



Emerging Materials for Nanophotonics and Plasmonics: Roads Ahead



BUILDING NANOSCALE PHOTONIC TECHNOLOGIES OF THE FUTURE

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OUTLINE

- Plasmonics: Loss and Gain
- Expanding Materials Playground for Plasmonics and Nanophotonics
- Metal Nitrides
- Transparent Conducting Oxides
- Material Requirements: Tunability & T-Stability
- Ultra-Thin Plasmonic Metal Nitrides
- MXenes: Novel Quasi-2D Materials
- Outlook





BASIC LAWS OF OPTICS

Refraction



www.passmyexams.co.uk





Diffraction



Reflection







Wikipedia

5102



PLASMONICS/NANOPHOTONICS

- Localized Surface Plasmons = Optical Nano-Antenna (imaging, sensing, therapy, energy...)

E-field Free – electrons Λ Negative epsilon Λ







= Optical Metasurfaces/Metamaterials





F. Capasso

- Propagating SP = Nano-Waveguide (on-chip photonics/optoelectronics, lab-on-a-chip...)



Epsilon-Near-Zero = Enhanced nonlinearities, ultra-fast switching, tunnelling, etc



POTENTIAL TECHNOLOGY IMPACT

- On-chip optics/Hybrid photon./electronic circuits
- \circ Sub- λ photodetectors
- Data recording/storage
- Single molecule sensors
- Medical/Drug delivery/Therapy
- \circ Sub- λ imaging
- Optical nanolithography
- Optical nanotweezers
- Solar cells/PV
- Photo-catalysis
- Novel energy conversion schemes
- Quantum information technology





Images from Wikipedia



PLASMONICS & LOSS

Plasmonic building blocks NOBLE METALS:

Much light is absorbed!(Ohmic loss)









LOSS CAN BE USEFUL!

APPLIED PHYSICS

Plasmonics-turning loss into gain

The optical losses usually associated with plasmonic materials could be used in applications

By Justus C. Ndukaife,^{1,2} Vladimir M. Shalaev,¹ Alexandra Boltasseva¹

he light-induced electronic excitations that occur at the surface of metals plasmons—provide the extraordinary ability to confine electromagnetic energy to the subwavelength scale. Such extreme optical confinement can enhance the light-matter interaction and enable miniaturized optical and optoelectronic devices. However, this confinement requires that plasmonic materials possess free carriers, which unavoidably results in light being lost or absorbed in the system (*1*). This optical loss has hampered the realization of device designs with ultracompact, on-chip optical components and nanometer-scale resolution imaging. Because of the detrimental effects of plasmonic losses, several avenues are being explored to mitigate the high absorption, such as using gain to compensate for the losses, and synthesizing alternative low-loss plasmonic materials (2). Rather than continuing to pursue low-loss plasmonics approaches, we draw attention to the benefit of losses by high-

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sciencemag.org SCIENCE

Published by AAAS

W. Li, J. Valentine "Harvesting the Loss: Surface Plasmon-Based Hot Electron Photodetection", Nanophoton. 7, 177, 2017
Ndukaife, Shalaev & Boltasseva. "Plasmonics: Turning Loss into Gain", Science 351, 6271 (2016)
See J. Khurgin regarding plasmonic losses
J. B. Khurgin and G. Sun, "In search of elusive lossless metal", APL 96, 181102 (2010)
J. B. Khurgin and G. Sun, "In search of elusive lossless metal", APL 96, 181102 (2010)



PLASMONICS FOR HYBRID ON-CHIP CIRCUITRY

Low-loss plasmon-assisted electro-optic modulator



SEM image of a plasmonic ring resonator and the corresponding transmittance

Operation

On State (non-resonant)

Light passes through the WG

Off State (resonant)

- OEO changes refractive index under applied voltage
- Light couples into resonator

Si waveguide mode couple SURFACE PLASMON when LOSS is ON! COMPACT (footprint of a few square micrometres) HIGH SPEED (> 100 GHz) and LOW LOSS (< 3 dB)

C. Haffner, et al., *Nature* (April 26, 2018) In collaboration with ETH, J. Leuthold , VCU, N. Kinsey, & U Wash

Plasmonic circuitry: Berini, Bozhevolnyi, Zhang, Brongersma, Atwater, Zayats and other



