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
PLASMONONICS

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

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

© MMP A/S

Plasmonics and metamaterials offer an unprecedented ability to control light. Numerous examples of extraordinary science.
Metamaterial is an arrangement of artificial structural elements, designed to achieve advantageous and/or unusual properties.

\( \mu \varepsilon \alpha = \text{meta} = \text{beyond} \) (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?
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
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
$\varepsilon(\omega) = \varepsilon_{ib} - \frac{Ne^2 / m\varepsilon_0}{\omega^2 + i\omega\gamma_m(\omega)}$

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

**Real and Imaginary $\varepsilon(\omega)$ 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 $\varepsilon_{\text{effective}} \sim 0$: cloaks, hyperlens etc.
- Real permittivity of metals must be comparable to that of dielectrics (for example, $\varepsilon_{\text{dielectric}} \sim 2$ requires $\text{Re}(\varepsilon_{\text{plasmonic material}}) \sim -2$ while $\text{Re}(\varepsilon_{\text{Ag}}) \ll -2$)

Ag: threshold for uniform continuous films is around 12-23 nm
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.
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 $\varepsilon'$ of metal and dielectric
    - Epsilon-near-zero (ENZ) materials
    - Effective permittivity nearly zero: e.g. optical cloaks, hyperlens etc.

- **Switchable** devices
  - E. Feigenbaum et al., Nano Lett. 10 (2010) 2111 – Atwater group

- **SC-compatible** components
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
ALTERNATIVE MATERIALS

THE PAST AND PRESENT

Looking for intermediate carrier density materials

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)
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!**

---

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 ($\text{Al}_2\text{O}_3$ 2.5~3nm)

ALKALI

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

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 $\omega_p$
- Shifting the threshold for interband transitions
- Reducing the absorption at a specific wavelength

“Band Engineering”
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

"LESS-METALLIC" MATERIALS?

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

SEMICONDUCTORS $\rightarrow$ "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 $\rightarrow$ TO "LESS-METALS"

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

AZO: Lowest Drude damping, Longest cross-over wavelength ($5 \times 10^{20}$ cm$^{-3}$)
GZO: Cross-over wavelength as low as 1.2 µm

Theoretical studies: with Norfolk and Navy Research Lab

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

SPPs ON TCO FILMS AT 1.55 µm

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

*Source: SPP excitation on ITO films using prism-coupling: Franzen, Noginov groups
TCO LSPR STRUCTURES (Size and Doping)

![Graphs showing transmittance vs. wavelength for different disk sizes and doping densities.]

GAP SP IN TCO/DIELECTRIC/TCO

- \( H_{\text{ZnO}} = 40 \text{ nm}, H_{\text{GZO}} = 120 \text{ nm} \)
- Metal: Gallium doped ZnO
- Dielectric: Undoped ZnO

- **1.8 \( \mu \text{m} \): LSPR**
- **2.9 \( \mu \text{m} \): Gap Surface Plasmon Resonance**
- **5.2 \( \mu \text{m} \): LSPR + GSPR**

See work by Sergey Bozhevolnyi, OE (2013)
Surface Enhanced Infrared Spectroscopy

- 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
GZO metasurface and Phase difference ($\Delta$) of reflected light between two orthogonal polarizations (s and p) at $18^\circ$ angle of incidence

Current QWP
- Bulk birefringent material with optical anisotropy
- Narrow band

QWP metasurface
- Fabrication simplicity/1D design
- Nano-scale
- Broadband

See work by Hasman, Capasso, Zheludev, Alu groups
EPSILON NEAR ZERO (ENZ)

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

See work by Engheta, Alu, Muskens and other groups
ANTENNAE/EMITTERS ON ENZ

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

By H. Caglayan

With Nader Engheta and Orest Glembocki Groups
ANTENNAE ON ENZ

TCO (Al:ZnO or Ga:ZnO)
Glass

With Nader Engheta and Orest Glembocki Groups
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

---

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

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

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

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 $\lambda_0$) at IR

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

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

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

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)