

# REFRACTORY PLASMONICS

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**Major collaborator: Alexandra Boltasseva**

# The International Year of Light



**Optical technologies promote sustainable development and provide solutions to worldwide challenges in energy, education, agriculture, communications and health**

**<http://www.light2015.org/Home.html>**



Isamu Akasaki



Hiroshi Amano



Shuji Nakamura

Nobel prizes in physics 2014

Blue LED



Andre Geim



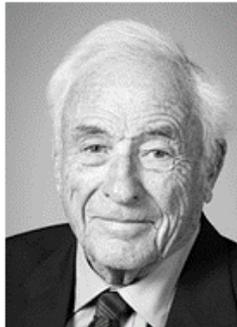
Konstantin  
Novoselov

Nobel prizes in physics 2010

Graphene



Charles Kuen Kao



Willard S. Boyle

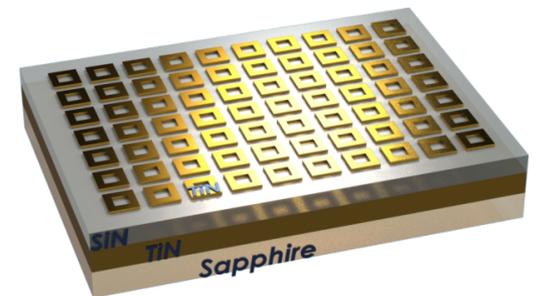


George E. Smith

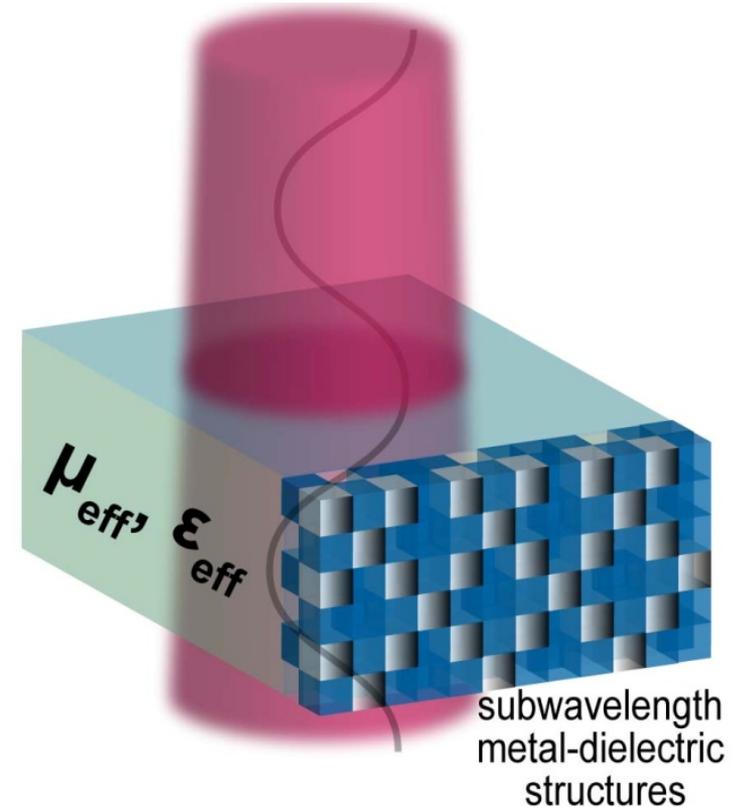
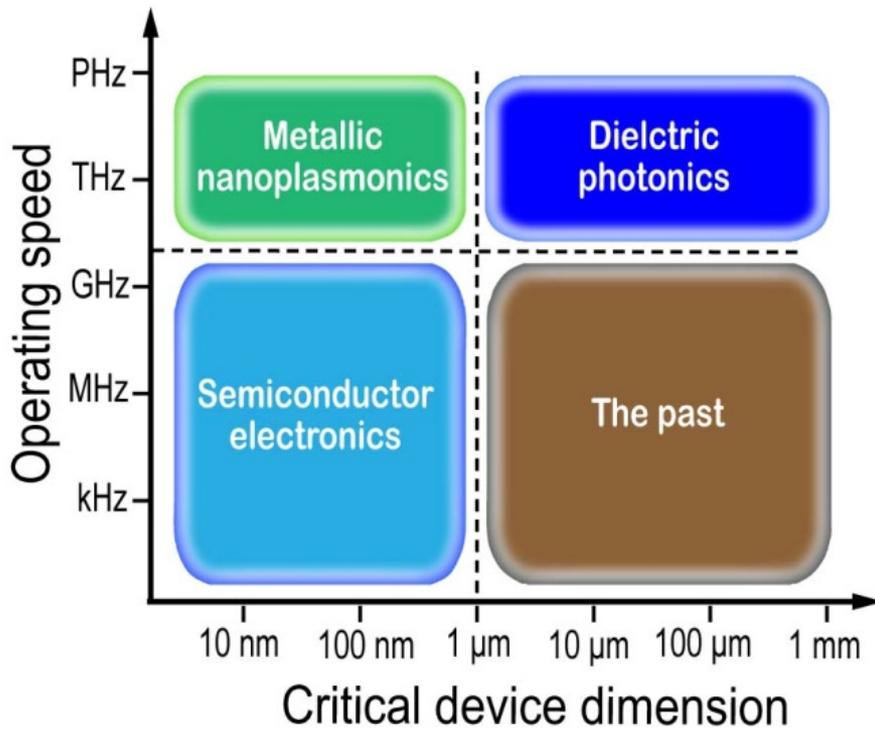
Nobel prizes in physics 2009

Low-loss optical fiber

- **Introduction: Plasmonics & Metamaterials**
- Material Requirements & Alternative Materials
- Transition Metal Nitrides
- Applications with Plasmonic Metal Nitrides
  - High Temperature
    - Thermophotovoltaics
    - Heat Assisted Magnetic Recording
    - Coherent thermal sources
  - Plasmonic photothermal therapy
  - Quantum Photonics Application

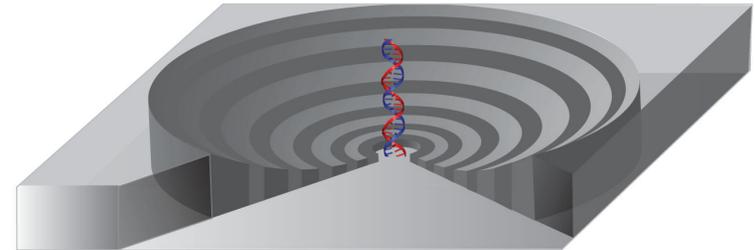
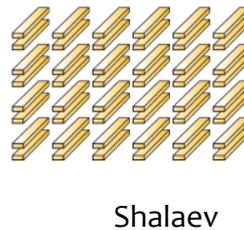
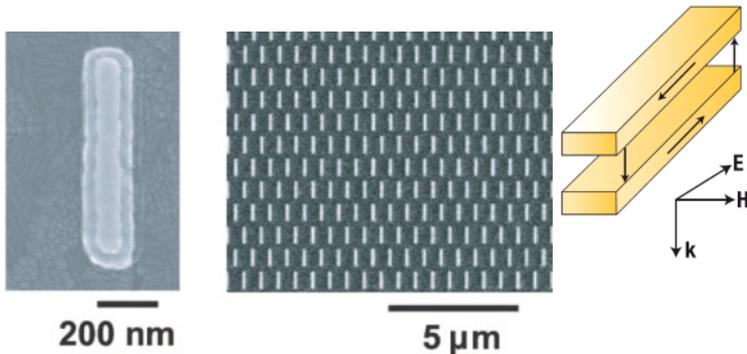


# WHY PLASMONIC TECHNOLOGY?

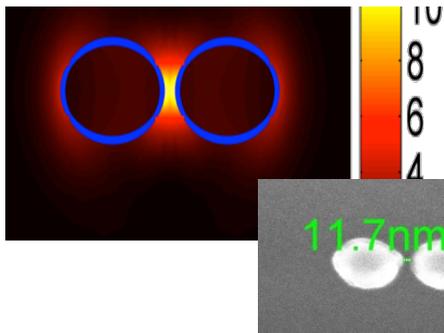


- Improved synergy between electronic and photonic devices
- Solution to the size-compatibility problem
  - Plasmonics naturally interfaces with *similar size electronic components*
  - Plasmonics naturally interfaces with *similar operating speed photonic networks*
- METAMATERIALS

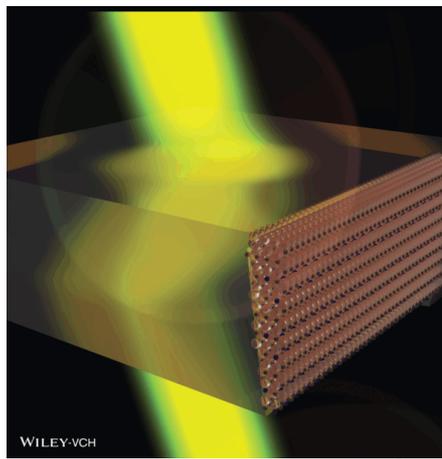
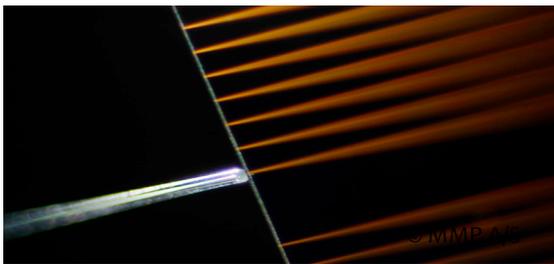
# PLASMONICS/METAMATERIALS



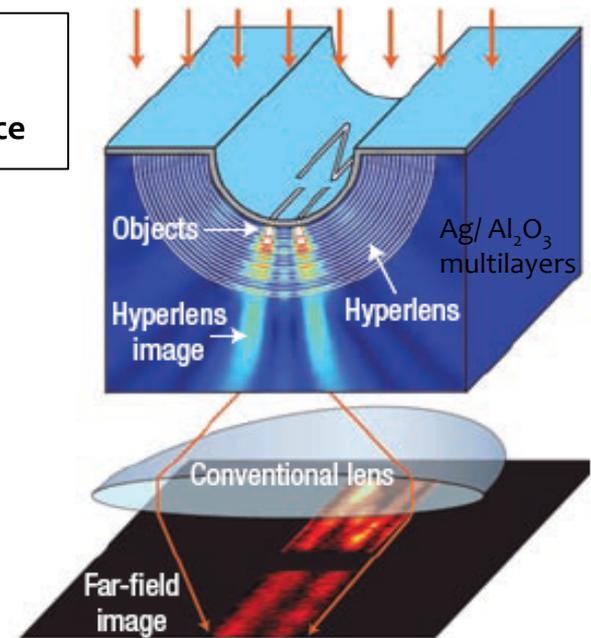
Narimanov, Engheta



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

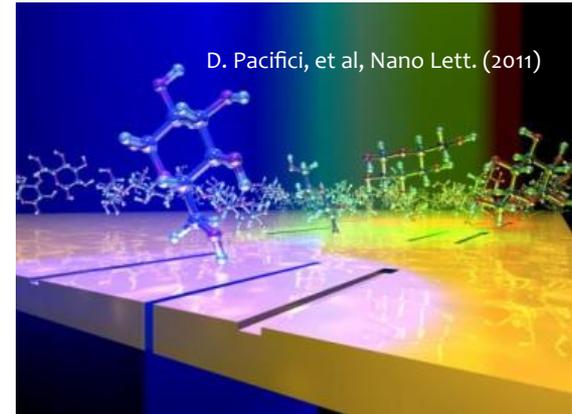


Purdue

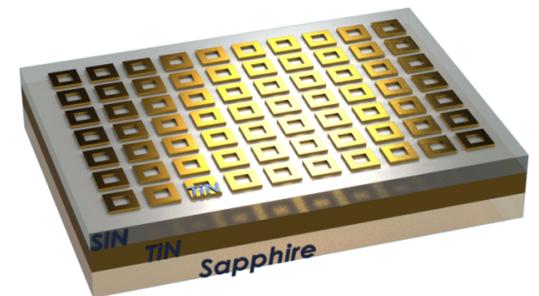


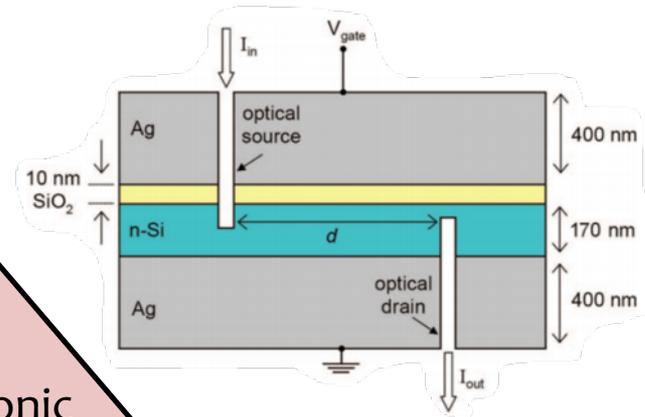
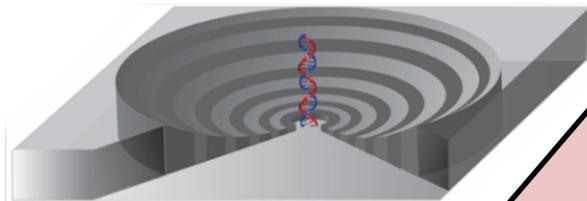
Z. Liu et. al, Science (2007)

- Interconnects/Hybrid photonic circuits
- On-chip optics and optoelectronics
- Data recording/storage
- Sub- $\lambda$  photodetectors
- Sensors
- Solar cells
- Novel energy conversion schemes
- Imaging
- Medical applications
- Quantum information technology



- Introduction: Plasmonics & Metamaterials
- **Material Requirements & Alternative Materials**
- Transition Metal Nitrides
- Applications with Plasmonic Metal Nitrides
  - High Temperature
    - Thermophotovoltaics
    - Heat Assisted Magnetic Recording
    - Coherent thermal sources
  - Plasmonic photothermal therapy
  - Quantum Photonics Application





## Devices:

Nanoantennas, Plasmonic waveguides, Metamaterials

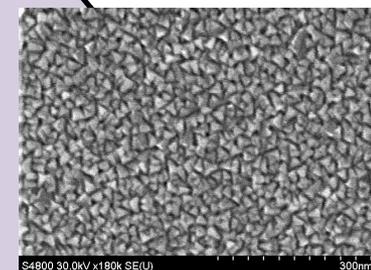
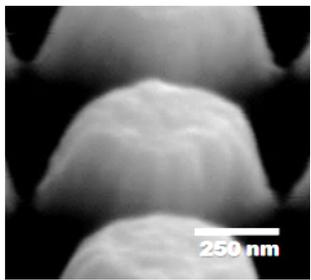
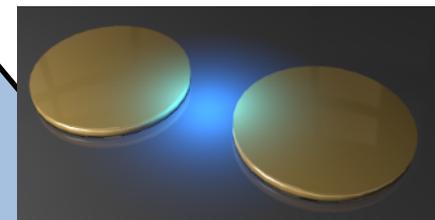
## Design:

Nanoscale building blocks, nanometer-thin films, nanoparticles

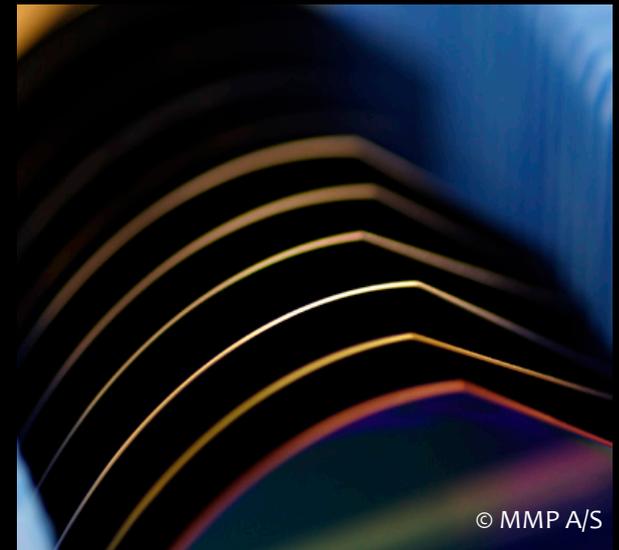
## Constituent Materials:

Metals (lossy, not tunable, challenging fabrication and integration)

**NEW PLASMONIC MATERIALS**



- GOLD and SILVER used so far...
  - High cost
  - Not adjustable optical properties
  - Not CMOS-compatible
  - Cn't sustain high T
  - Not mechanically robust
  
- Refractory (high-T) plasmonic materials
  - Adjustable / Tunable
  - SC-compatible
  - Low cost



- **Low loss** components
  - Dielectrics can be nearly loss-less
  - Metals have large losses

J. B. Khurgin and A. Boltasseva, MRS Bulletin (2012)

- **Adjustable / Tunable** optical properties  
Some Metamaterial + TO designs require comparable magnitudes of  $\epsilon'$  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. Feigenbaum et al., *Nano Lett.* 10 (2010) 2111 – Atwater group

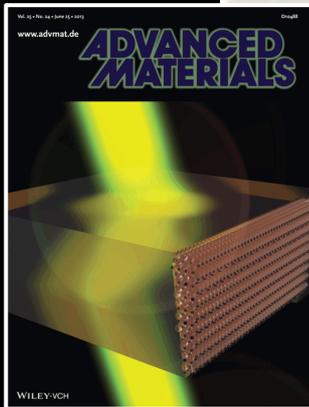
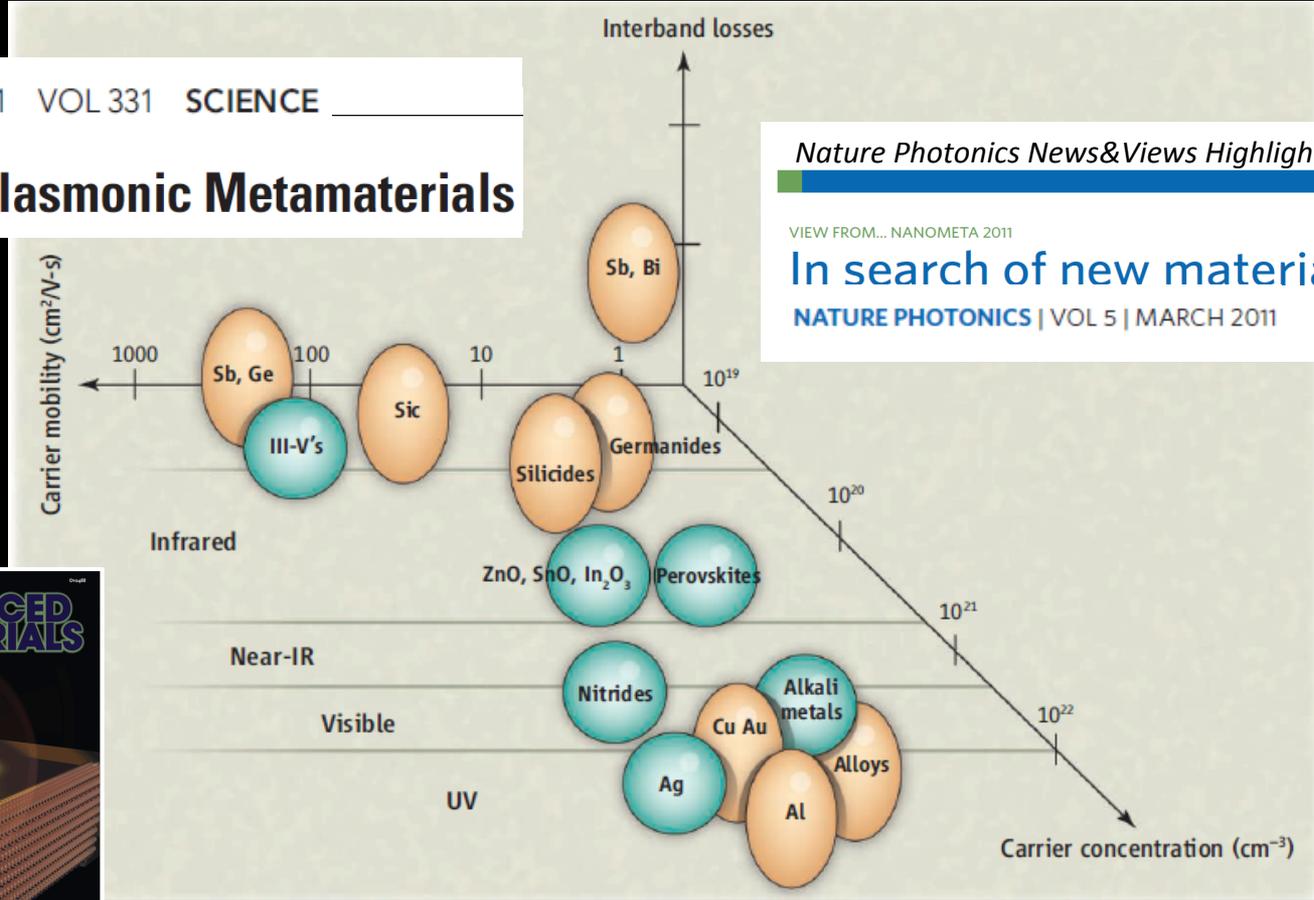
- **SC-compatible** components

# New CMOS-Compatible Plasmonic Materials

SEMICONDUCTORS TO METALS or METALS TO LESS-METALS:  
 Doped semiconductors + Intermetallics (nitrides, borides, silicides, ...)

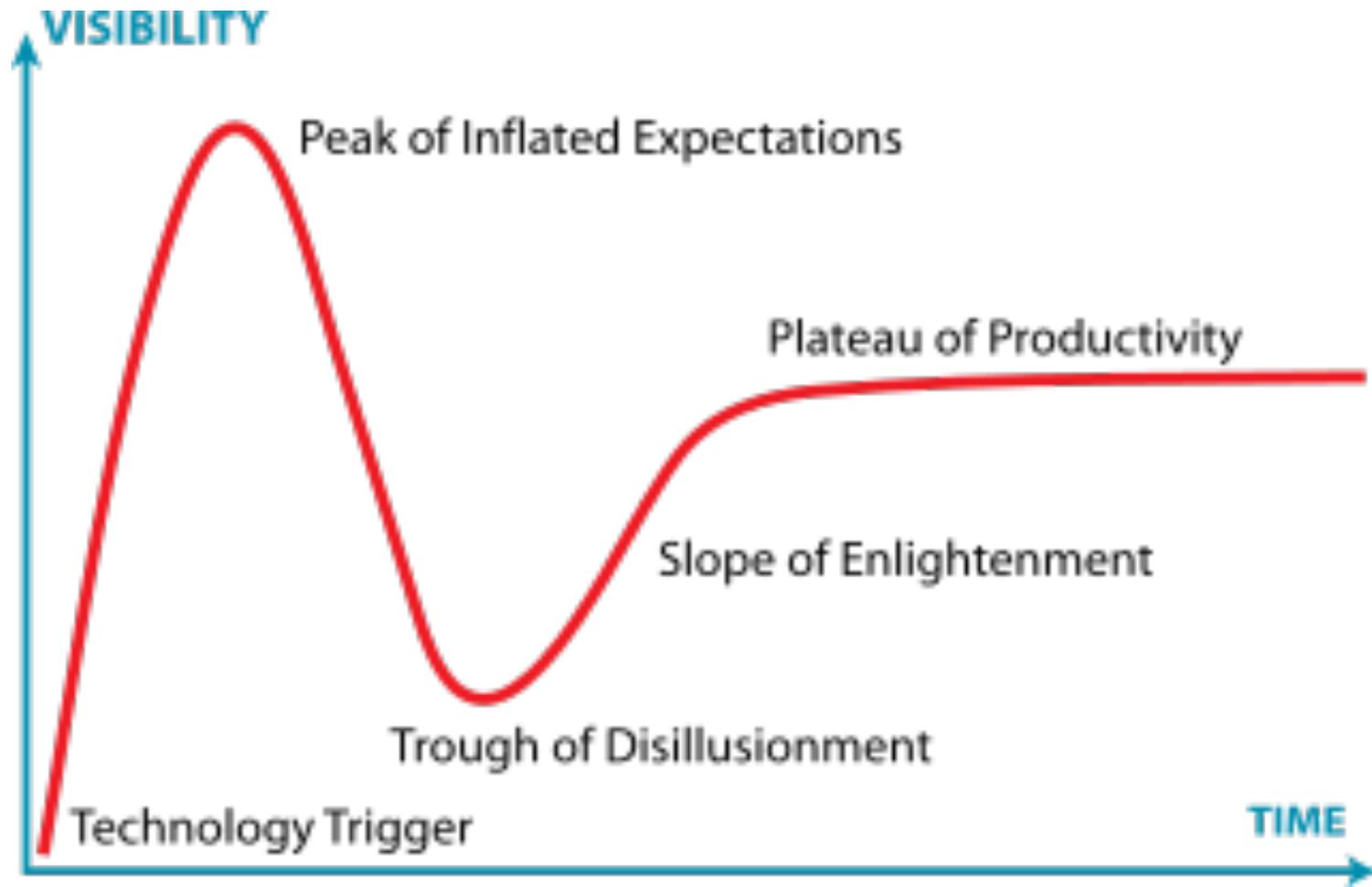
21 JANUARY 2011 VOL 331 SCIENCE  
 MATERIALS SCIENCE  
**Low-Loss Plasmonic Metamaterials**

*Nature Photonics News&Views Highlight*  
 news & views  
 VIEW FROM... NANOMETA 2011  
**In search of new materials**  
 NATURE PHOTONICS | VOL 5 | MARCH 2011

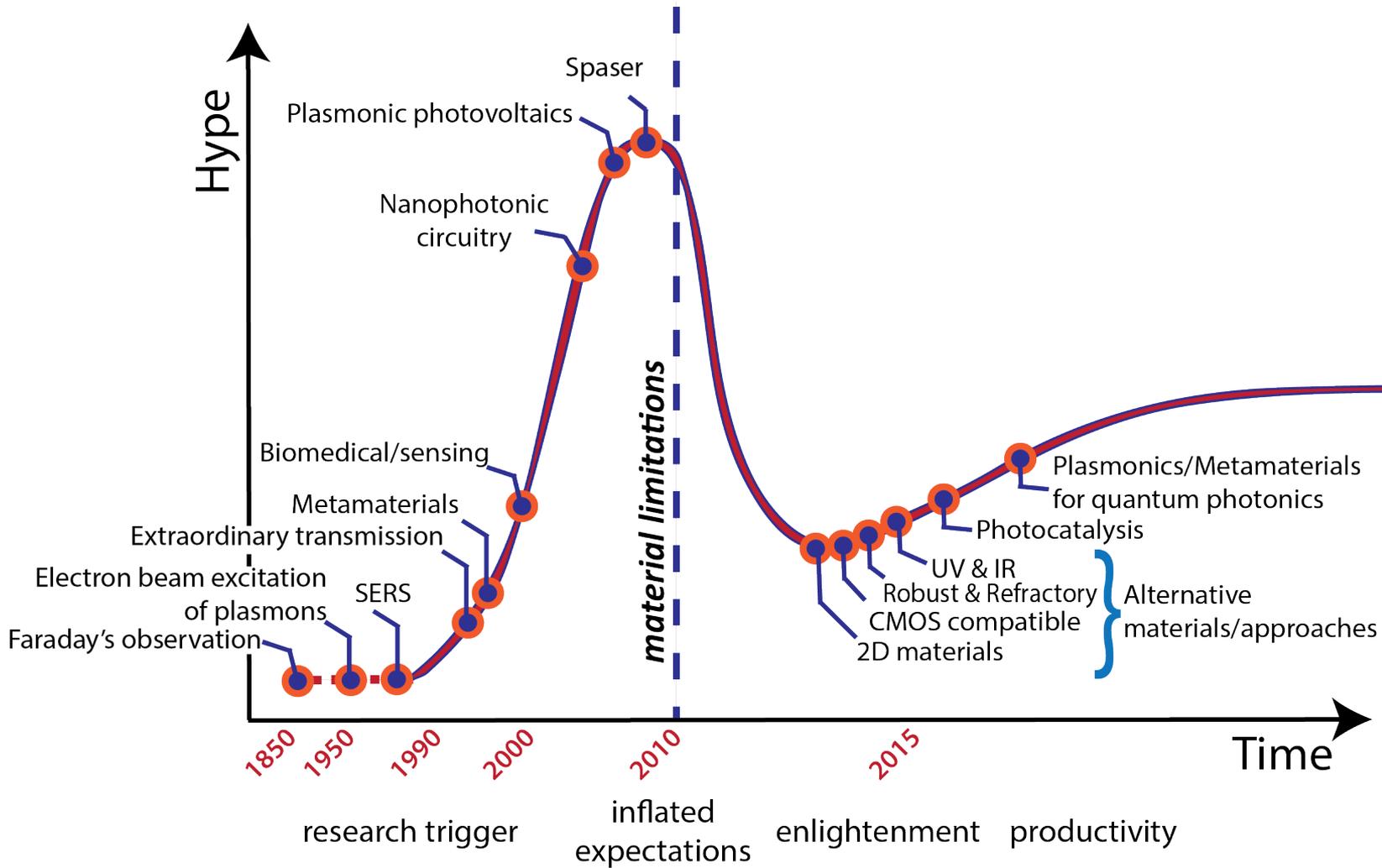


A. Boltasseva and H.A. Atwater, Science **331**, 290 (2011)  
 G. Naik, V. Shalaev, A. Boltasseva, Advanced Materials **25** (24), 3264 (2013)

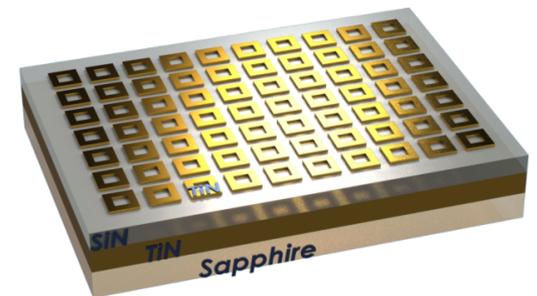
# Hype (Gartner) Cycle



# Hype Cycle for Plasmonics



- Introduction: Plasmonics & Metamaterials
- Material Requirements & Alternative Materials
- **Transition Metal Nitrides**
- Applications with Plasmonic Metal Nitrides
  - High Temperature
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    - Heat Assisted Magnetic Recording
    - Coherent thermal sources
  - Plasmonic photothermal therapy
  - Quantum Photonics Application

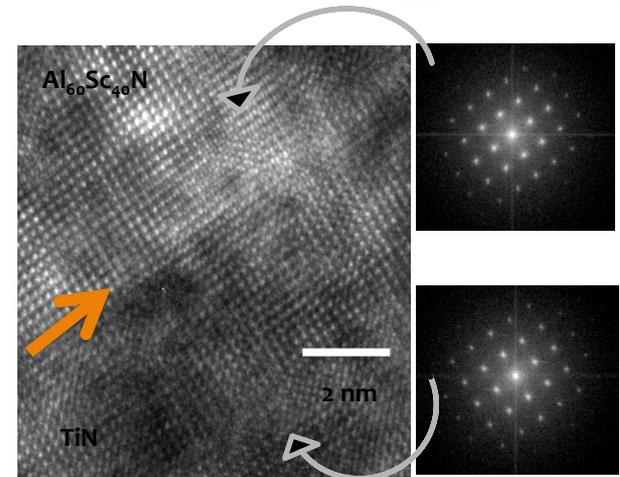
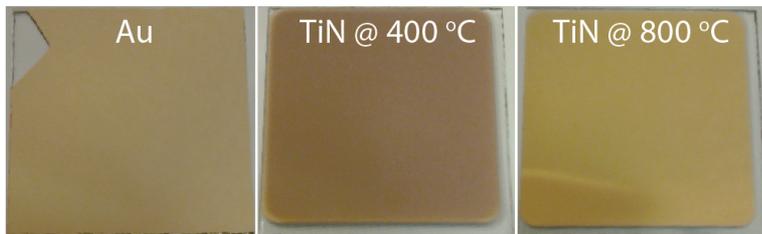