PLASMONICS FOR HYBRID ON-CHIP CIRCUITRY

Low-loss plasmon-assisted electro-optic modulator

- Compact footprint (6 µm diameter) smaller than conventional SOI modulators and plasmonic MZIs
- 72Gbps speed demonstrated experimentally
- Low Q (~30) higher thermal stability
- Low energy consumption (12 fJ bit-1 at 72 Gbit s-1)



• High bandwidth (~100 GHz)



PLASMONIC NANOTWEEZERS



Juan et al. Nature Physics (2009)



Amr et al. Nano letters (2012)

See also works from the groups of:

R. Quidant, K.Crozier, L. Hesselink, K. Touissaint, X. Zhang, Y. Tsuboi, J. Dionne and other

The Hybrid Electrothermoplasmonic Nanotweezer (HENT)

Yuanjie et al. Nano letters (2011)



HENT Features:

- Laser + AC electric field: on-demand fluid flow
- Fast and precise delivery to plasmonic hotspots
- High resolution nanoparticle trapping
- Ability to immobilize trapped object

With S. Wereley, Purdue Ndukaife *et al., Nature Nanotechnology* (2016) Ndukaife, Shalaev & Boltasseva. *Science 351, 6271* (2016)

R. Quidant: ETP- enhanced LSPR chip



FROM SOLAR STEAM TO WATER SPLITTING



- Plasmon enhanced solar water splitting
- Hematite bandgap 2.0-2.2eV (solar spectrum)
- Earth abundant/Commercially viable
- Photochemically stable
- Grown with Pulsed Laser Deposition





Photocurrent enhancement with gap plasmons (See work by S. Bozhevolnyi)

With A. Naldoni

See work by N. Halas & P. Nordlander on solar steam, S. Link and other



MATERIALS BUILDING BLOCKS

Plasmonic NOBLE METALS:

- Much light is absorbed (Ohmic LOSS)
- Not adjustable optical properties
- Hard to switch/tune
- Challenging fabrication
- Challenging integration
- Not CMOS-compatible
- Soft
- Low melting point
- High cost

TUNABLE/SWITCHABLE response and STABILITY remain a challenge!





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PLASMONIC MATERIALS RESEARCH

Looking for intermediate carrier density materials TUNABLE & ROBUST/STABLE & Sustainable



See work by E. Hu, H. Giessen, L. Dal Negro, M. Brongersma, T. Odom, H. Atwater, N. Zheludev, A. Zayats, M. Ford, M. Blaber, O. Muskens, M. Noginov, R. Soref, M. Wegener, M. Polini and other groups

TiN, TiAIN, Zr_xN_y, HfN, ScN, TaN, YN, VN, NbN, Cu₃N, WN SnO_2 , In:SnO₂, ZnO. Al:ZnO, Ga:ZnO. InGa:ZnO, CdO, CdSb₂O₆, \ln_2O_3 , $GalnO_6$, $Mgln_2O_4$, TiO₂, SrTiO₃, SrSnO₃, $Cd_{3}TeO_{6}$, BaSnO₃, SrGeO₃, IrO₂, VO₂, RuO₂ CoSi₂, CrSi₂, FeSi₂, HfSi₂, IrSi₂, NbSi₂, Ni_xSi_x, Os₂Si₃, Pt₂Si, Pd₂Si, ReSi₂, RhSi₂, Ru₂Si3, TaSi₂, TiSi₂, V_xSi_y, WSi₂, ZrSi₂, Ca₂Si, Mg₂Si

Ru₂Ge₃, Os₂Ge₃, BaGe₃, SrGe₂, Ca₂Ge, Mg₂Ge, CrGe₂ GaAs, AlGaAs, InGaAs, InP, AlInAs



Al, Cu, Ag, Au

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

C. Zhang et al., Advanced Materials, 1521, 2017; N. Kinsey et al, JOSA B 32(1), 2015



METALS TO 'LESS-METALS'

 \circ $\,$ Reduce carrier concentration: Mixing them with non-metals \Rightarrow

Many compounds: Intermetallics Ceramic materials

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



Wiki: Ceramics = metal + non-metal



Transition metal nitrides Mimic Au optical properties High melting point! REFRACTORY Hard materials

