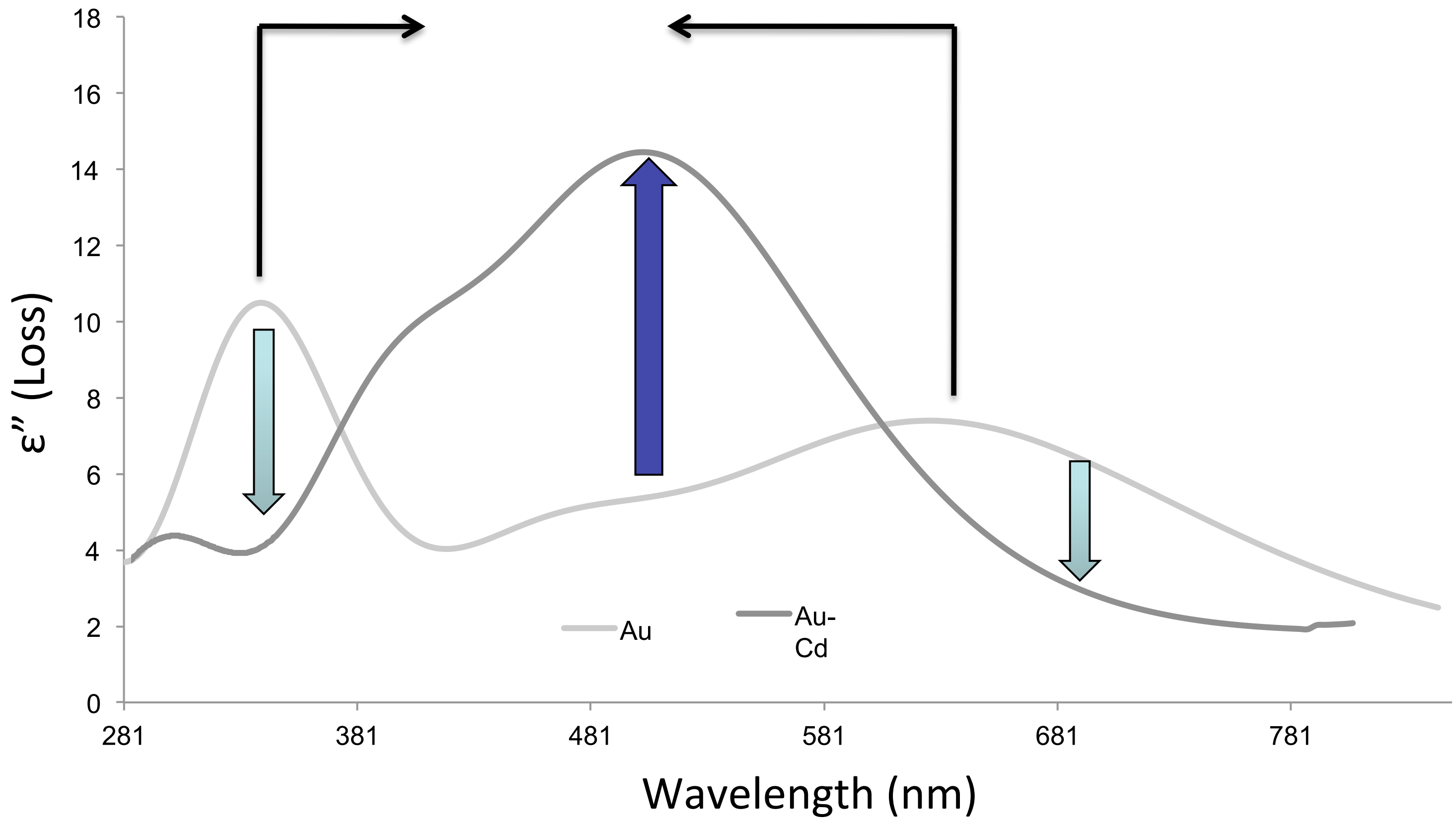
D. A. Bobb, G. Zhu, M. Mayy, A. V. Gavrilenko, P. Mead, V. I. Gavrilenko, and M. A. Noginov, Appl. Phys. Lett. 95, 151102 (2009) - Norfolk University

NOBLE-TRANSITION ALLOY

Cadmium + Gold ⇒ Additional electron to free electron gas

Shift of the Lorentz resonance peaks ⇒ Tuning of the optical parameters

Optimum – 3.3% Cadmium in Gold



D. A. Bobb, G. Zhu, M. Mayy, A. V. Gavrilenko, P. Mead, V. I. Gavrilenko, and M. A. Noginov, Appl. Phys. Lett. 95, 151102 (2009) - Norfolk University

"LESS-METALLIC" MATERIALS?

- Metals: Too large carrier concentration
  - Large plasma frequency (ω_P)
    - $\omega_P \alpha \sqrt{n}$: $n \sim 10^{22}$ cm^{-3} in metals
  - Large loss ($\varepsilon'' \alpha \omega_P^2$) + large magnitude of ε'

METALS ARE TOO METALLIC…

SEMICONDUCTORS → "METALS"

- Semiconductors: Doping can control carrier concentration
  - Conventional semiconductors: too low carrier concentration (dielectrics)
  - Doping density of $10^{21} cm^{-3}$ could produce $\varepsilon'<0$ in NIR

METALS → TO "LESS-METALS"

- Lower carrier concentration in metals
  - Abstract electrons by non-metal inclusions
  - Non-stoichiometric: controllable properties

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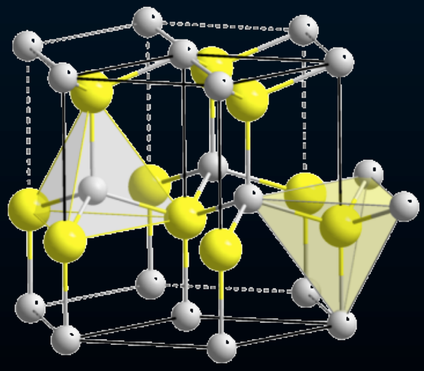


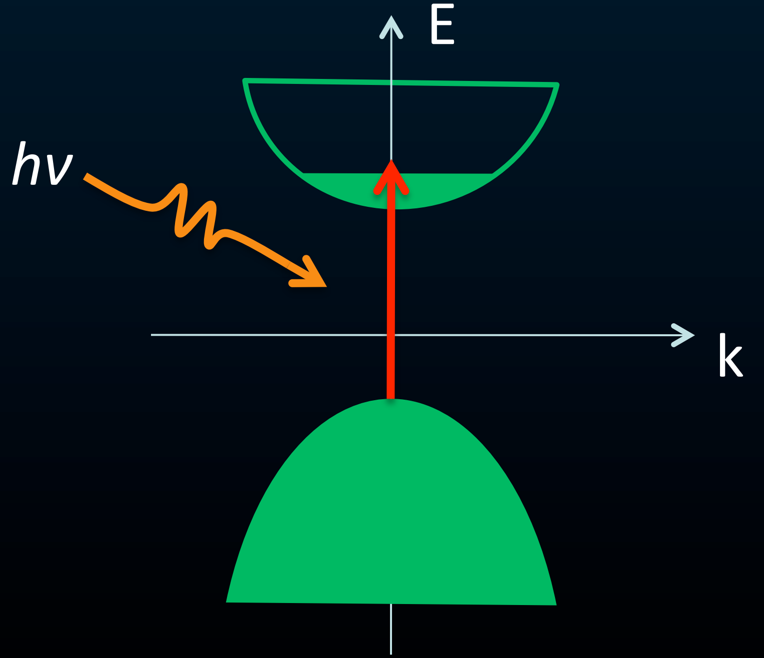
SEMICONDUCTOR-BASED "METALS"

- Make semiconductors more metallic:
  Increase carrier concentration to 10^{21} cm^{-3}
- Wide Bandgap Semiconductors:
  Negligible interband transition losses
- Bandgap should be larger than frequency of interest

  Material Bandgap (eV):