# Titanium Nitride

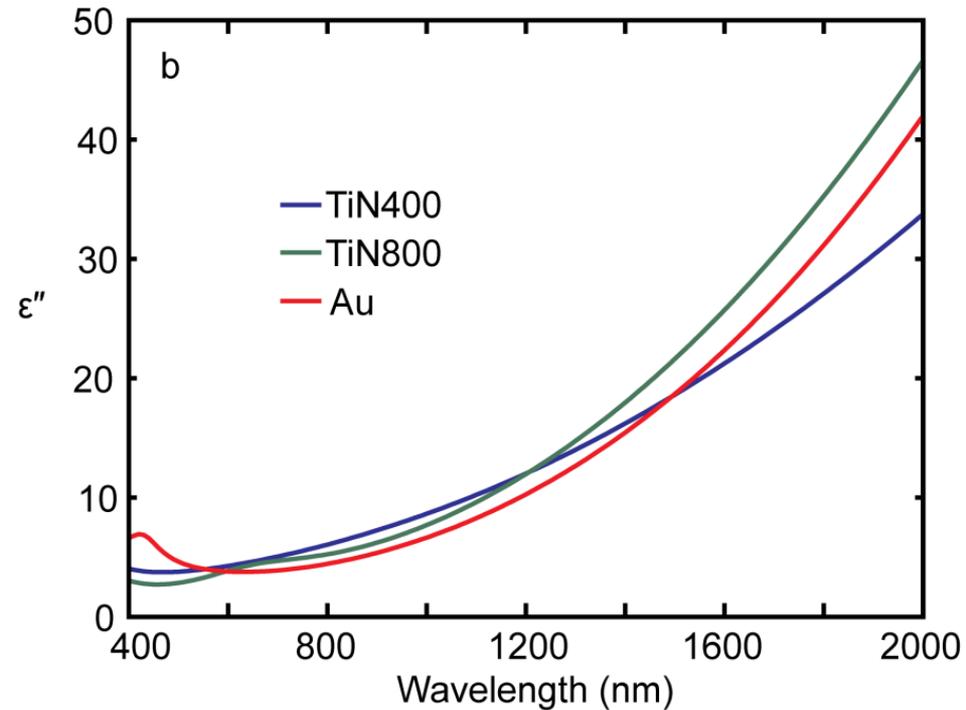
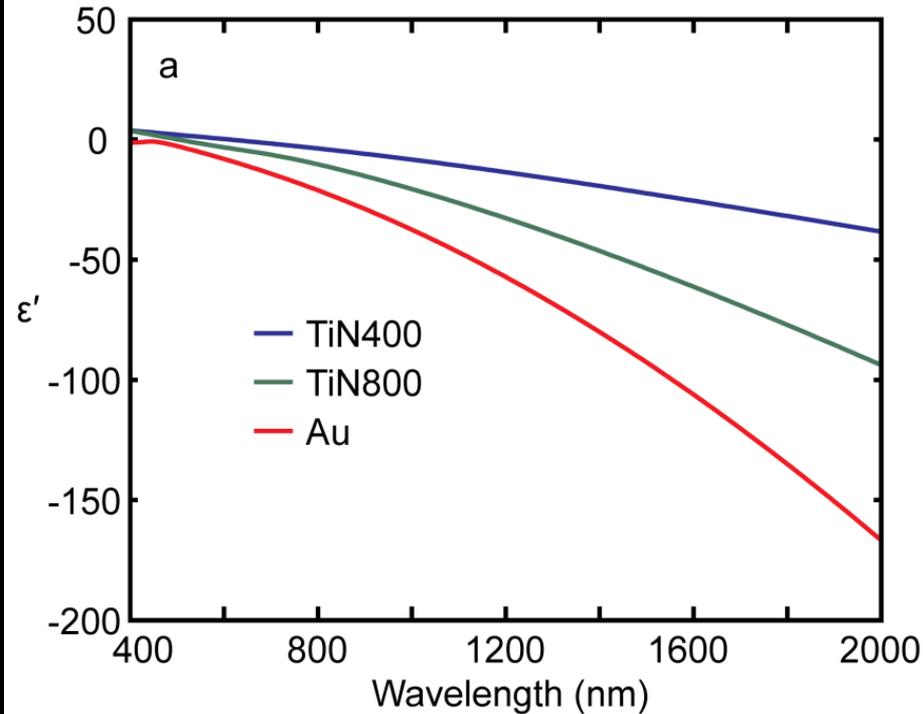
- Hard & tough: high speed drill-bits
- Well-established processing
- Thermally and chemically stable
- High melting point ( $> 2700^{\circ}\text{C}$ )
- Epitaxial growth
- CMOS-compatible
- Bio-compatible



## Golden Luster



**Plasmonic and tunable!**

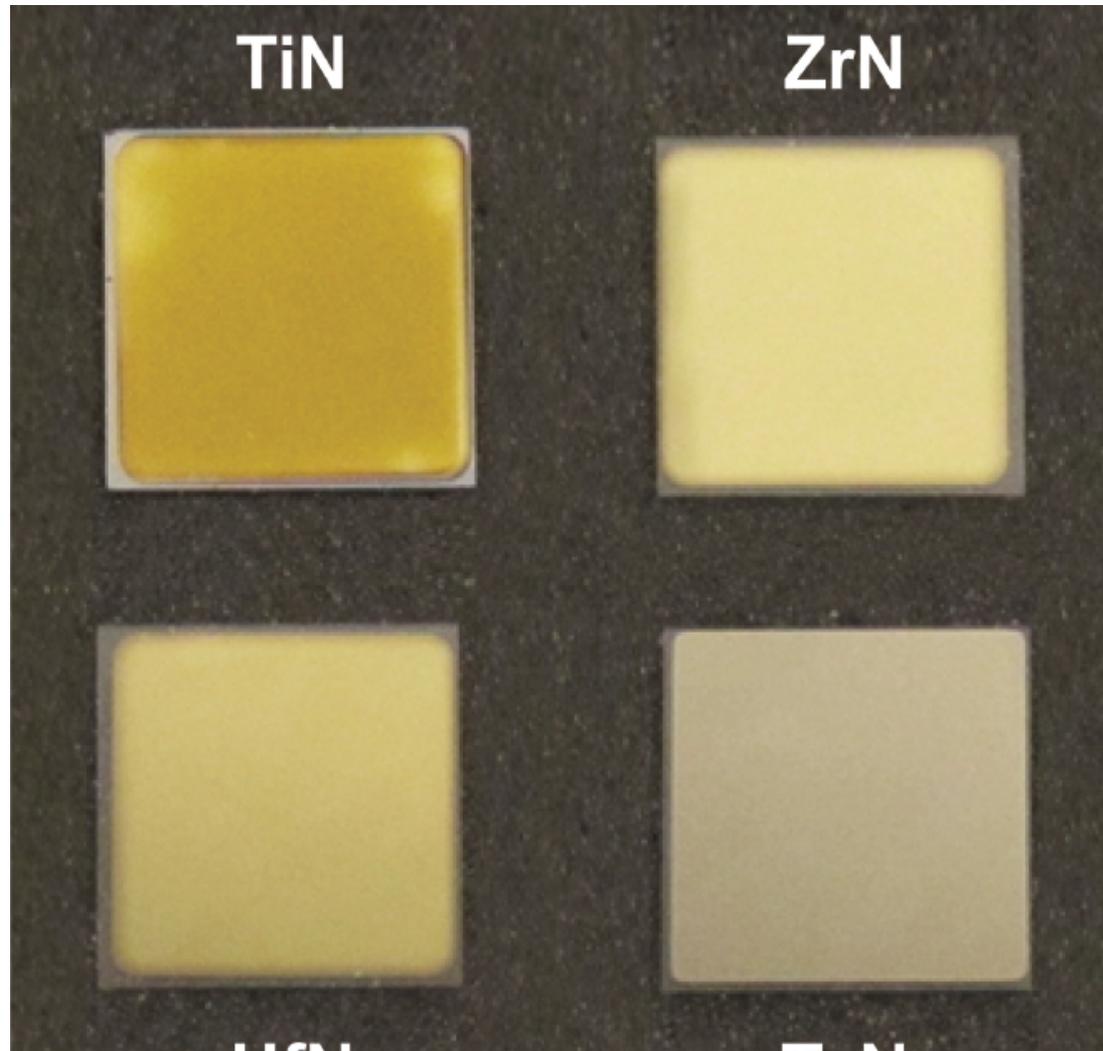


Transition metal  
nitrides

Mimic Au optical  
properties

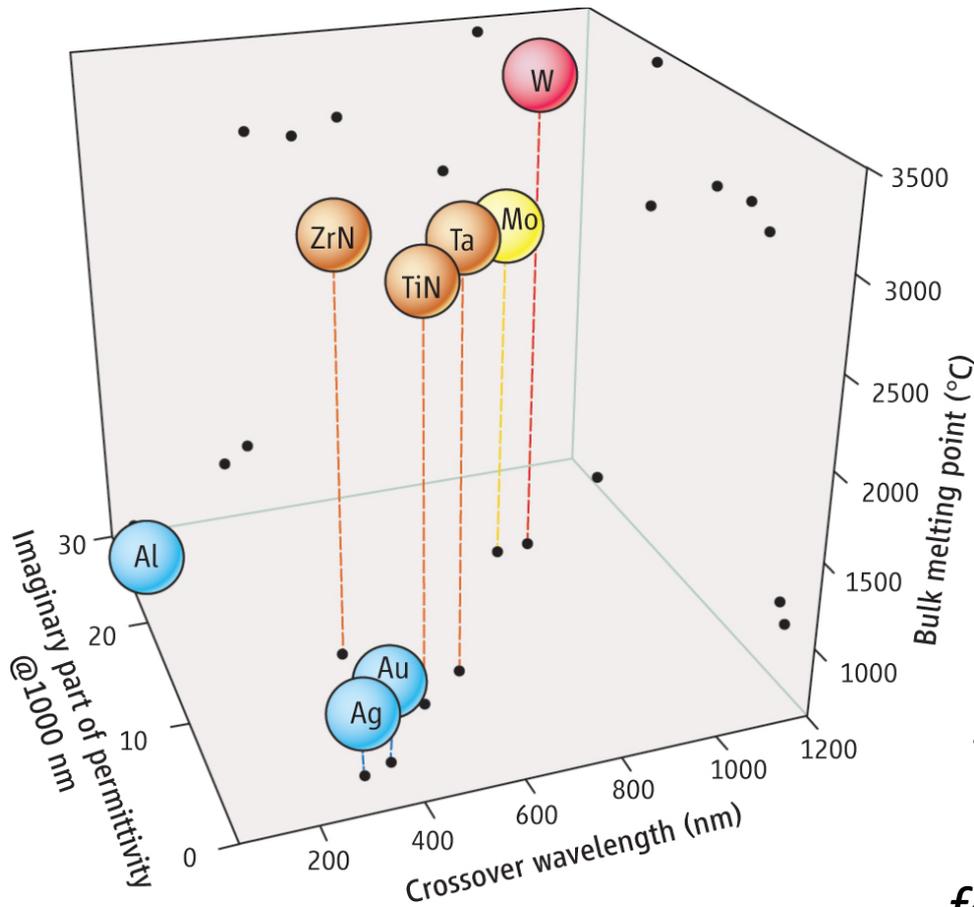
High melting point!  
REFRACTORY

Hard materials



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

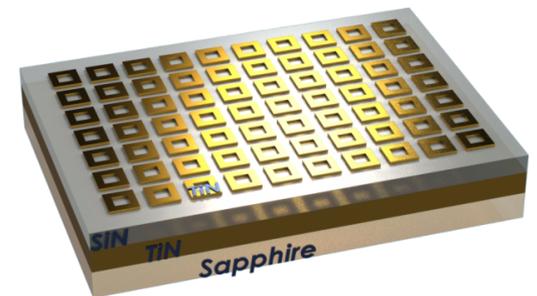
U. Guler, V. Shalaev, A. Boltasseva, *Materials Today* 18 (4), 227-237 (2015)



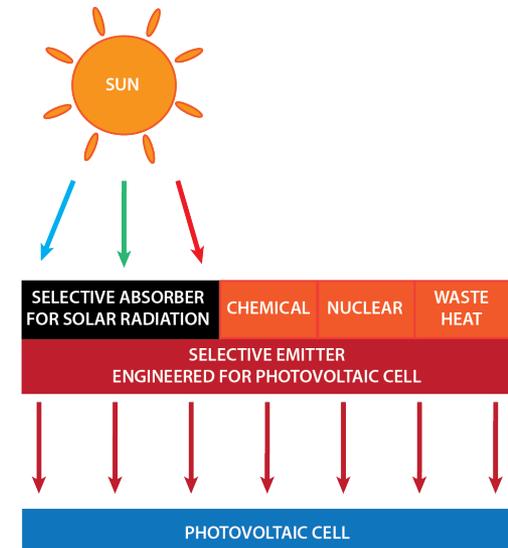
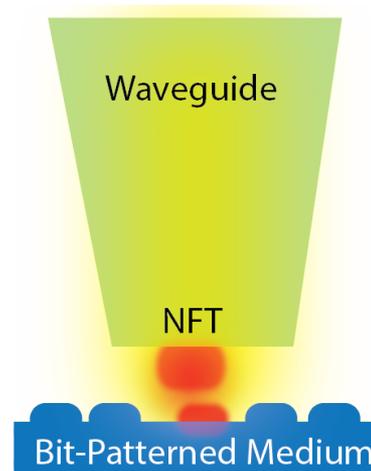
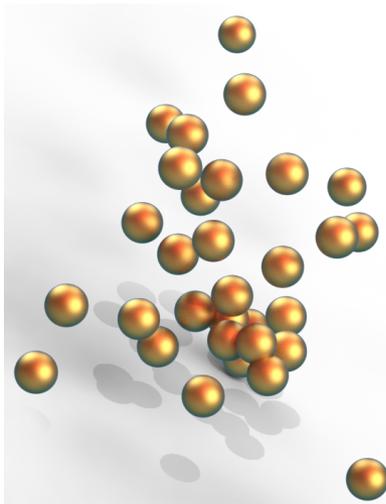
- Plasmonic metals
  - Low melting points
  - Soft
- Refractory metals
  - Lossy, non-plasmonic
- **Transition metal nitrides**
  - **Mimic Au optical properties**
  - **High melting point**
  - **Hard materials**

*Transition Metal Nitrides can be the solution for high temperature applications*

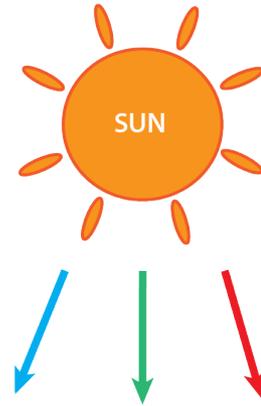
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- Plasmonic ceramics for
  - Photothermal therapy
  - Heat-assisted magnetic recording (HAMR)
  - Solar/Thermophotovoltaics (S/TPV)



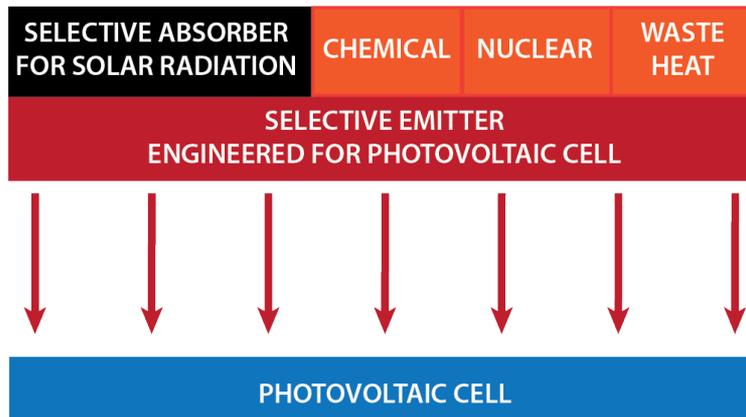
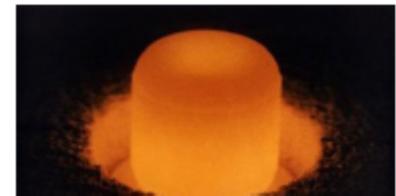
# Thermophotovoltaics



**Fuel-fired cells**  
TPV is well-suited for fuel-based power generation for military needs or as a backup energy source. They can also complement solar TPV devices.