See work by E. Hu, H. Giessen, J. Dionne, G. Naik, H. Atwater, S. Ishii, M. Blaber, M. Ford, Soref, L. Dal Negro, A. Zayats, A. Calzolari, P. Patsalas and other



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TITANIUM NITRIDE

Plasmonic, Tailorable, REFRACTORY



G.V. Naik et al., OMEx 2, 478 (2012), U. Guler et al., Nano Letters 13, 6078 (2013)

TMNs HIGHLIGHTS/RESULTS

- New functional devices and new physics unlocked by tailorable TMNs
 - Plasmonics/Metamaterials/Metasurfaces in VIS
 - Robust/high-T Stable/CMOS, bio-compatibility







POTENTIAL OF PLASMONIC CERAMIC MATERIALS

Ceramic (high-T stable) materials with plasmonic properties

NFT

- Photothermal biomed apps/therapy/drug delivery
- Heat-assisted magnetic recording •
- Harsh environment sensing \bullet
- Solar/Thermophotovoltaics (S/TPV) •
- **Plasmon-assisted photocatalysis** •
- **Optical trapping/nanomanufacturing** •







Mater. Today 2014



Photonic Spin Hall Effect in TiN Metasurface

Photonic SHE: Reflects the two photonic spins (left and right circular polarizations, LCP and RCP) in opposite directions with ROBUST Nitrides



Phase gradient for the two opposite polarizations, created by anisotropic antenna unit cells Reflection mode unit cell supporting gap-plasmon type resonance

See work by X. Zhang, F. Capasso, E. Hasman, and other



PLASMON-ENHANCED WATER SPLITTING

Enhancing hot electron collection with TiN nanoparticles



TiN and Au NPs: TiN produces higher photocurrent enhancement than Au NPs!

TiN has a broader LSPR and produce more hot electrons than Au, higher transmission of hot electrons at the interface with TiO₂



A. Naldoni et. al Nanophotonics 2016 & Adv Opt Mat 2017 See work by N. Halas, P. Nordlander, P. Christopher, S. Ishii, A. Zayats and other

With A. Naldoni



THERMOPLASMONIC TIN NANOFURNACE

- High temperatures can be obtained using thermoplasmonic TiN nanofurnace under solar illumination
- Enables thermally induced nanochemistry with attolitre volume precision





TiN nanofurnace formed by nitridation of TiO_2 at 600^0 C





With A. Naldoni

See work by N. Halas, P. Nordlander, P. Christopher, S. Ishii and other





Biomimetic TiN as Broadband Absorbers

Plasmonic Biomimetic Nanocomposite with Spontaneous Subwavelength Structuring as Broadband Absorbers



Corrugated TiN coatings: Broadband absorption (90%) FAST, FLEXIBLE, ENVIR. FRIENDLY



Layer-by-layer assembly of TiN nanoparticles with polyelectrolytes: out-of-plane topography with subwavelength dimensions.

With N. Kotov, UMich

ACS Energy Letter, 2018



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APPROACHES TO SWITCHING/TUNING



Phase Transition in VO₂¹



Electrical Injection in Semiconductors⁴



Mechanical Stretching² "Plasmomechanics" Electromechanical





Optical Control³

Key issues

- Speed vs Magnitude
- Electrical control
- Modulation in VIS/NIR
- Tunable plasmonic materials

¹T. Driscoll et. al., Science (2009) ³K. F. MacDonald et. al., Nat. Phot. (2008) ²I. M. Pryce et. al., Nano Lett. (2010) ⁴H. T. Chen et. al., Nature (2006)

⁵S. Xiao et. al., APL (2009) Zheludev, Atwater, Brongersma, Mortensen, other



GRAPHENE AS TUNABLE PLATFROM

- High degree of optical confinement **PLASMONIC** MATERIAL
- Easy and high dynamic tunability TUNABLE PLATFORM
- Stackable with other 2D materials for new properties
- Zero bandgap, uniform optical absorption a promising material for photodetection



C.T. Phare, ...& M.Lipson, Nature Photonics (2015)

Graphene plasmons in IR Z. Fei et al, Nature (2012)