  Si - 1.12, GaAs - 1.42, SiC - 2.36-3.05
- Large carrier mobility:
  Low damping losses

Required min $3x10^{20}$ cm^{-3}

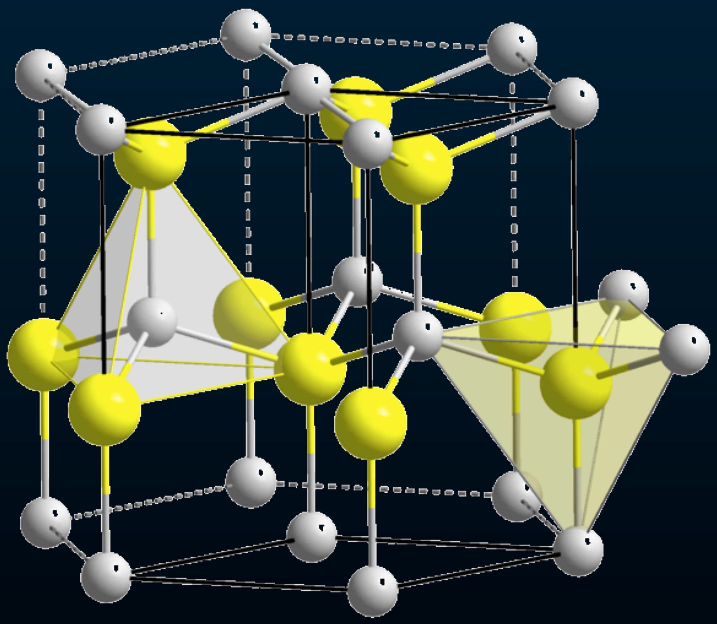


ZINC OXIDE

- II-VI semiconductor
- Wide band-gap of 3.37 eV at 300 K

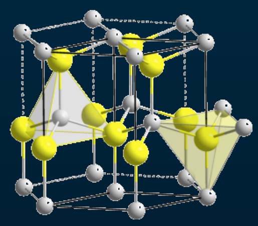
- Applications:
  - Display flat panels
  - Piezo-electric devices
  - Paints, anti-corrosive coatings
  - Bio-compatible devices
  - Optoelectronic devices
  - Gas-sensing

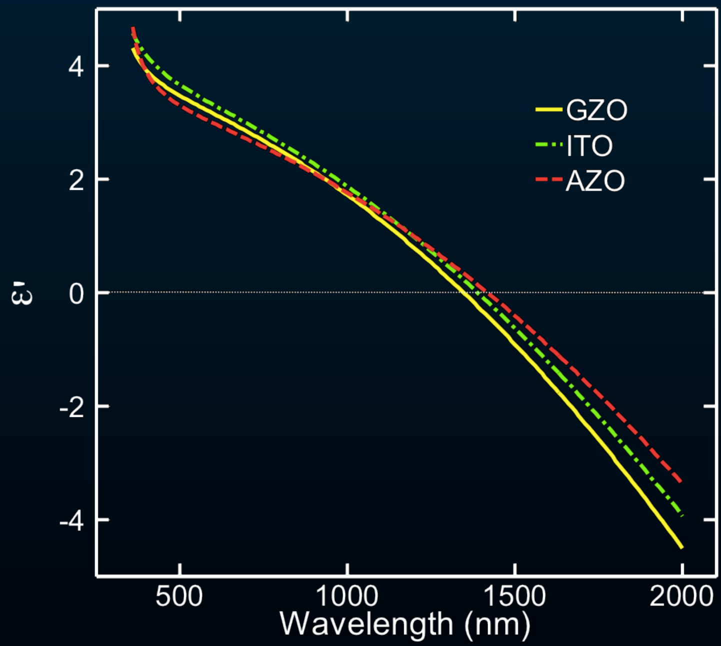
- Heavy doping:
  - Al or Ga (up to 10^{21} cm^{-3})
  - Challenging

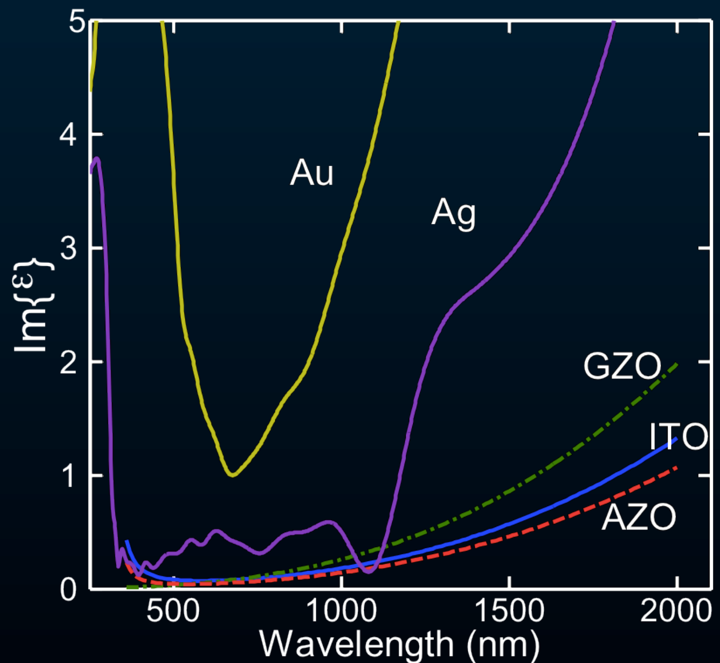


SEMICONDUCTOR "METALS": TCOs

- DOPED ZINC OXIDE: Wide band-gap (3.37 eV@300K)
- Al or Ga (up to 10^{21} cm^{-3})
- Can be adjusted/tuned!