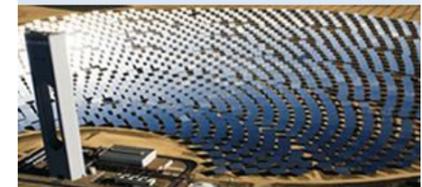
**Radioisotopic cells**  
use arrays of thermocouples to convert heat released by radioactive decay into electricity. Their energy efficiency, about 10%, can be surpassed using TPV.



**Waste heat harvesting**  
TPV is capable of waste heat recovery in various applications such as metal casting and fossil-fuel based power generation, including various diesel- and gas powered engines.



**Solar Energy Concentration**  
S/TPV is perfect for solar energy concentration plants as it is designed for high-temperature operation. Arrangement of cells in small (10-20x) clusters will increase cost effectiveness.



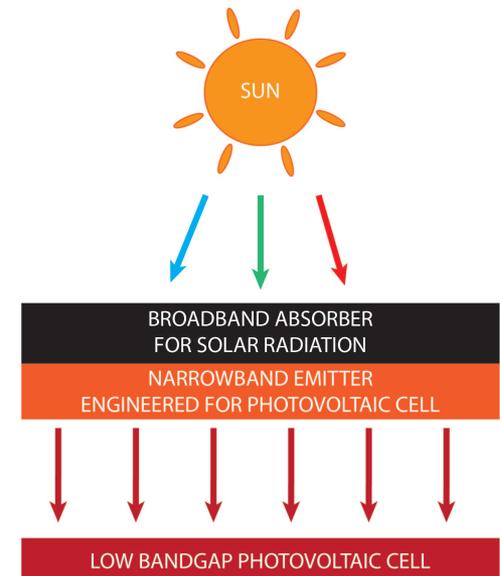
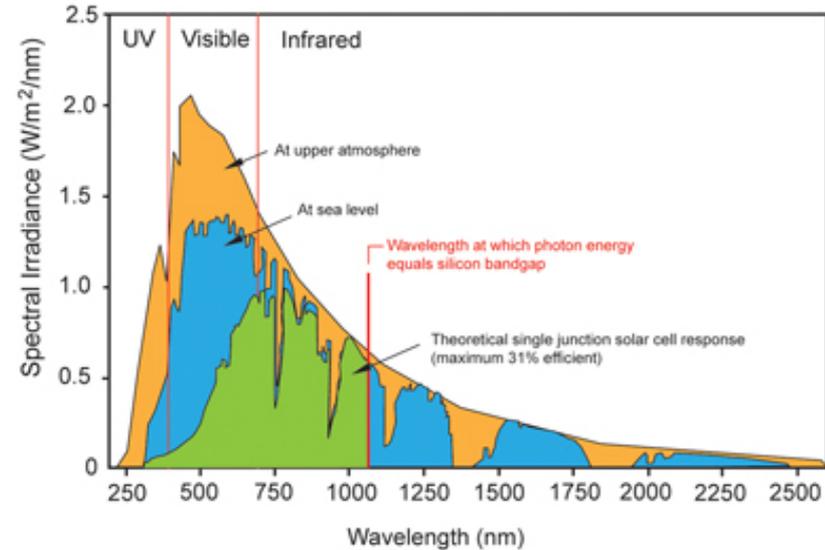
# Solar Thermophotovoltaics

Lower energy photons are not absorbed

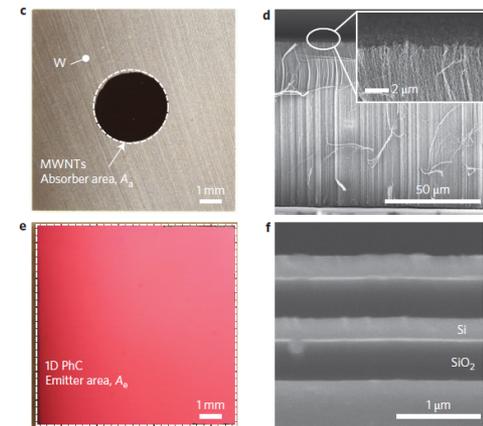
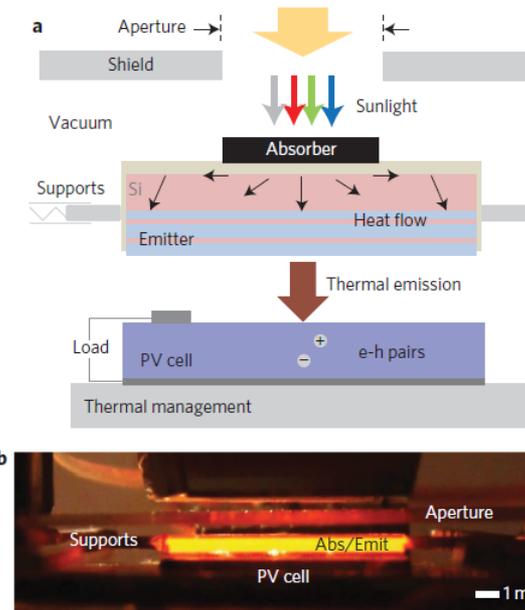
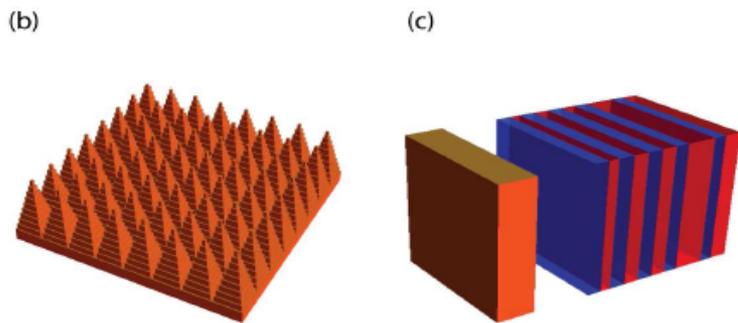
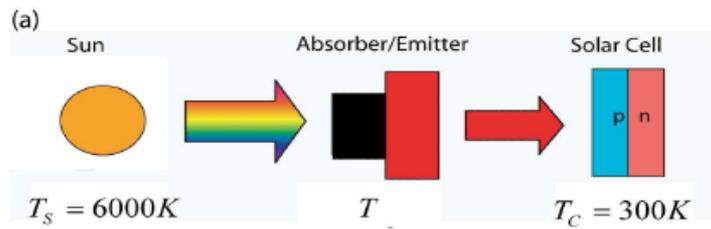
- Higher energy photons are not efficiently converted
  - Excess energy is lost as heat
  - Heated semiconductor efficiency drops
  - Long term high temperature operation shortens lifetime

## Solar/Thermophotovoltaics:

- Provide broad absorption at sun emission peak
- Emit all the collected energy at wavelengths optimized for maximum absorption
- Protect semiconductor against environmental factors
  - UV degradation
  - Humidity

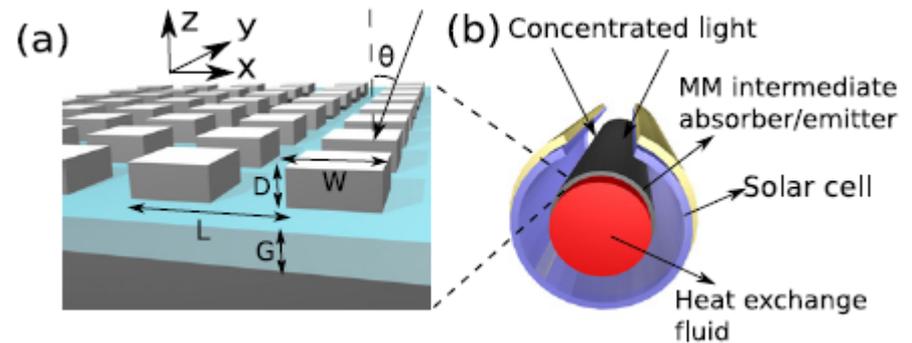
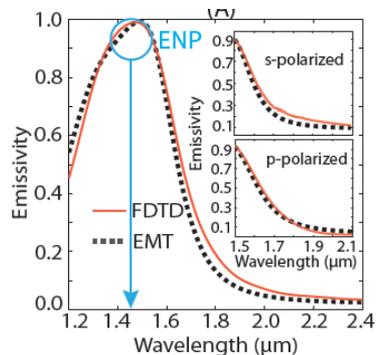
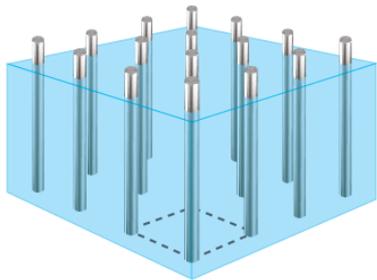


# S/TPV Absorbers & Emitters



E. Rephaeli and S. Fan, Opt. Exp. 17, 15145 (2009).

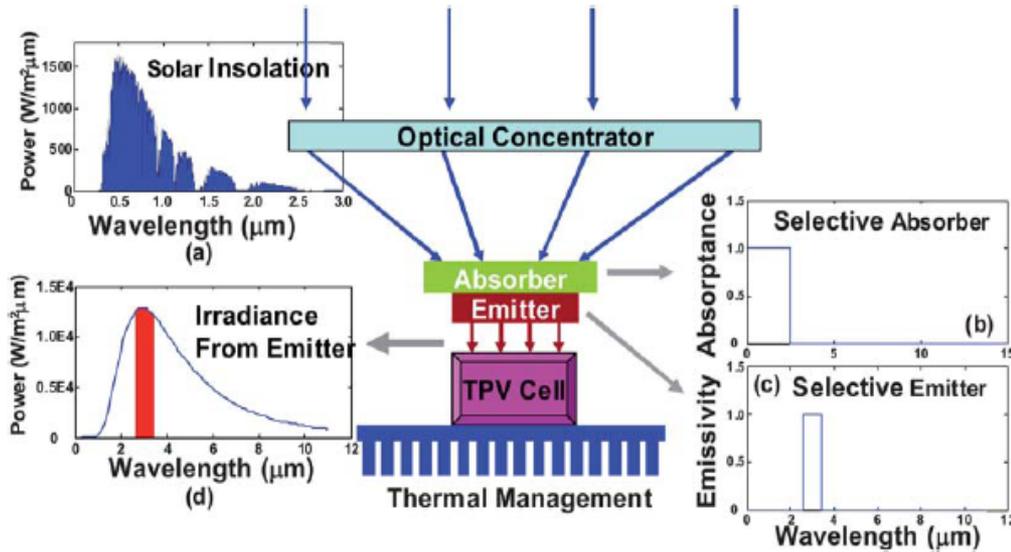
A. Lenert et al., Nat. Nano. 10.1038/nnano.2013.286 (2014).



S. Molesky, C. Dewalt and Z. Jacob, Opt. Exp. 21, A96 (2013).

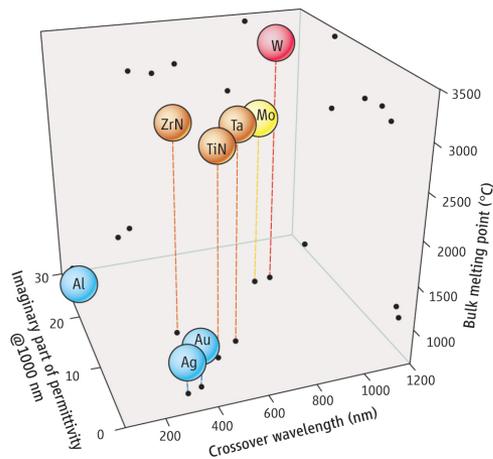
C. Wu et al., J. Opt. 14, 024005 (2012).

# Solar Thermophotovoltaics

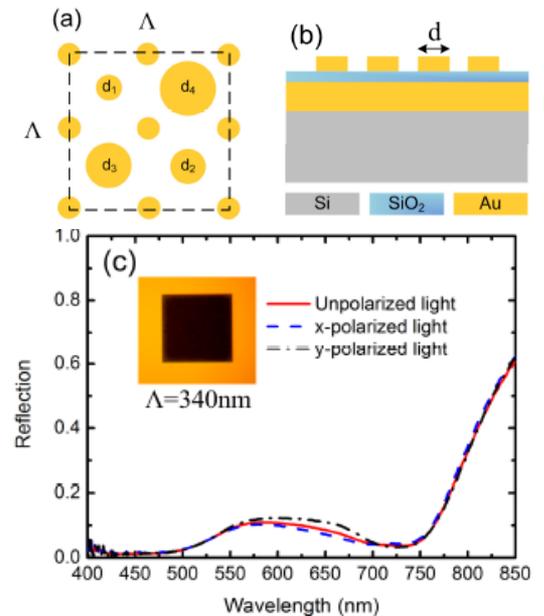


**Metamaterials!**

Baxter et al, Energy Environ. Sci. **2**, 559 (2009)

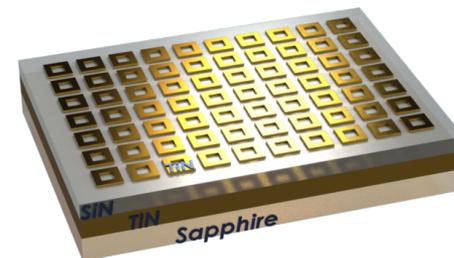
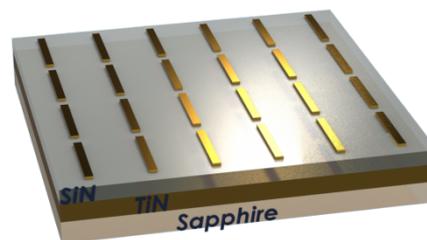
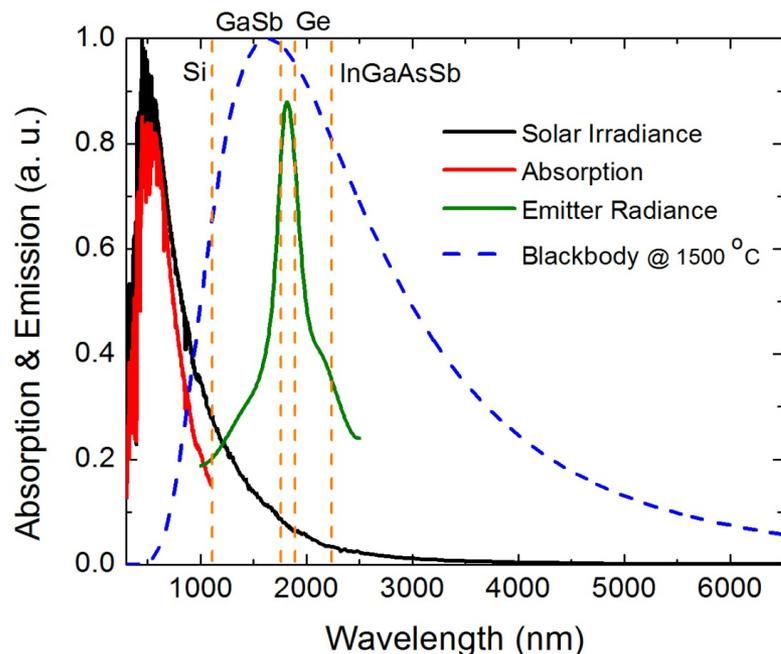