D. Basov, X. Garcia de Abajo, F. Koppens, M. Lipson, N. Halas, N. A. Mortensen, H. Altug, N. Zheludev and other



TCOs AS DYNAMIC MATERIALS

- Transparent Conducting Oxides with extremely high dopant solubility (10²¹ cm⁻³)
- Indium Tin Oxide (ITO)/Doped Zinc Oxide/Vanadium Oxide/Cadmium Oxide
- Numerous advantages for photonics
- Mature fabrication processes
 - Sputtering, PLD, ALD, CVD, etc.
- Non-stoichiometric materials
 - Plasma frequency highly tunable from VIS to NIR
- Ultra-fast response
- Electrical- and all-optical switching



ITO-based touch screens



IGZO-based highly resolved flexible screen

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

Also work by H. Atwater, R. Boyd, H. Li, O. Muskens, M. Brongersma, I. Brener, H. Li, N. Zheludev and other



ULTRAFAST NONLINEARITIES



Engineered nonlinearities by controlling delay between two pumps: UV (262nm) and IR (787 nm)

Strong modulation with change in T/R $\,\sim 100\%$ With ultrafast response ~ 100 fs

fast NLOs – see also work by Zheludev group NLO in TCOs – see also work by Muskens group



M. Clerici, et al. Nat. Comm (2017)

ENZ ENHANCED NONLINERITIES





L. Caspani, et al Phys. Rev. Lett. 116, 233901 (2016); see also work on ITO by Boyd group, Science (2016)

TCO HIGHLIGHTS/RESULTS

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- New functional devices and new physics unlocked by LOW-LOSS TCOs
 - Plasmonics/Metamaterials/Metasurfaces in NIR
 - Ultra-fast switching/Enhanced Nonlinearities





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TUNING THE PROPERTIES OF METALS?

- High carrier density in metals: no appreciable tuning
- Change in the carrier density

$$\Delta n = \frac{O_s}{t}$$



• Thinner the film larger the tunability!

 Tuning of carrier density close to 15-20% has been theoretically predicted in atomically thin films



J. Garcia de Abajo, Nat. Comm. (2014)



ULTRA-THIN PLASMONIC FILMS

• Electrical (optical) control over the properties



J. Garcia de Abajo's group Nature Communications, 2014

• Unique light-matter interactions in highly confined light regime





QUANTUM CONFINEMENT ENHANCED NONLINEARITIES

• Energy level discretization enhanced nonlinearities

- ħθ
- Enhanced nonlinear properties have been shown in Au quantum wells



Zhaowei Lu's group, Nat. Comm (2016)



PLASMONIC ULTRATHIN TIN FILMS

- Plasmonic noble metals
 - Difficult to grow smooth, continuous films <7-10nm
- Titanium Nitride
 - Epitaxial growth on c-sapphire and MgO
 - Potentially epitaxial growth of *ultrathin* (~1-2nm) films on Si
 - Enhanced nonlinearities
 - High T- and High-Intensity Stability and Robustness





N. Kinsey et al., Opt. Express (2014) Chen et al., Nanoscale Research Letters (2014)



OPTICAL PROPERTIES OF ULTRATHIN TIN

- Lower metallicity (~2-nm-thick TiN_xO_y layer on the surface)
- Agrees with theory; plasma frequency acquires the spatial dispersion (~ 2D)
- Films remain highly metallic, even at a thickness of 2 nm (n $\approx 10^{22}$ cm⁻³)
- Higher losses in thinner films
- Increase in scattering rate
 - Defect scattering: TiN_xO_y layer
 - Surface scattering rate, $\Gamma_{ss} \sim 1/t, t$ = film thickness



D. Shah, H. Reddy, N. Kinsey, V. Shalaev, A. Boltasseva, Advanced Optical Materials (2017)



CONFINEMENT FACTOR CALCULATIONS



- Computed confinement factor of tightly confined plasmons λ_0/λ_p
- Maximum confinement of close to 50 in 2 nm films

With M. Soljacic



EFFECT ON PLASMA FREQUENCY



The plasma frequency acquires the spatial dispersion \sim typical for 2D materials: shifted to the red at all fixed k with dielectric losses enhanced as the film thickness d \downarrow

$$\omega_p = \omega_p(k) = \frac{\omega_p^{3D}}{\sqrt{1 + (\varepsilon_1 + \varepsilon_2)/\varepsilon kd}}$$

D. Shah, et al, Adv Opt Mat (2017) Bondarev et. al, OMEx (2016)



ULTRATHIN TIN: TUNABLE METAL?!