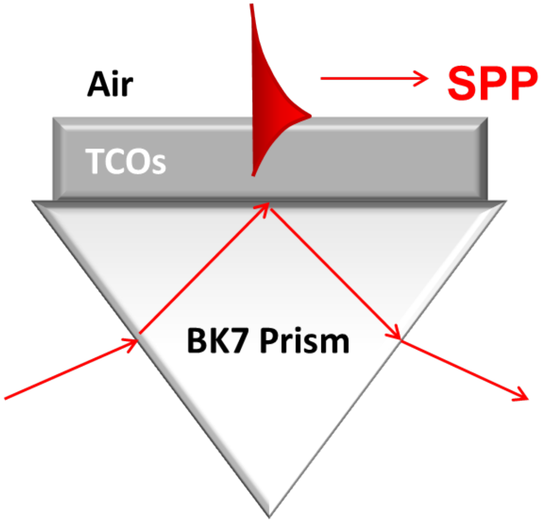


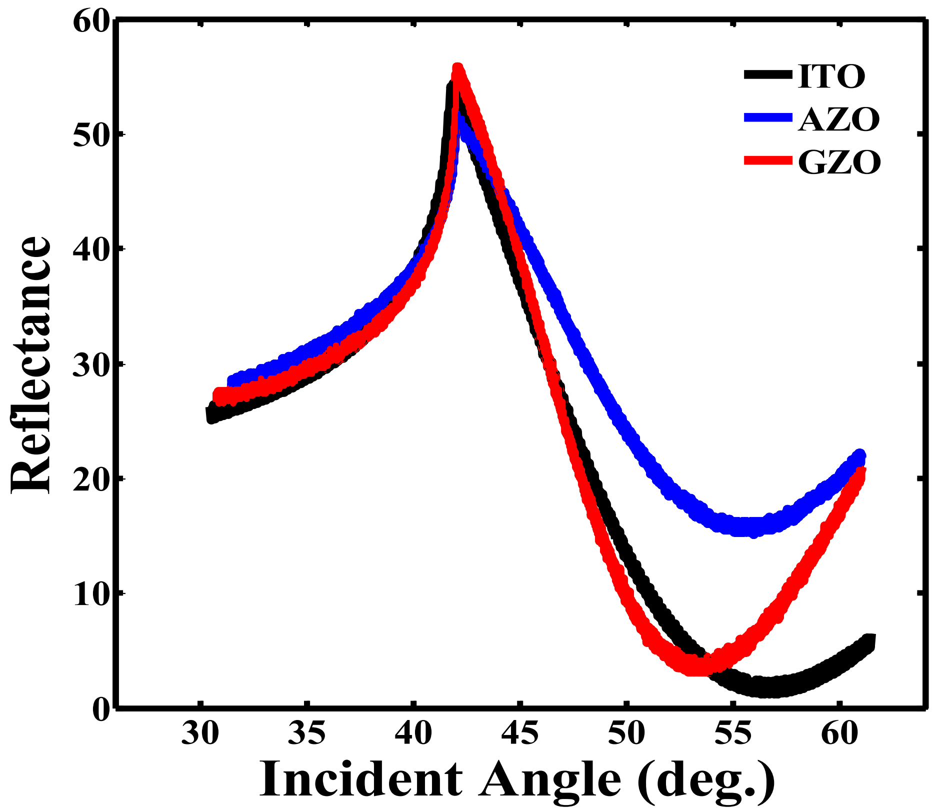
Also see :
O. L. Muskens
H. A. Atwater
M. A. Noginov
C. B. Murray
D. J. Milliron
V. J. Sorger
R. P. H. Chang
M. Wegener
S. Franzen
T. W. Odom
V. A. Podolskiy

AZO: Lowest Drude damping, Longest cross-over wavelength ($5x10^{20}$ cm^{-3})
GZO: Cross-over wavelength as low as 1.2 µm
Theoretical studies: with Norfolk and Navy Research Lab

G.V. Naik, et al, Optical Mater. Exp. 1 (2011)
J. Kim, et al, PRX (2013)

SPPs ON TCO FILMS AT 1.55 μm



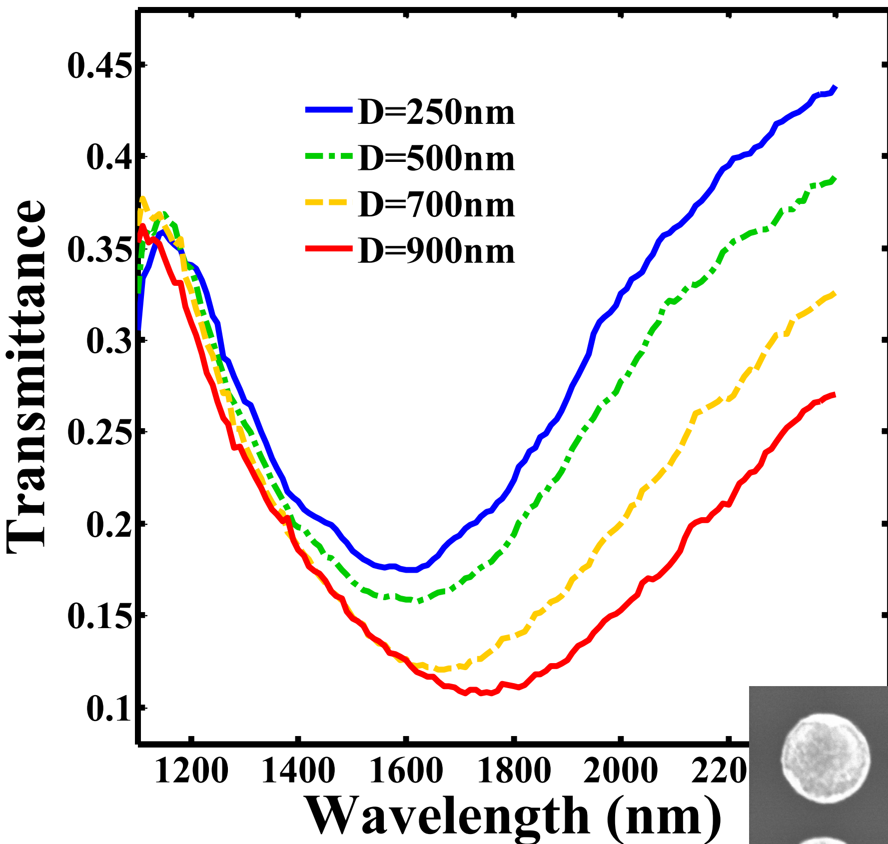


- **TCO is directly deposited onto BK7 glass prism**
- **Re{ε_{TCO}} < -1 (at 1.55um)**
- **Angular reflectance shows dip at angles corresponding to excitation of SPPs**

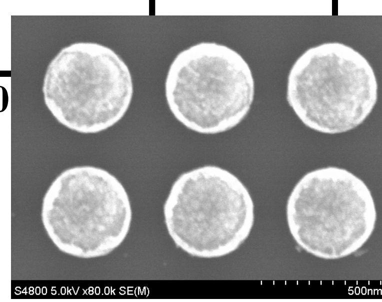
SPP excitation on ITO films using prism-coupling: Franzen, Noginov groups

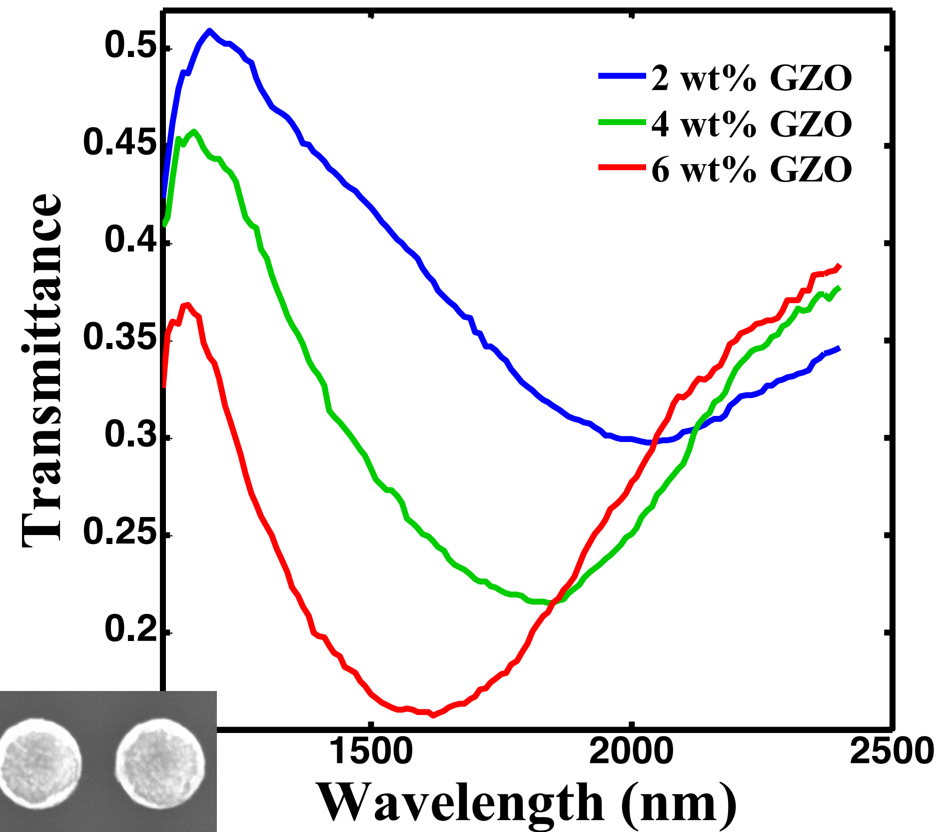
J. Kim, et al., IEEE J. Select. Topics Quant. Elec. 19, 4601907 (2013)

TCO LSPR STRUCTURES (Size and Doping)