U. Guler et al, Science **344**, 263 (2014)



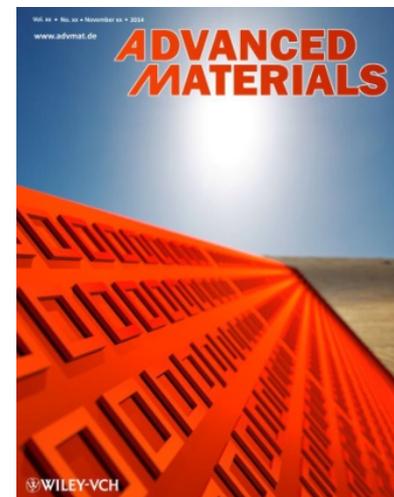
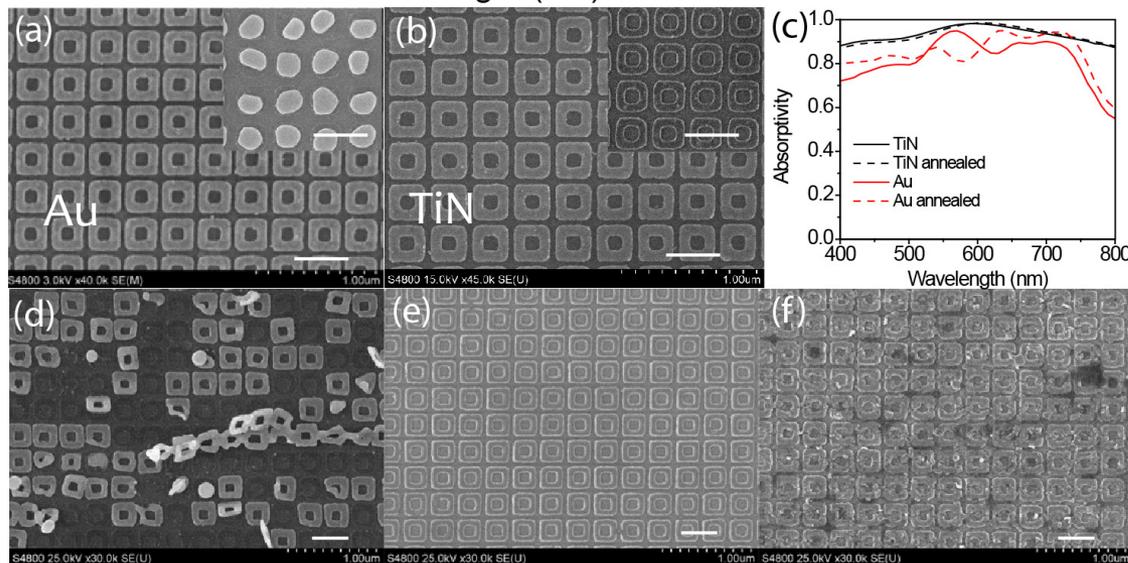
M. G. Nielsen et al, Opt. Express **20**, 13311

# Example: TiN Absorber for S/TPV



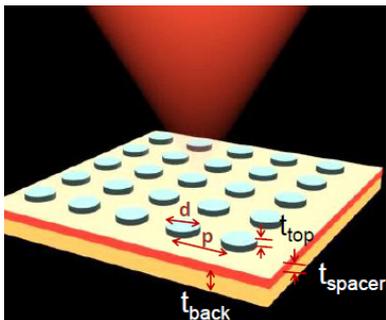
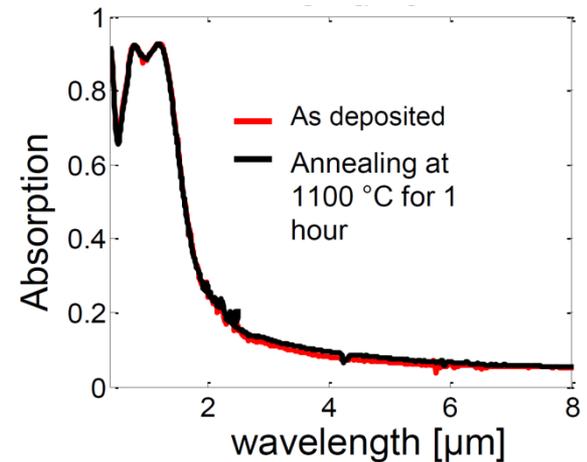
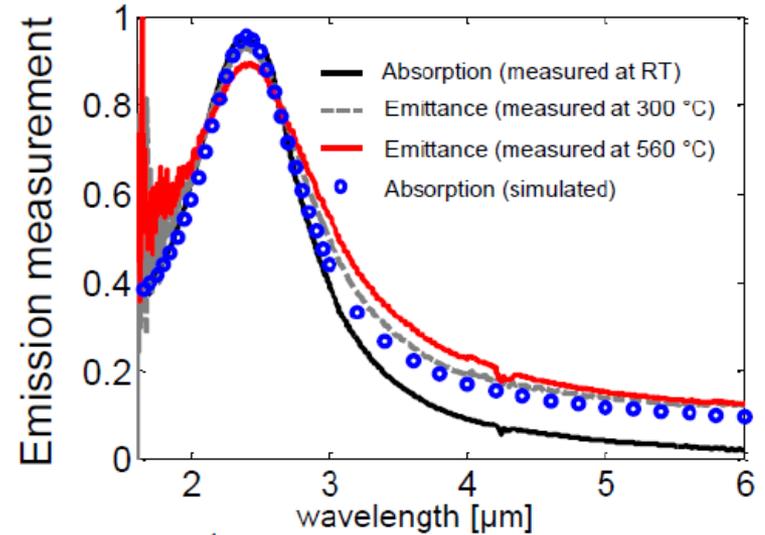
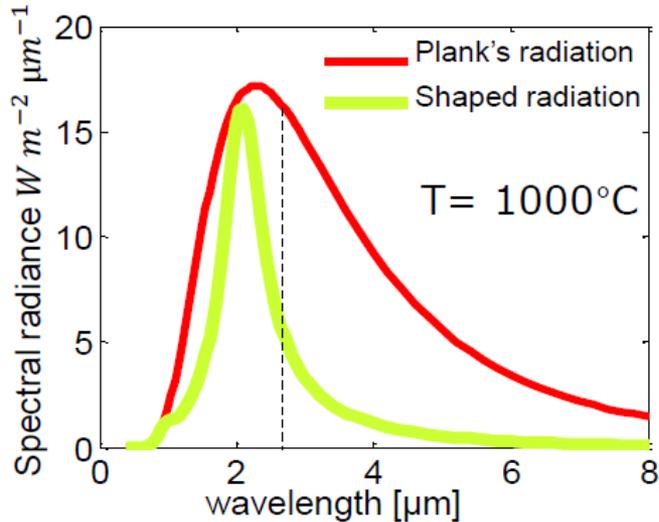
Furnace, 800 °C

Pulsed Laser 550 nm

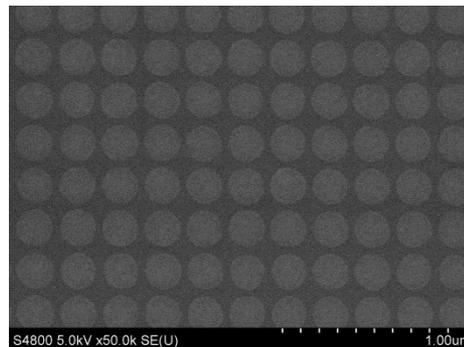


# Example: TiN Emitter for S/TPV

Emitter in the TPV cell: reshape the broadband spectrum of input thermal energy into emission above the bandgap of photovoltaic cells.



SEM image after annealing at 1100°C for 1h in the atmosphere



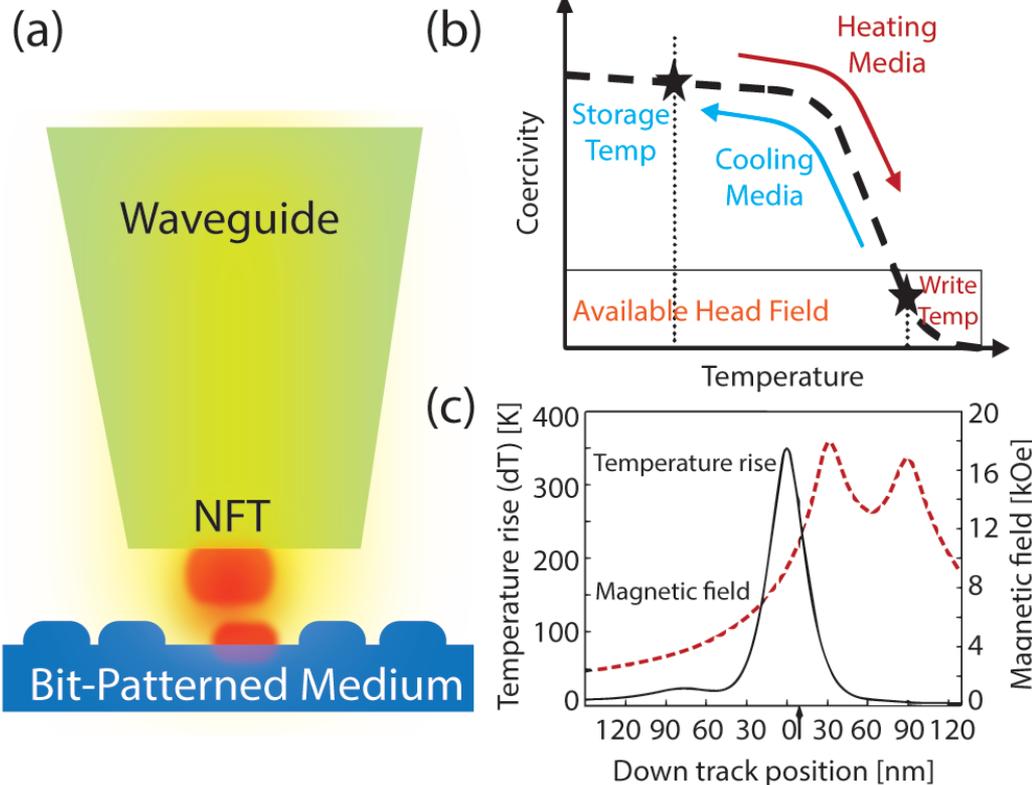
# Heat Assisted Magnetic Recording

Denser storage required - **smaller bit sizes**

Smaller bit sizes bring instabilities - **higher coercivity materials**

Higher coercivity material requires higher writing temperatures - **light induced heating**

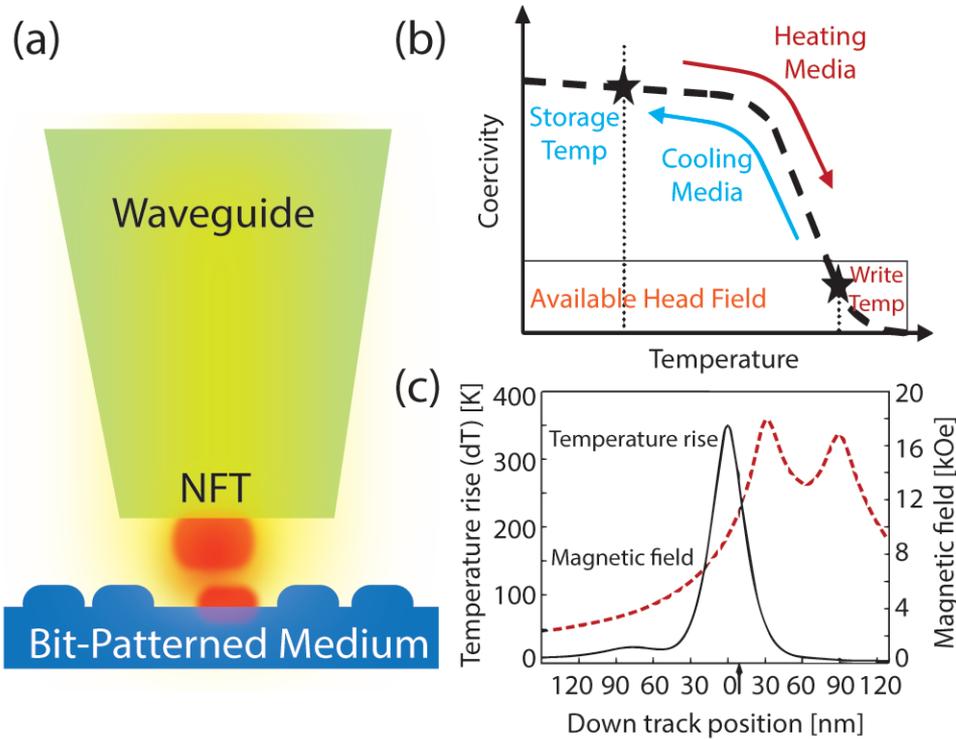
Sub-diffraction focusing required - **antenna for visible light**



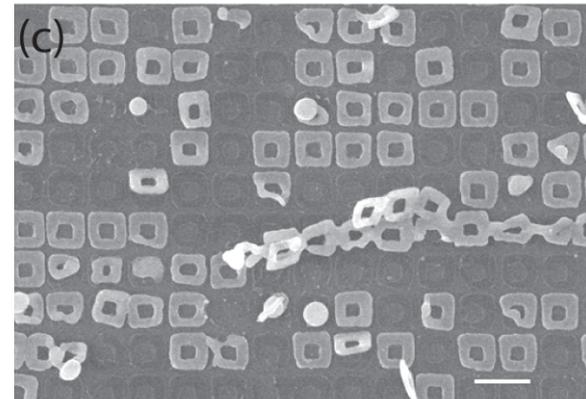
HAMR promises  
10 – 16X greater  
HDD storage  
densities!