• Epitaxial quality films with thicknesses down to 1 nm are fabricated



- Close to 16% relative change in the carrier density is expected in monolayer TiN film

- Inversely proportional to film thickness



8.5% change in 1nm TiN films!



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MAX Phases

The MAX Phases: a family of ternary carbides with the general formula $M_{n+1}AX_n$ **M** is an early transition metal

A is an A-group element (mostly IIIA and IVA),

X is C and/or N





ceramics, M. Radovic, M. W. Barsoum, American Ceramic Society Bulletin (2013)

- \rightarrow Unique, combination of properties: **METALS & CERAMICS**
- → Conduct heat and electricity like metals
- → Elastically stiff, strong, brittle, and heat-tolerant like ceramics
- \rightarrow Chemically-, thermally stable, readily machinable, damage tolerant
- \rightarrow Fatigue, creep, and oxidation resistant



MAX/MXenes

The next generation of sustainable, cost-effective materials for technological use



2D materials: unique properties! Graphene – just Carbon!

"MAX" & "Graphene" = "MXene"

MAX Layered structure \rightarrow Kink and delaminate during deformation \rightarrow 2D early TM carbides/carbonitrides

MXenes: M₂X, M₃X₂, and M₄X₃

- Bare: metallic (similar to multilayer graphene)
- OH or F terminated: semiconductors with small band gap
- Can be intercalated

With Y. Gogotsi, Drexel

Ti₃C₂T_x MXene thin FILMS







RMS roughness ~ 15 nm

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\Gamma_p)} + \frac{f_1\omega_1^2}{\omega_1^2 - \omega^2 - i\omega\Gamma_1} + \frac{f_2\omega_2^2}{\omega_2^2 - \omega^2 - i\omega\Gamma_2}$$

Optical losses

- Inter-band transitions
- Scattering in the rough/disordered structure



MXene BROADBAND ABSORBER



Ti₃C₂ disks/pillar-like structures: LSPR in NIR



- The first experimental exploration of MXene Ti₃C₂T_x as a functional plasmonic broadband absorber
- Simple design of the absorber: utilizes both the inherent absorption in MXene, as well as the scattering enhancement at the plasmonic resonances at longer wavelength
- Optimized to design: efficiency in NIR >80% in λ~0.5 1.6um

With Y. Gogotsi, Drexel

MXenes FOR RANDOM LASING









With Y. Gogotsi, Drexel

- Active system composed of 2D graphene nanoflakes can operate as cavity-free random lasers due to the ultra low threshold of saturable absorption of graphene. Phys. Rev. Lett. 116, 217401 (2016)
- Experimentally demonstrated random lasing with $Ti_3C_2T_x$ nanoflakes (diameter ~ 85 nm) and dye molecules
- The lasing effect can be tunable by varying the concentration of $Ti_3C_2T_x$ nanoflakes



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SWITCHABLE/DURABLE/FLEXIBLE PHOTONICS

PLASMONIC CERAMICS

- Durable//high-T/intensity stable/nonlinear
- Ultra-thin/CMOS-compatible

CONDUCTING OXIDES

- Plasmonic materials in NIR
- Great switching opportunities

Ultra-Thin Plasmonic Films

- Quantum confinement enhanced nonlinearities
- Dynamic control over optical response
- Highly confined plasmons

GRAPHENE/2D/MXenes

- Strong electrical tunability/Highly confined SPs

Applications

- Flat Optics, Flexible/Conformal Optics, TPV
- Optical Modulators, NIR/VIS photodetectors, Lasers, THz polarization controllers

Groups of N. Halas, H. Giessen, H. Atwater, N. Zheludev, M. Brongersma, L. dal Negro, O. Muskens, D. Basov, J. Garcia de Abajo, F. Koppens, and other







TEAM AND SUPPORT





TEAM AND SUPPORT

Students

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