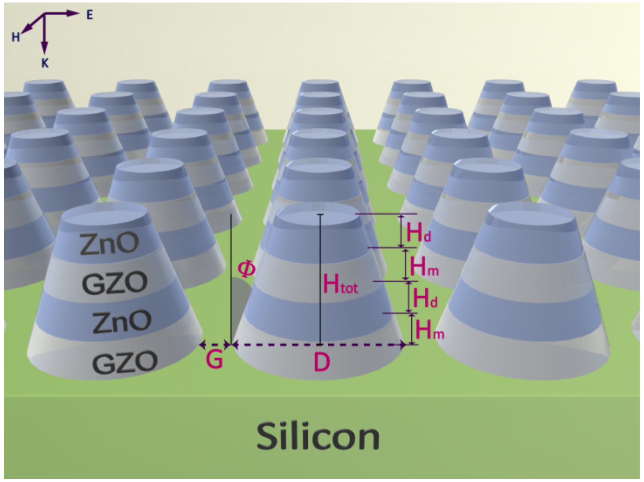
<Disk Size>





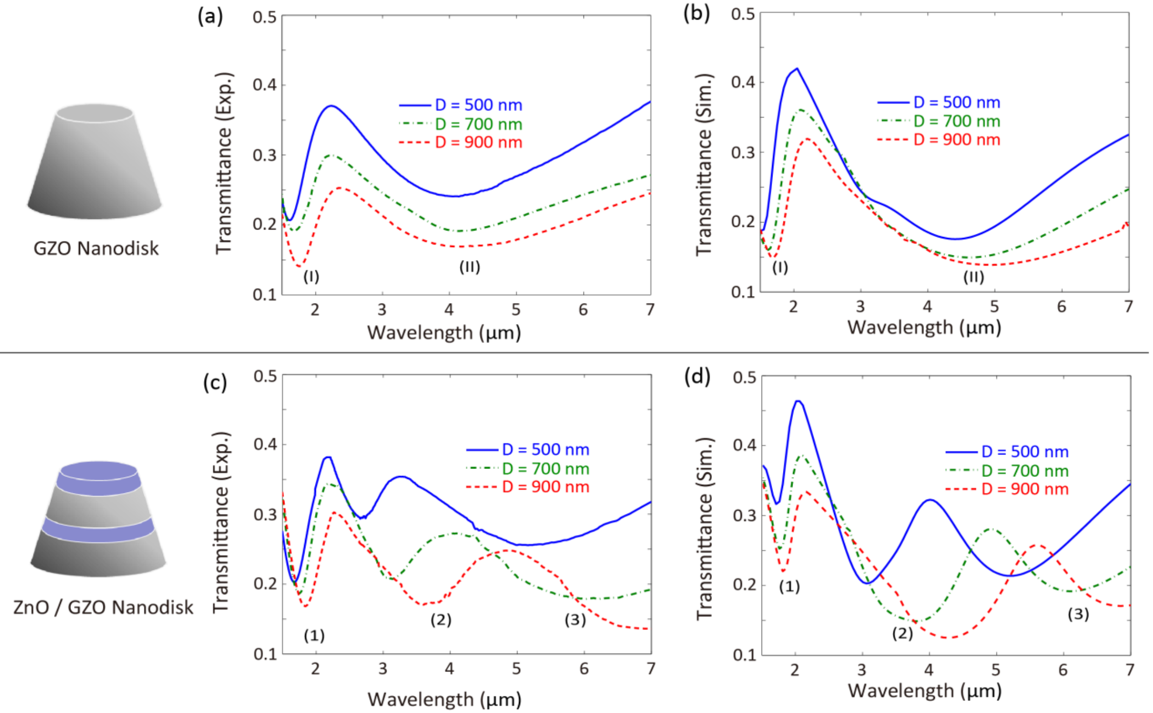
<Doping density>

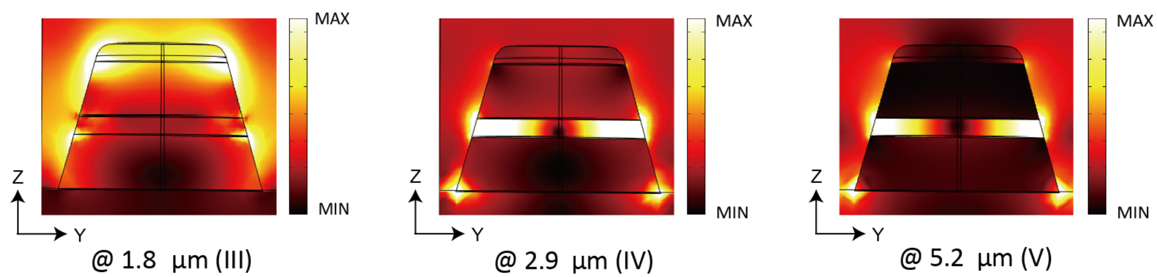
GAP SP IN TCO/DIELECTRIC/TCO



- H_{ZnO} = 40 nm, H_{GZO} = 120 nm
- Metal : Gallium doped ZnO
- Dielctric : Undoped ZnO

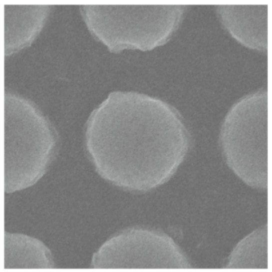
- ***1.8 µm: LSPR***
- ***2.9 µm : Gap Surface Plasmon Resonance***
- ***5.2 um : LSPR + GSPR***



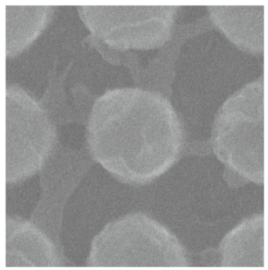


Surface Enhanced Infrared Spectroscopy

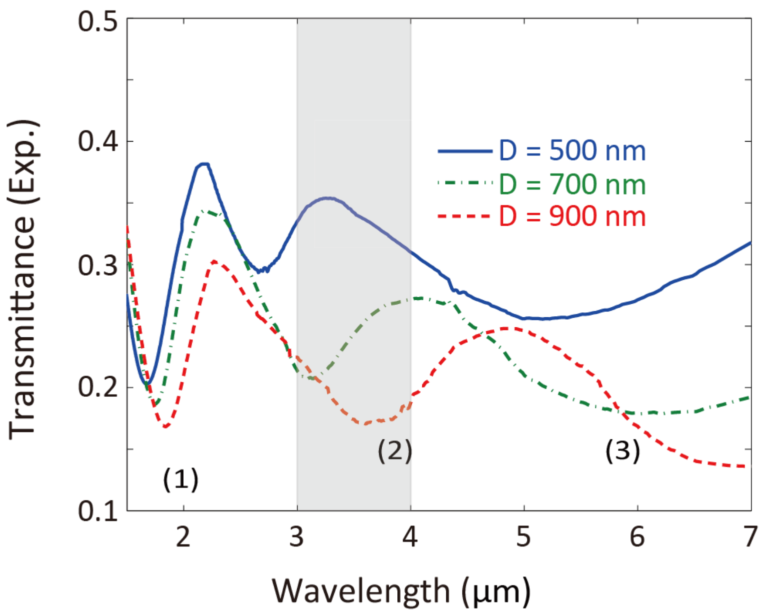
Nanodisk without ODT layer

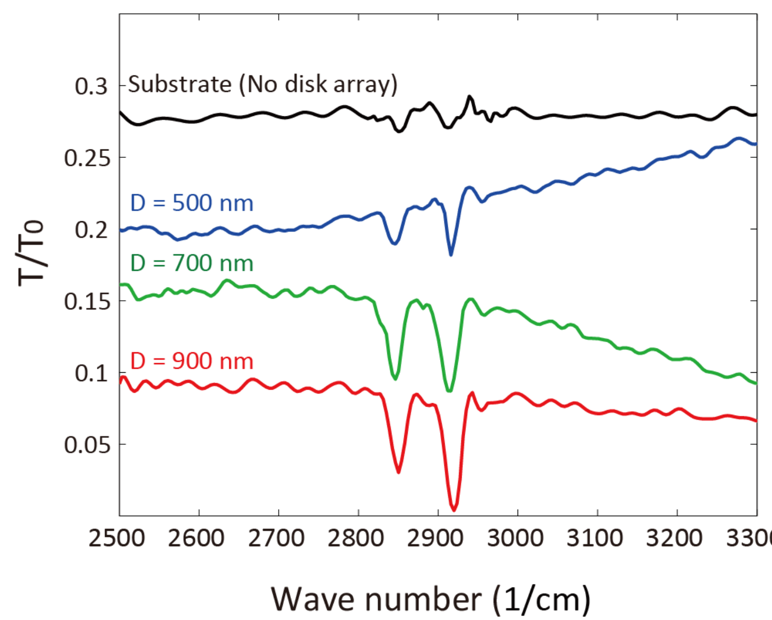


Nanodisk with ODT layer



- Octadecanethiol (ODT) Polymer layer (20nm)
- Absorption from vibrational modes of ODT molecules are located very close to the GSP resonance
- Strong enhancement of absorption due to interaction with GSPR on MIM TCO based nanodisk resonator