**Temperatures up to 500 °C**

*Noble metals are good plasmonic materials,  
but not mechanically robust for HAMR operation.*



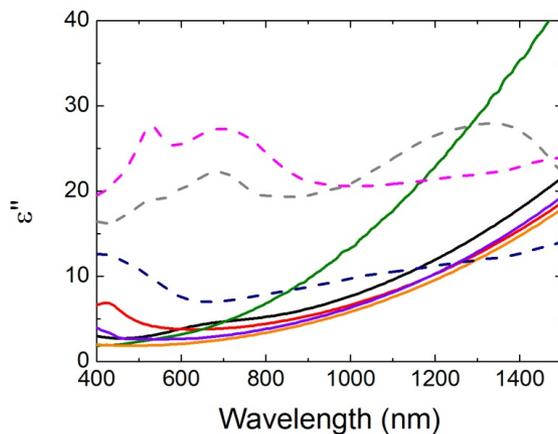
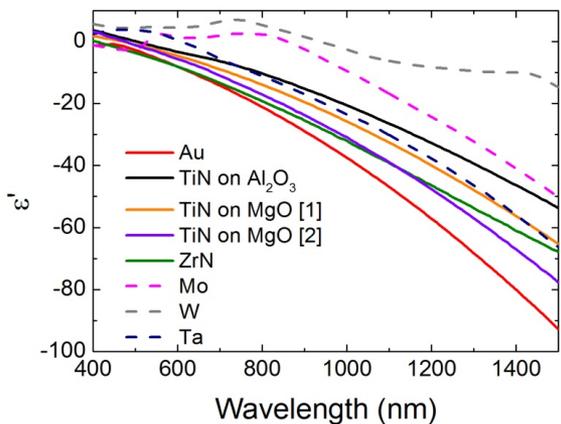
**OEMs can't devise robust heat source.**



*HAMR operation principles*

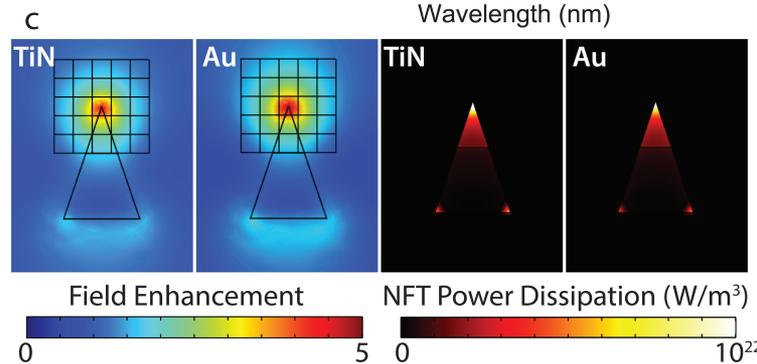
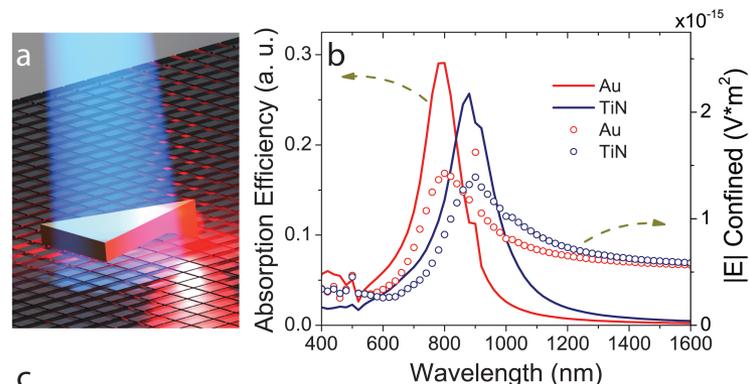
*Gold nanostructures after laser illumination.*

# TiN for HAMR

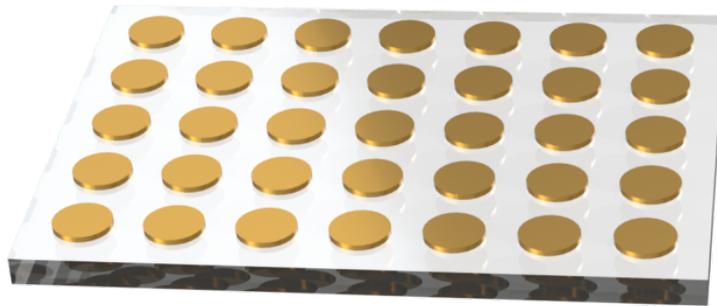


Optical Figure of Merit for TiN is close to Au

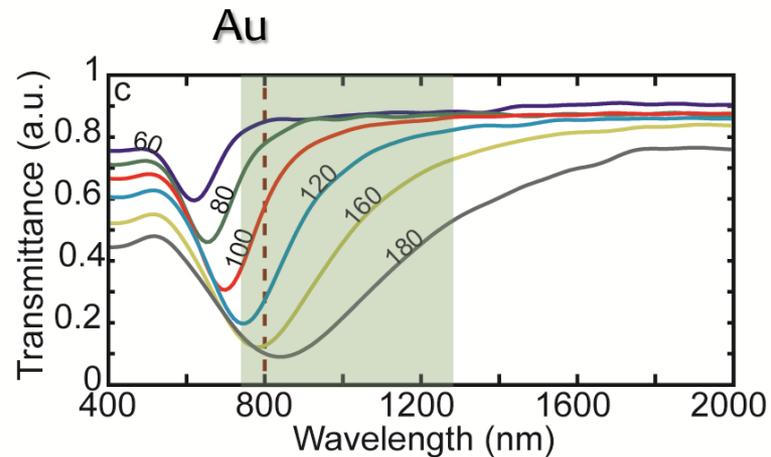
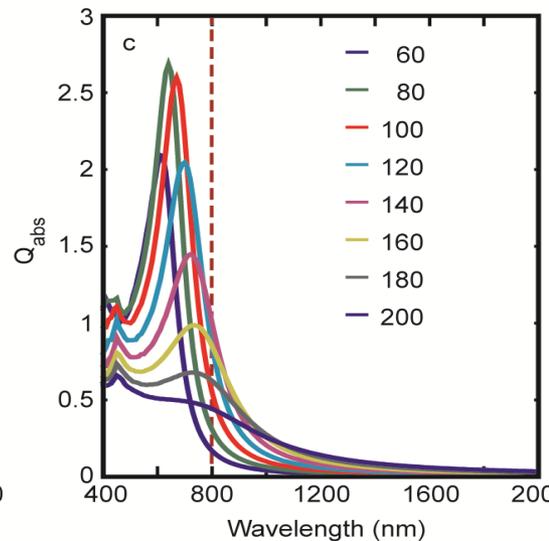
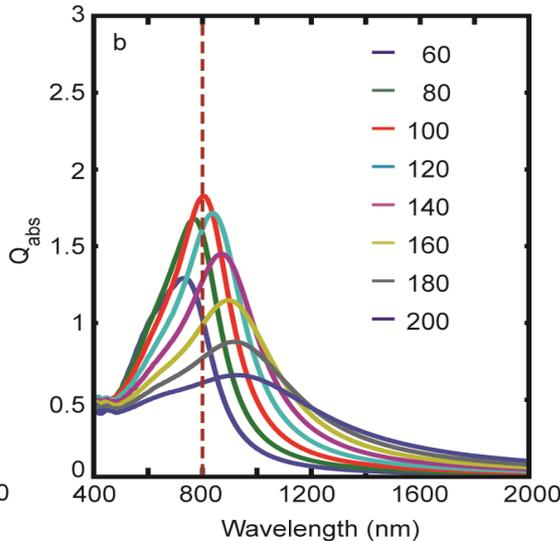
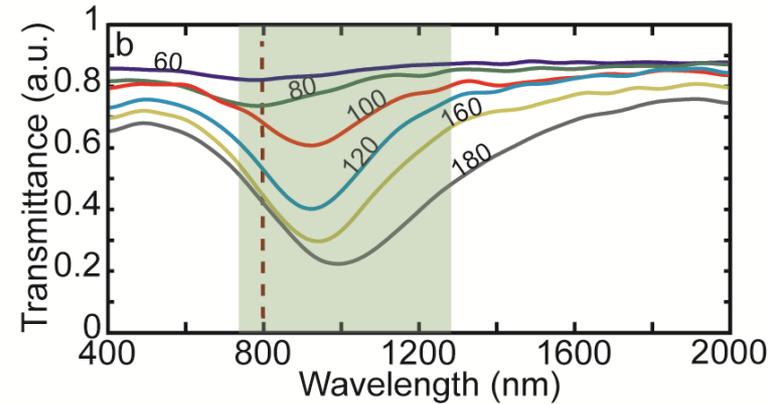
Material	Permittivity (real)	Permittivity (imaginary)	FOM ( $ \epsilon' /\epsilon''$ )
Au	-23.39	4.67	5.01
TiN ( $\text{Al}_2\text{O}_3$ )	-11.73	5.47	2.14
TiN (MgO) [1]	-15.57	3.68	4.23
TiN (MgO) [2]	-19.08	4.11	4.64
ZrN	-21.15	7.64	2.77
Mo	1.43	23.16	NA
W	4.21	19.41	NA
Ta	-12.89	8.15	1.58



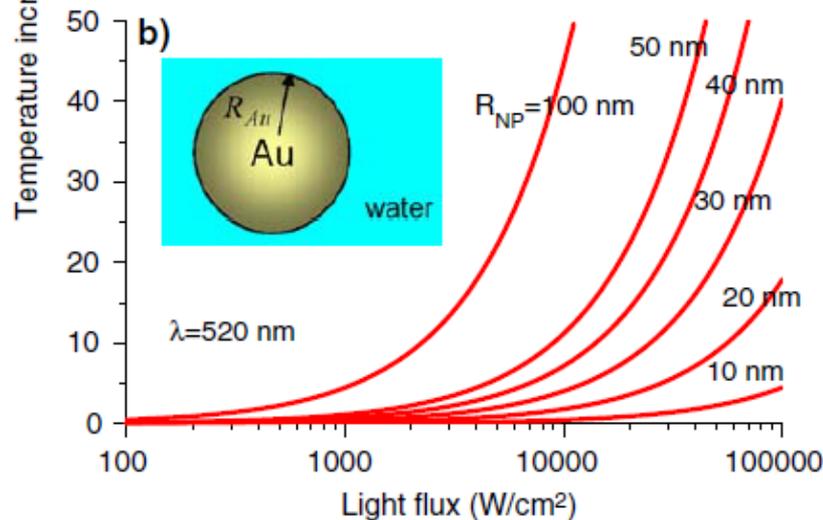
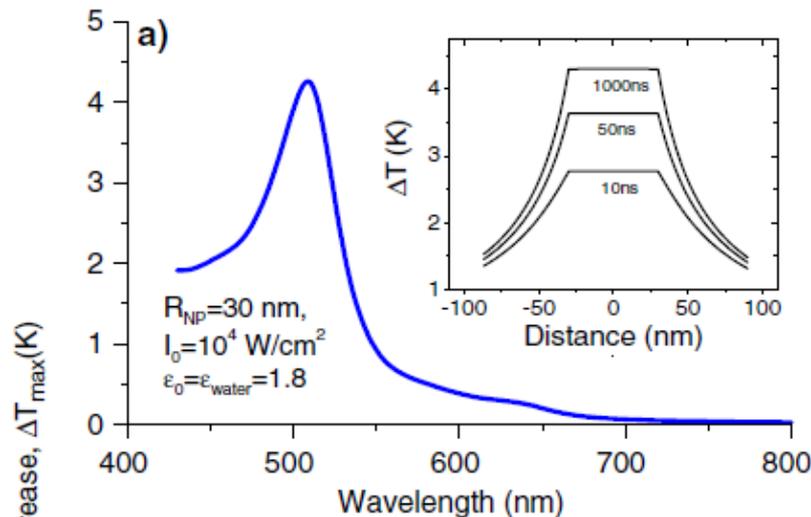
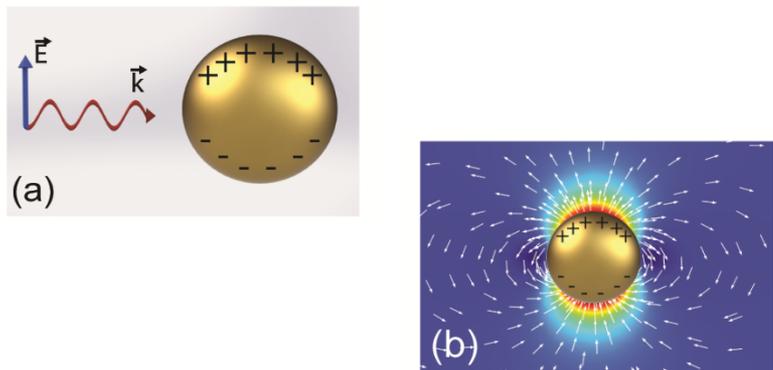
## Broad resonance with higher absorption in biological window: Therapeutical applications



TiN grown @ 800 °C



# Local heating



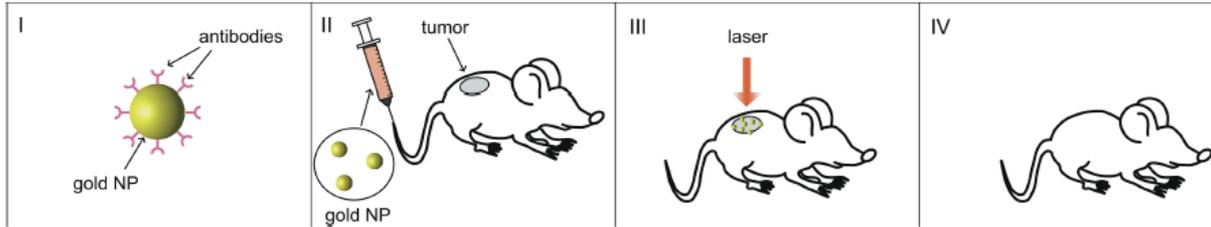
$$\Delta T(\mathbf{r}) = \frac{V_{NP} Q}{4\pi k_0 r} \quad (r > R_{NP})$$

$$Q = -\text{Re} \left[ i\omega \frac{\epsilon(\mathbf{r}) - 1}{8\pi} \mathbf{E}_0^2 \left| \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_m} \right|^2 \right]$$

$$Q = \sigma_{\text{abs}} I = \sigma_{\text{abs}} \frac{nc\epsilon_0}{2} |\mathbf{E}_0|^2$$

**TiN?**

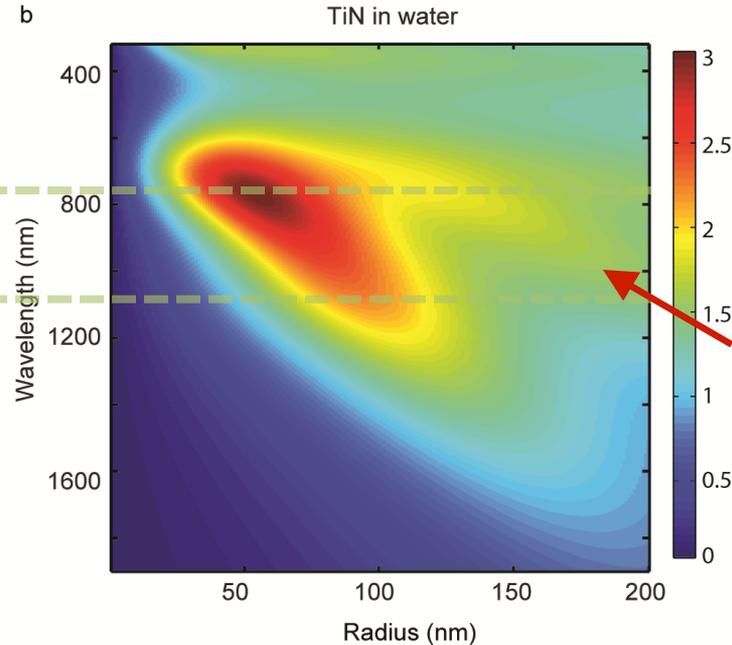
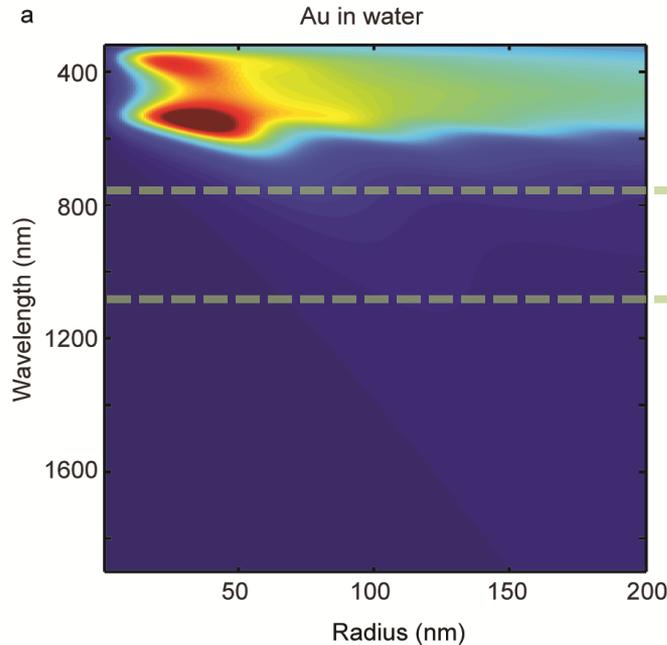
# Thermal Therapy - TiN