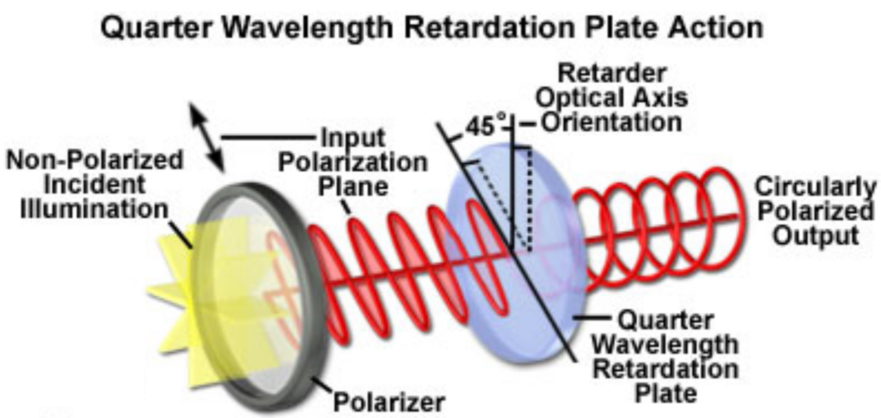




See work by Sergey Bozhevolnyi, *OE* (2013)

METASURFACES WITH CERAMICS With Andrea Alu

PURDUE UNIVERSITY

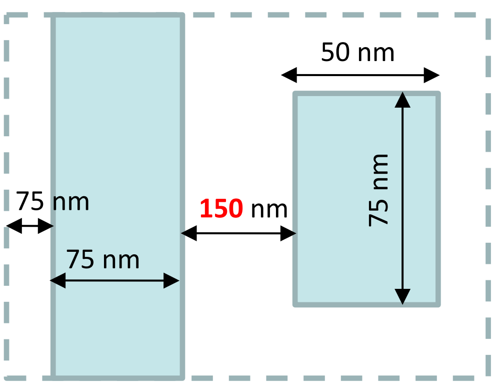


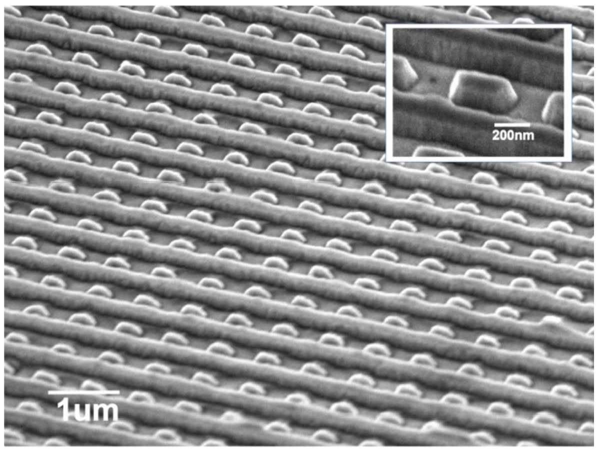
Current QWP

- ✓ Bulk birefringent material with optical anisotropy
- ✓ Narrow band

QWP metasurface

- ✓ Fabrication simplicity/1D design
- ✓ Nano-scale
- ✓ Broadband





GZO metasurface and Phase difference (Δ) of reflected light between two orthogonal polarizations (s and p) at 18^{o} angle of incidence

See work by Hasman, Capasso, Zheludev, Alu groups

EPSILON NEAR ZERO (ENZ)

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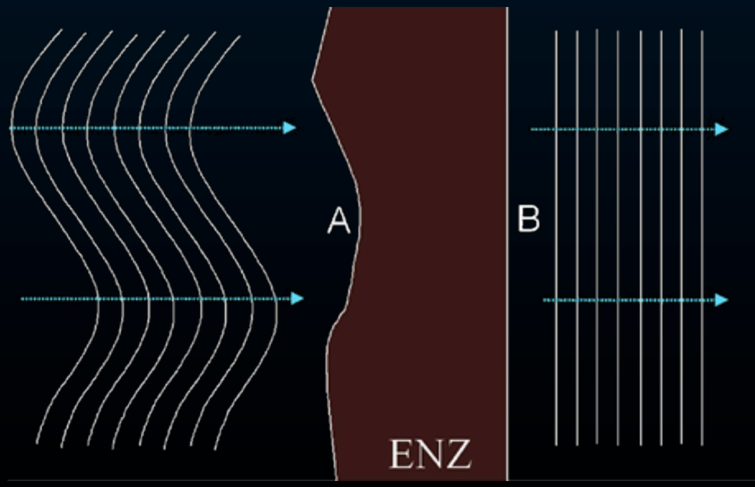
CONCEPT:

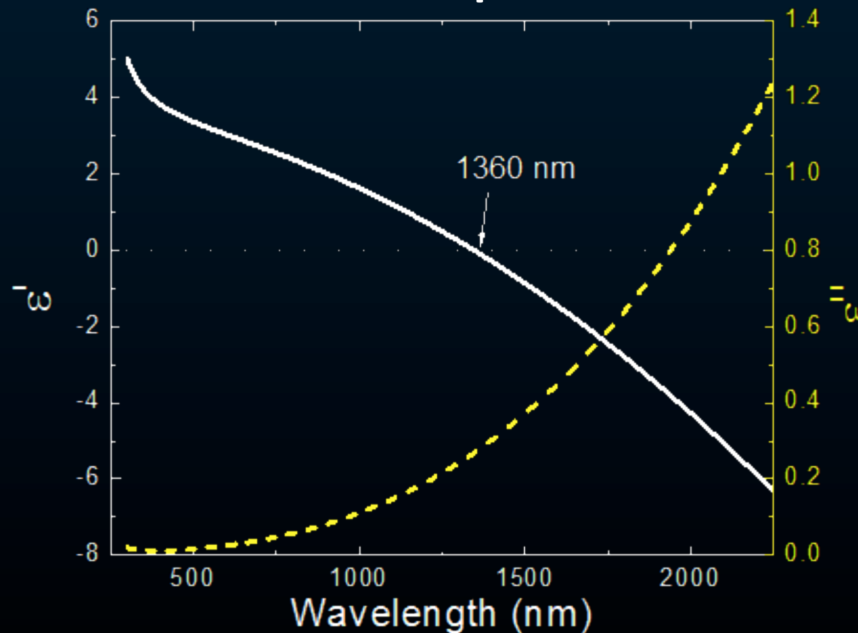
- Near Zero Refractive index (n) : Light propagates with almost no phase advance
  → Very small phase variation over a physically long distance

- **High impedance with the surrounding environment** $Z = \sqrt{\mu/\varepsilon}$
  → **Directive radiation or Isolation of devices for on-chip nanophotonic devices**

TCOs as ENZ :
Naturally occurring ENZ medium with low losses in NIR
Tunable ENZ by doping



TCO: Al doped ZnO



ENZ at around 1360 nm wavelength

See work by Engheta, Alu, Muskens and other groups

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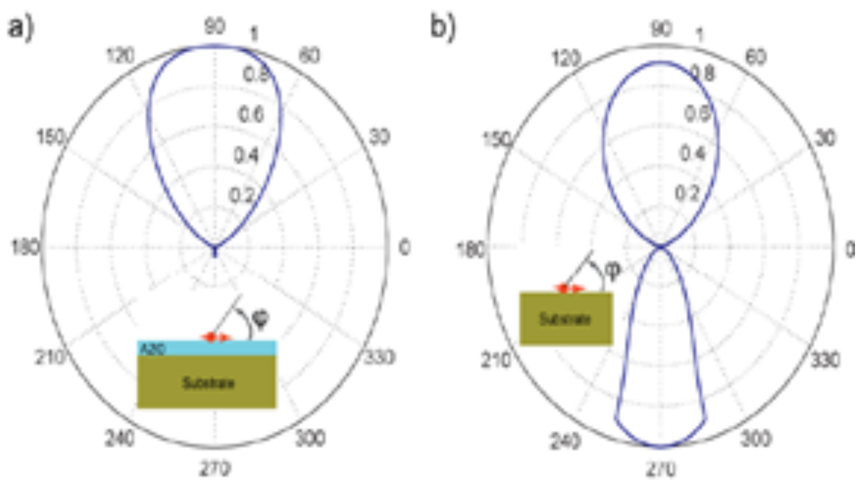
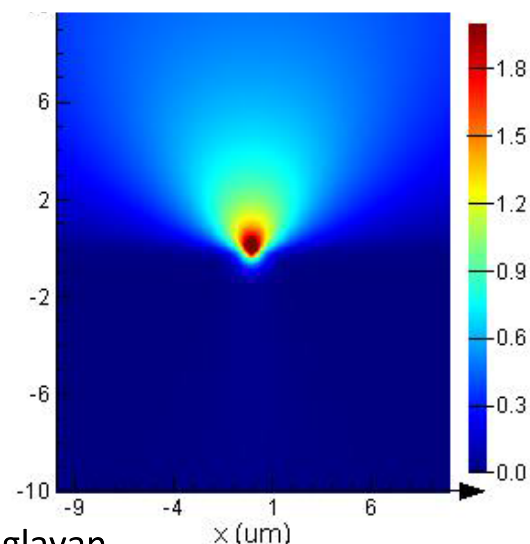
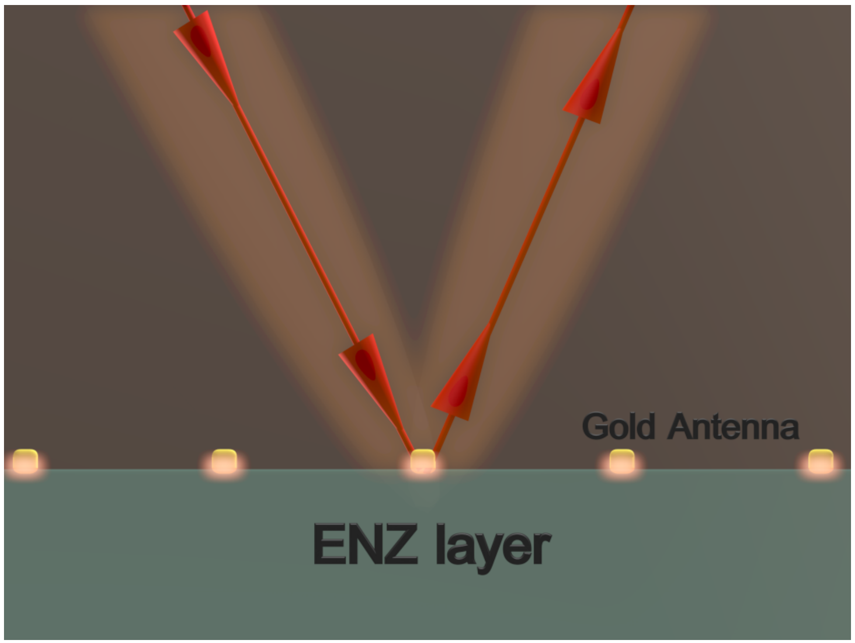
ANTENNAE/EMITTERS ON ENZ