G. Baffou et al., *LPR* **7**, 2 (2013).  
J. M. Stern et al., *J. Urol.* **179**, 748 (2008).

$$Q = \sigma_{\text{abs}} I = \sigma_{\text{abs}} \frac{nc\epsilon_0}{2} |E_0|^2$$

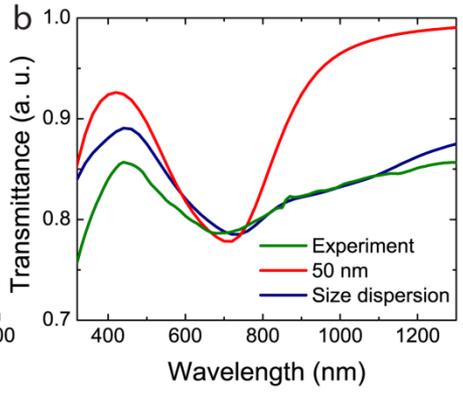
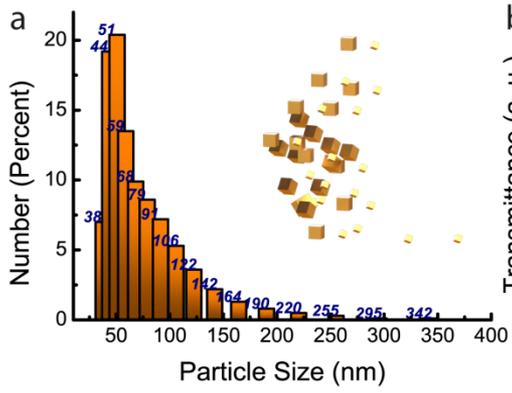
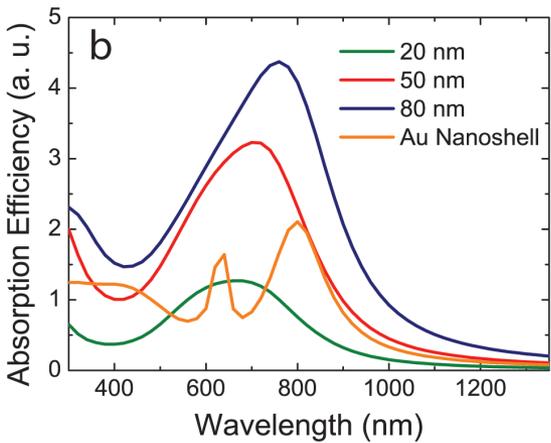
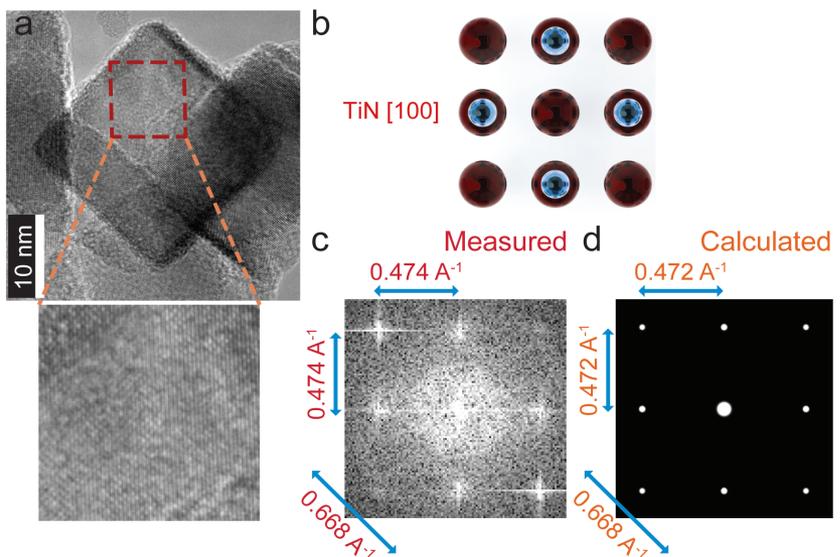
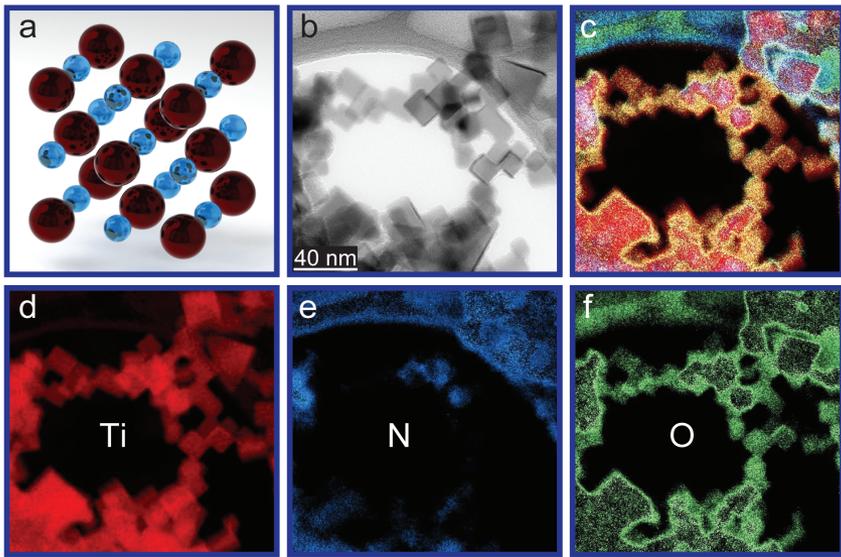
L. R. Hirsch et al., *PNAS* **100**, 13549 (2003).  
N. Halas, *MRS Bulletin* **30**, 362 (2005).  
B. E. Brinson et al., *Langmuir* **24**, 14166 (2008).



Transparency  
window

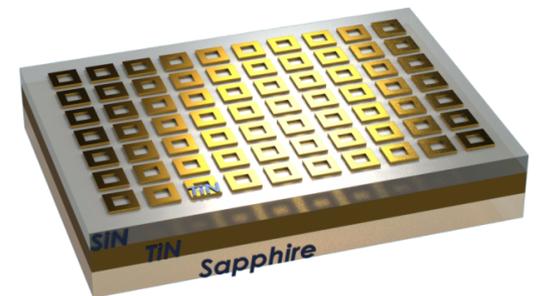
U. Guler et al., *Nano Letters* **13**, 6078 (2013)

# Plasmonic TiN in Colloids & photothermal therapy



Golden luster of dispersed TiN powder

- Introduction: Plasmonics & Metamaterials
- Material Requirements & Alternative Materials
- Transition Metal Nitrides
- Applications with Plasmonic Metal Nitrides
  - High Temperature
    - Thermophotovoltaics
    - Heat Assisted Magnetic Recording
    - Coherent thermal sources
  - Plasmonic photothermal therapy
  - **Quantum Photonics Application**



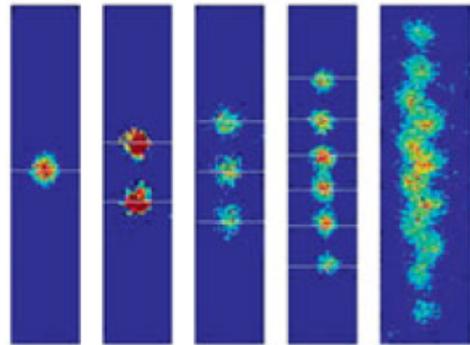
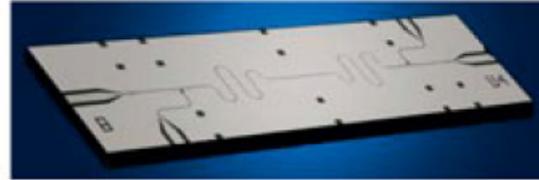


“Nature isn't classical dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical, and by golly it's a wonderful problem because it doesn't look so easy.”

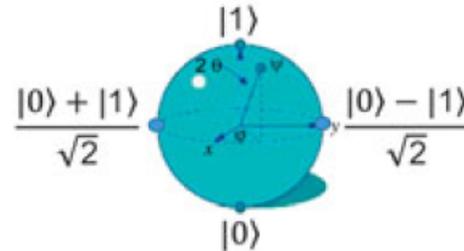
*R.P. Feynman, Int. J. Theor. Phys. 21, 467*

**Materials** **➔** **Quantum sensors, simulators & computers**

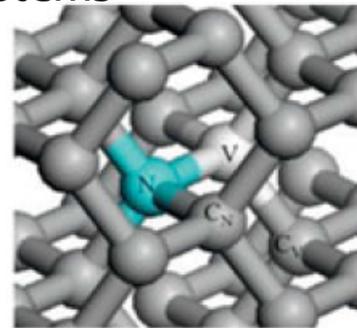
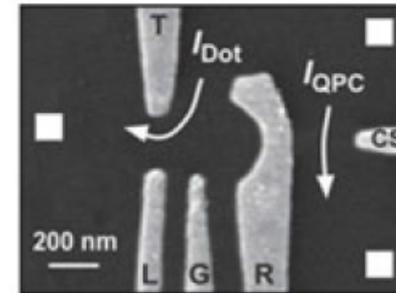
Superconducting resonators/Josephson junctions



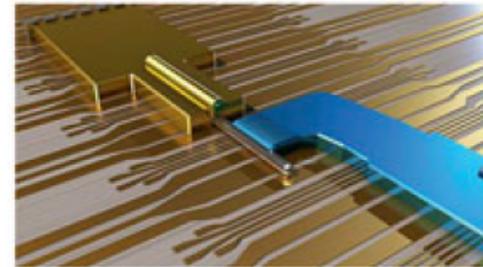
Trapped ion/atom systems



Gate-defined semiconductor structures



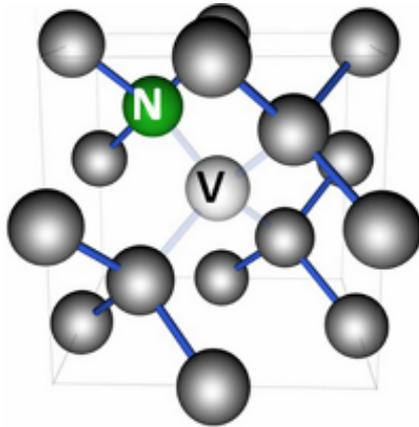
Atomic centers in solids



Majorana fermions in nanowire hybrid materials

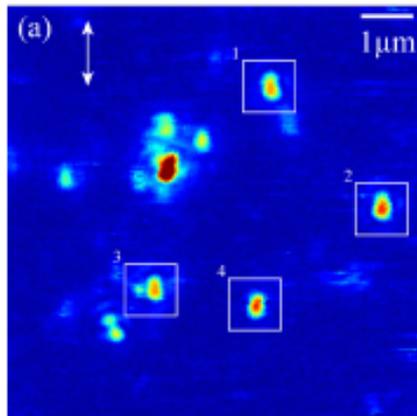
# Diamond NV center

Solid-state defect:  
artificial atom  
“with handles”



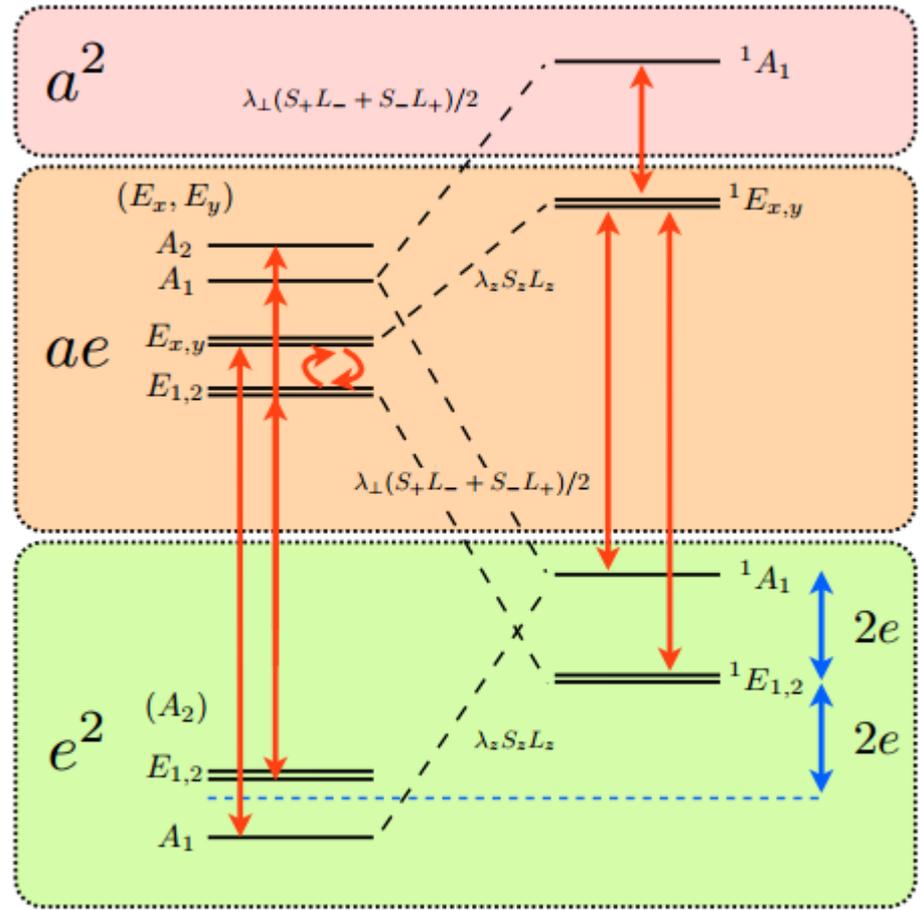
Jelezko et al., *Phys. Stat. Sol.* (2006)

Single-photon  
fluorescence  
at room  
temperature



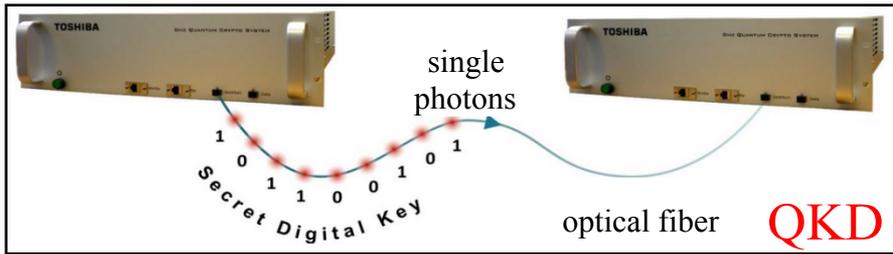
Dolan et al., *Opt. Express.* (2014)

Many degrees of freedom = many applications

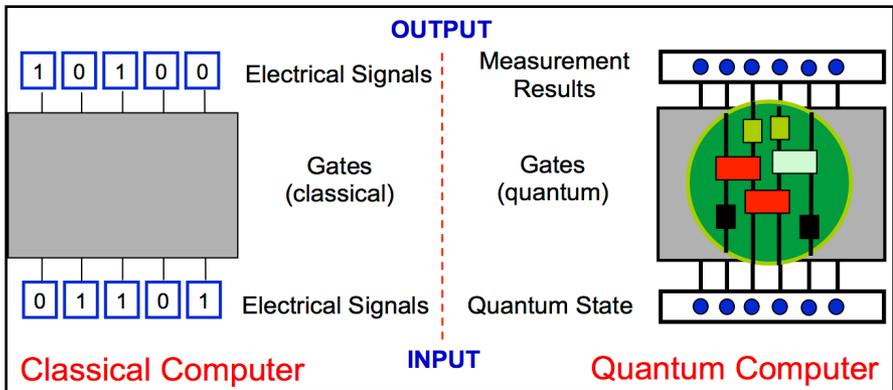


Maze et al., *New J. of Phys.* (2011)