Dipole on ENZ/air interface

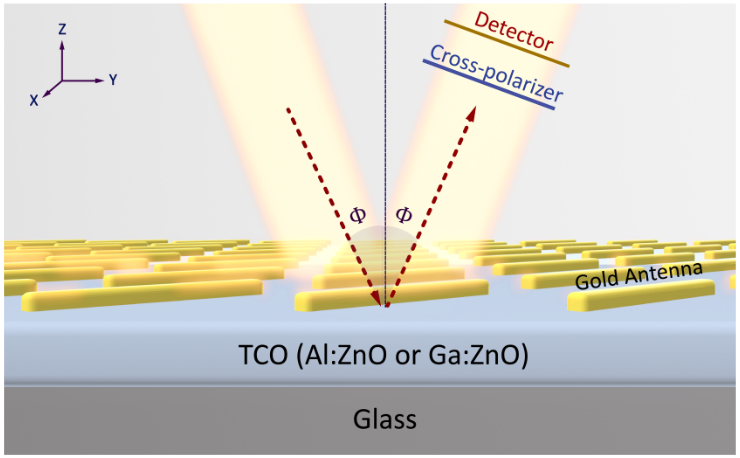


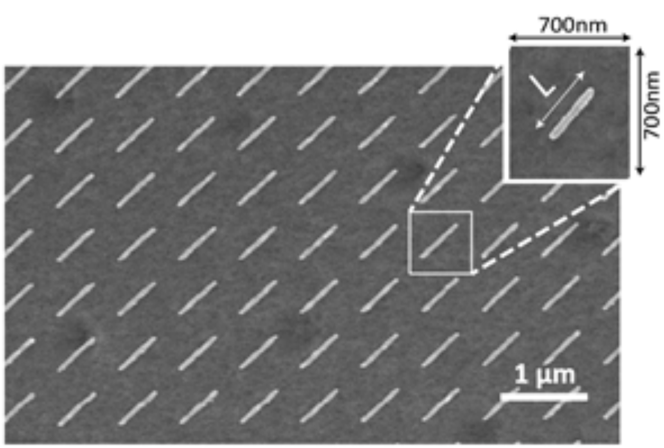
By H. Caglayan

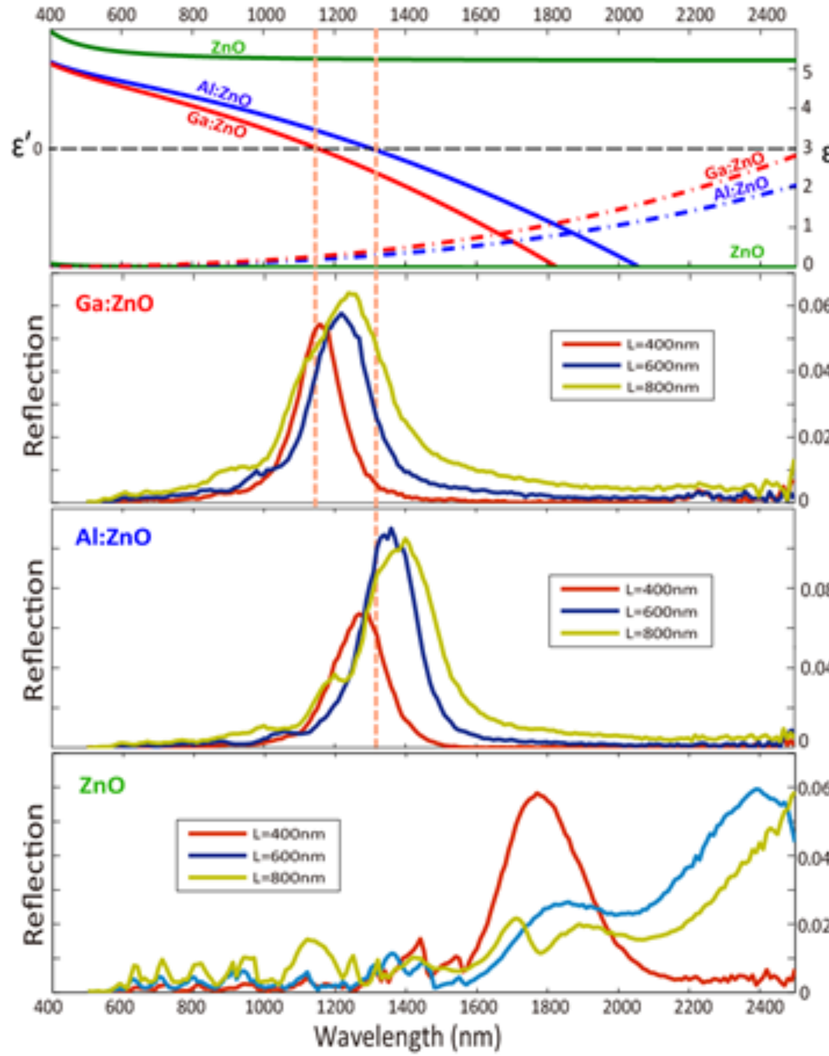


ENZ substrates alter radiation pattern and pin antenna resonances to ENZ wavelength!

ANTENNAE ON ENZ







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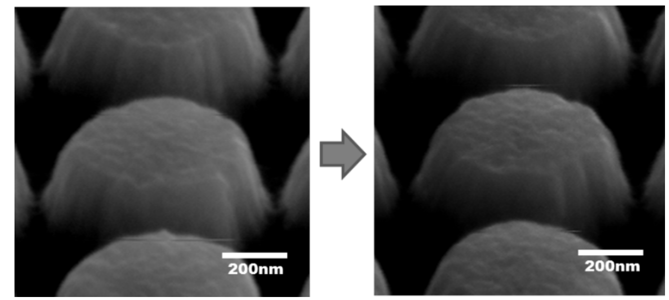
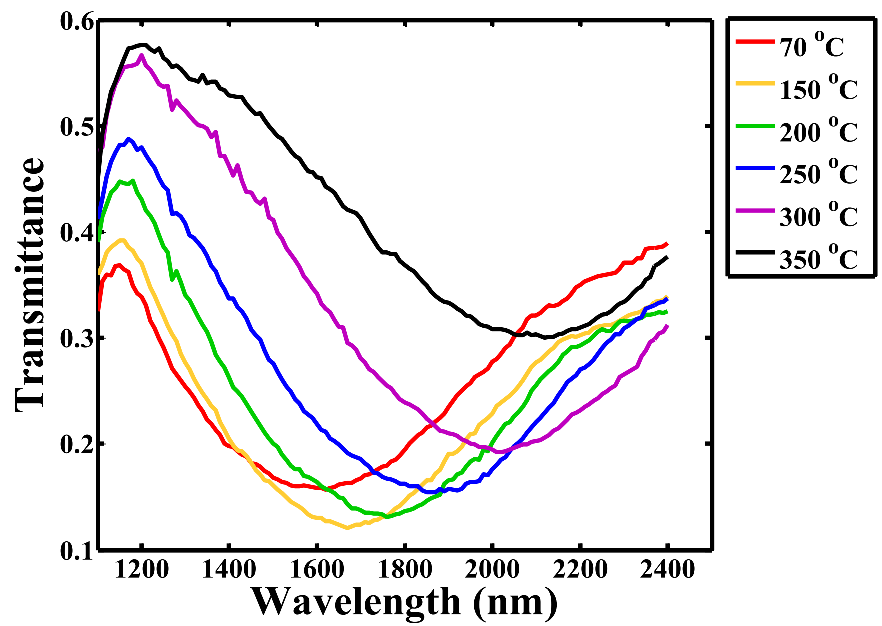
TUNING LSPR IN TCOs

- Resonance **tuning** by anneal process
- Nitrogen and oxygen anneal reduces carrier concentration
- Nitrogen anneal reduces defects and improves damping losses





Approaches:

- **Doping concentration change during solution-based synthesis (AZO)**
- **Dynamically change doping level by electrochemical means (ITO)**
- **Electrical means**

J. Kim, G.V. Naik, N.K. Emani, U. Guler, A. Boltasseva, IEEE-JSTQE, 2012

Groups of Sorger, Odom, Ketterson, Chang, Muskens, Brongersma, Atwater

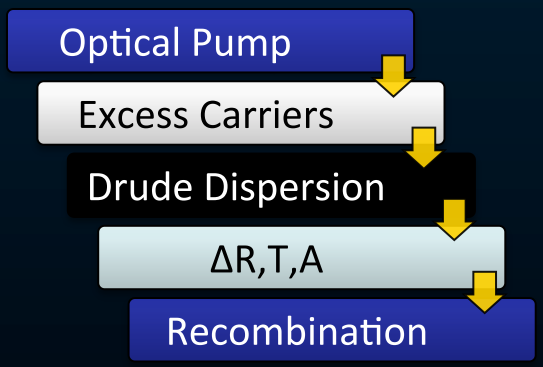
TUNABILITY OF TCOs

- Transparent conducting oxides are known for their dynamic nature
  - **Electrical**
  - **Optical**

- Reports of dynamic devices using TCOs, little evidence for the change of carrier concentration

- Use pump-probe techniques to investigate ALL-OPTICAL tuning of TCOs

Free Carrier Effect



Groups of Juerg Leuthold, Volker Sorger, Otto Muskens, Harry Atwater, Mark Brongersma, Robert Boyd, Robert Chang

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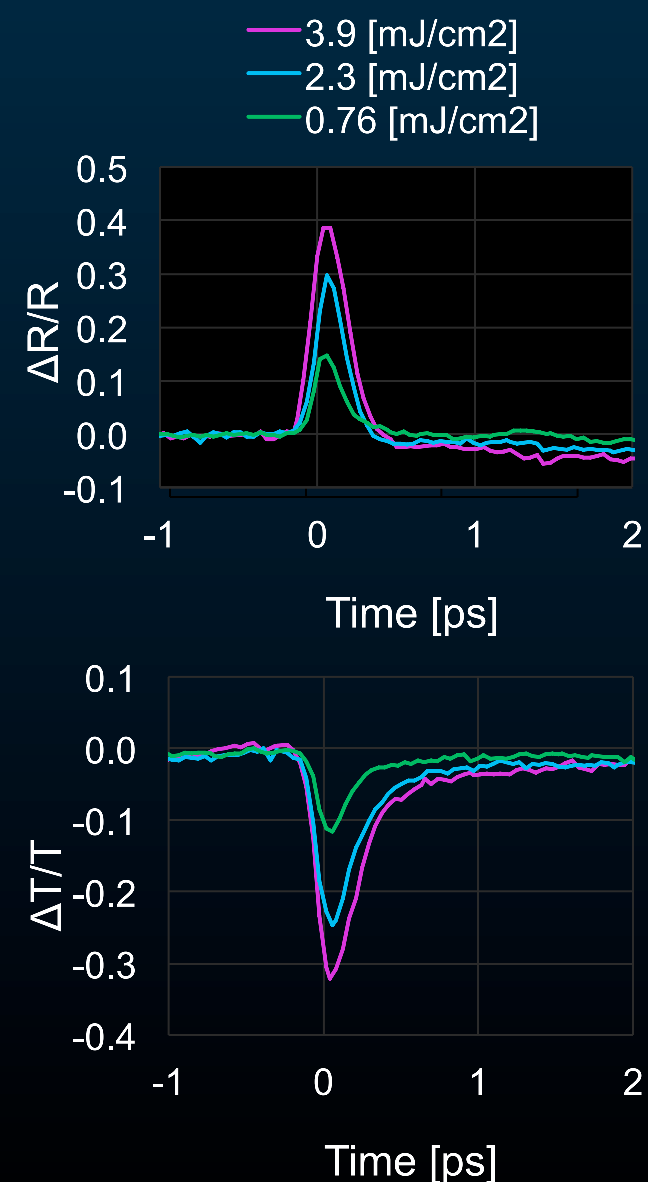
PUMP-PROBE RESULTS

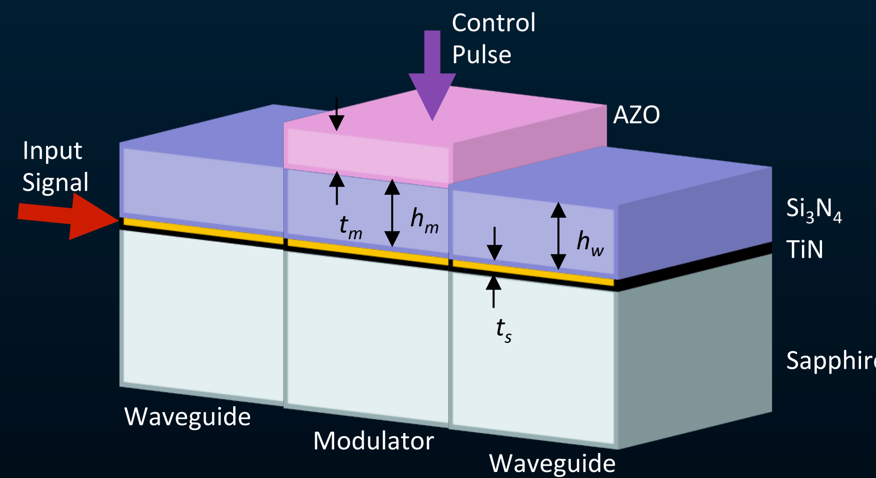
- Experimental results:
  - Large change in R & T (40% & 30%)
  - Ultrafast response zero-to-zero in < 1 ps
  - Small energy required
- The large response is due to ENZ operation
- Ultrafast recombination is believed to be the result of deep level defects which arise due to the growth procedure
  - Similar effect noted in low-T GaAs
  - However, this effect is still 2-3x faster



N. Kinsey et al, Optica, in press, 2015

ALL-OPTICAL MODULATOR

- The extracted values were used to design a high-speed modulator
- Based on the solid-state TiN waveguide
- Modulation achieved through two processes
  - Absorption
  - Mode disturbance
- Mode in waveguide exists only for a balanced effective index
- Modification of the AZO index disturbs this balance so the mode no longer is supported



See modulator work by Juerg Leuthold, Volker Sorger, Harry Atwater, Mark Brongersma

N. Kinsey et al, Optica, in press, 2015

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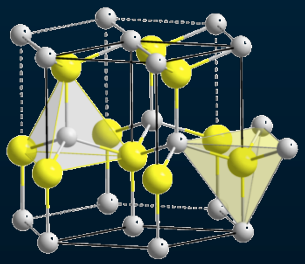
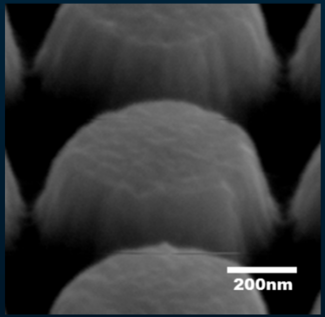
NOVEL TUNABLE/SWITCHABLE DEVICES

TRANSPARENT CONDUCTING OXIDES

- *Plasmonic materials in NIR*
- *Tune plasma frequency by doping*
- *Great switching opportunities*
- *Standard fab, SC-compatible*

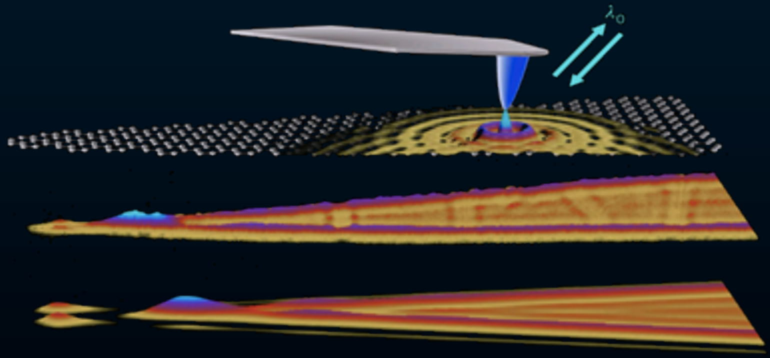




GRAPHENE

- *Strong electrical tunability*
- *Highly confined plasmons*

(40-60 times smaller than λ_0) at IR



Applications

- *Optical Modulators, NIR/VIS photodetectors*
- *Lasers, THz polarization controllers*

Reviews: G. Naik, V. Shalaev, A. Boltasseva, Adv. Mat. 25, 3264 (2013), J. Garcia de Abajo, Science 339 , 917 (2013)

GROUPS of H. Giessen, H. Atwater, N. Zheludev, O. Muskens, D. Basov, J. Garcia de Abajo

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TCOs: NEED FOR THEORY & MODELING

Doping of ZnO substantially affects

- Lattice parameters
- Band structure

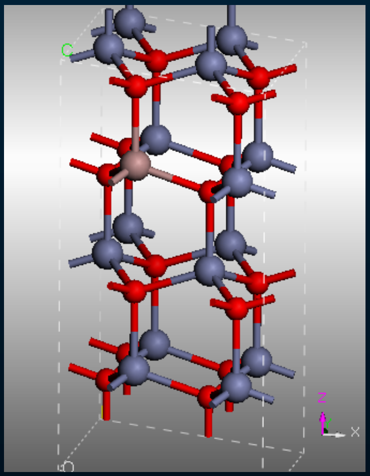
Optical response mechanisms in Ga:ZnO

- Burstein-Moss – Excitons –
- Atomic structure distortions – Alloying effects

Modeling and Simulation (NSU)

- Lattice expansion with Ga-doping
- Density of States : Strong charge redistribution due to d-Ga electrons

Ga: ZnO

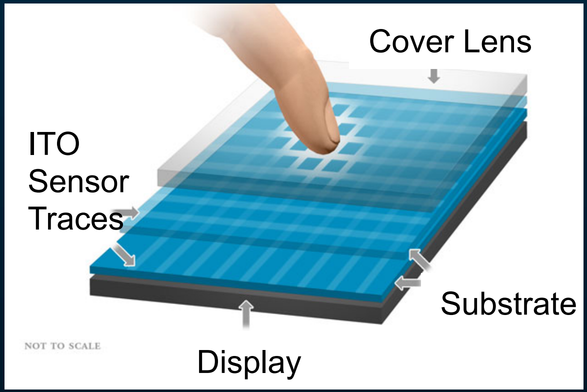


In highly doped materials the ATOMIC STRUCTURE TRANSFORMATIONS and ALLOYING EFFECTS provide increasingly important contributions to optical response

With V. Gavrilenko, Norfolk

TCOs AS DYNAMIC MATERIALS

- TCOs with extremely high dopant solubility
  - 10^{21} cm^{-3}
- Numerous advantages for plasmonic applications
- Mature fabrication processes
  - Sputtering, PLD, ALD, CVD, etc.
- Non-stoichiometric material
  - Plasma frequency highly tunable from VIS to NIR (ex. ITO 600 - 1600 nm)
- AZO and GZO can have significantly lower permittivity at telecommunication wavelengths



ITO-based touch screens

IGZO-based highly resolved flexible screen

G.V. Naik et al, Opt. Mater. Express **1**(6), 2011

See also work by O. Muskens, M. Brongersma, M. Noginov

TCOs: OUTLOOK

- TCOs: AZO, GZO, ITO, ICO…
- Great potential for nanophotonic/plasmonic applications in NIR!

- *Tunable plasma frequency by doping*
- *Great switching opportunities (electrical/optical)*
- *Low loss*
- *Small adjustable real part of permittivity*
- *Mature fabrication process*
- *Compatibility with SC-processes and other materials (TCOs, Graphene, YH2)*