## Quantum information



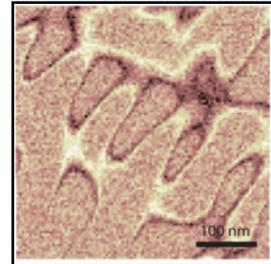
© 2013 Toshiba Research Europe Ltd



Andrew Daley, University of Strathclyde

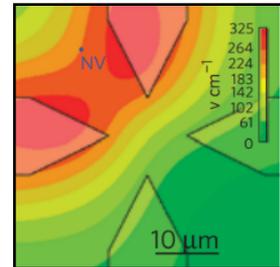
## Nanoscale sensing

Magnetic fields



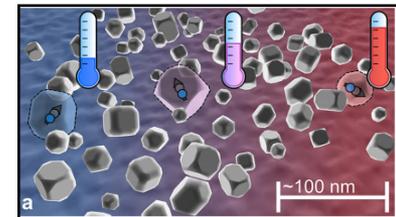
Hong et al. *MRS Bulletin* (2013)

Electric fields



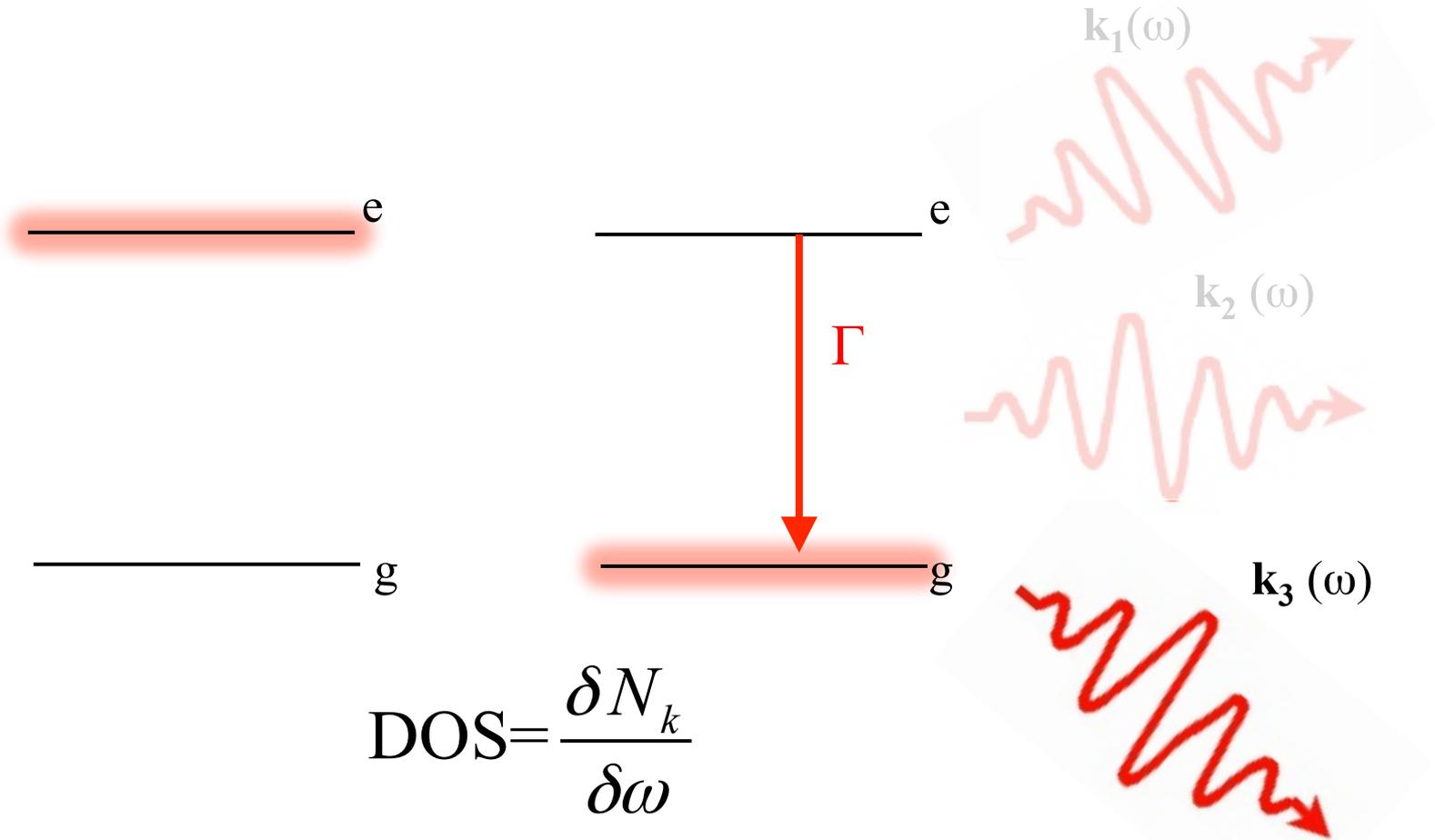
Dolde et al. *Nat. Phys.* (2011)

Temperature



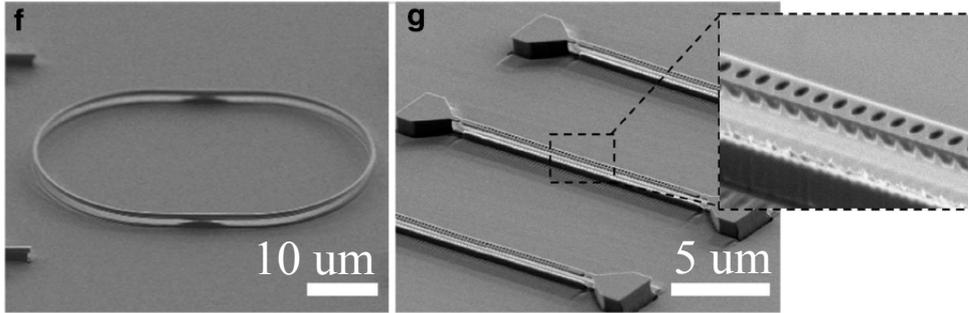
Neumann et al. *Nanolett.* (2013)

# Enhancing the emission rate



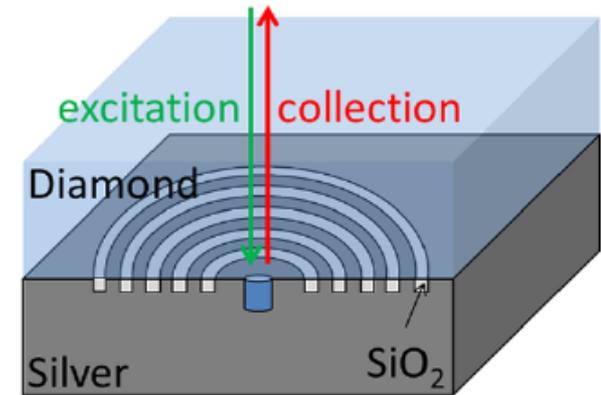
$$\Gamma \sim [\text{dipole matrix moment}]^2 \times \text{DOS}$$

# Resonant ways to enhance emission rate



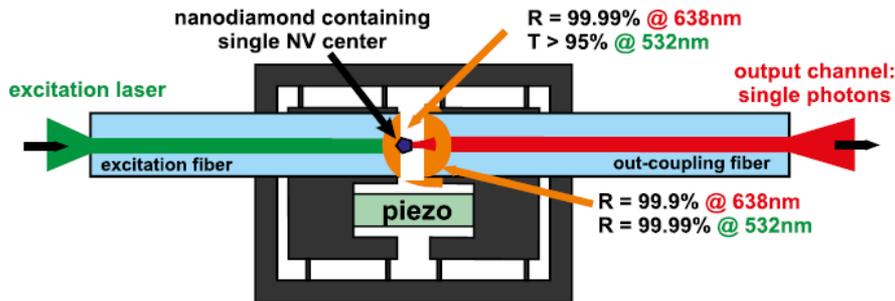
diamond racetrack resonator  
& nanobeam photonic crystal cavity

*M. J. Burek et al., Nat. Comm. 2014 (Lukin & Loncar)*



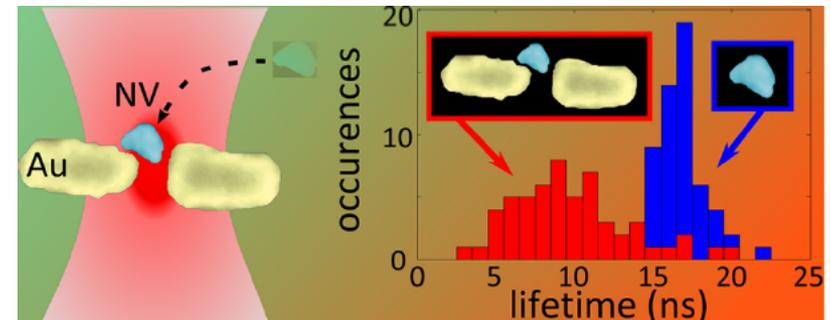
diamond-silver apertures

*J. T. Choy et al., APL 2013 (Loncar)*



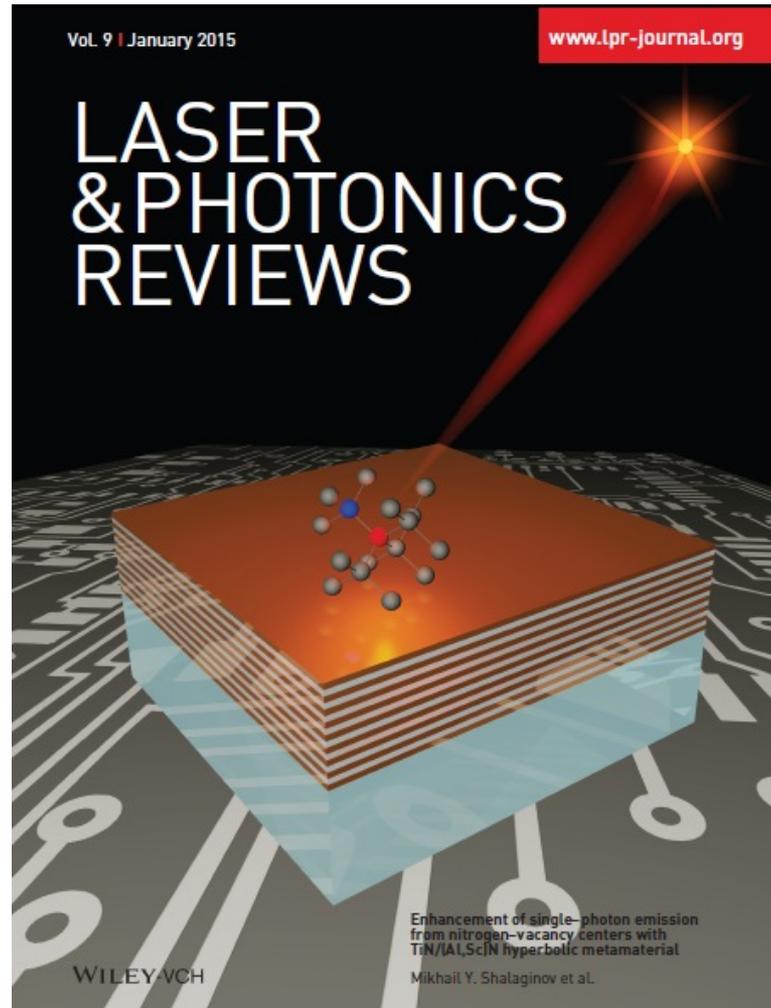
all-fiber cavity

*R. Albrecht et al., APL 2014 (Benson)*



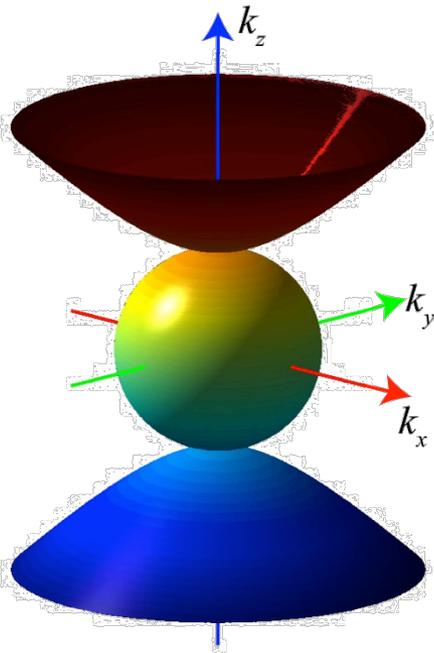
plasmonic gap-antenna

*M. Geiselmann et al., Nano Lett 2014 (Quidant)*



Shalaginov, et al, LPR (2105): Enhancement of single-photon emission from NV centers with TiN/(AlSc)N hyperbolic metamaterial

# Metamaterials with Hyperbolic Dispersion



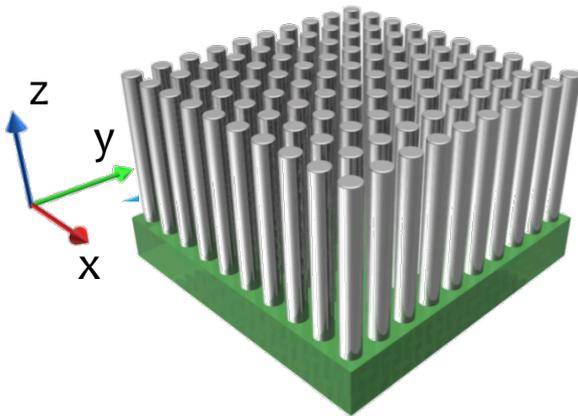
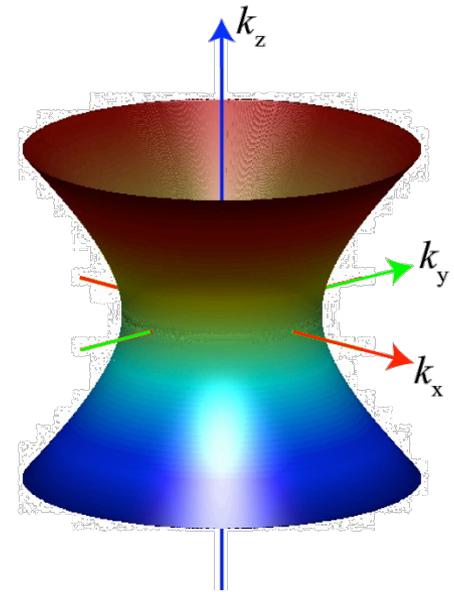
normal dispersion

$$\frac{k_x^2 + k_y^2 + k_z^2}{\epsilon} = \left(\frac{\omega}{c}\right)^2$$

hyperbolic dispersion

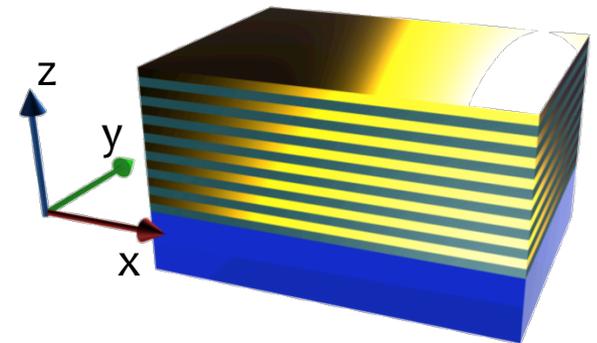
$$\frac{k_x^2 + k_y^2}{\epsilon_p} - \frac{k_z^2}{|\epsilon_{\perp}|} = \left(\frac{\omega}{c}\right)^2$$

$$-\frac{k_x^2 + k_y^2}{|\epsilon_p|} + \frac{k_z^2}{\epsilon_{\perp}} = \left(\frac{\omega}{c}\right)^2$$



transverse positive (type I)

Smith & Schurig PRL (2003)  
Jacob, et al, Opt. Express (2006)

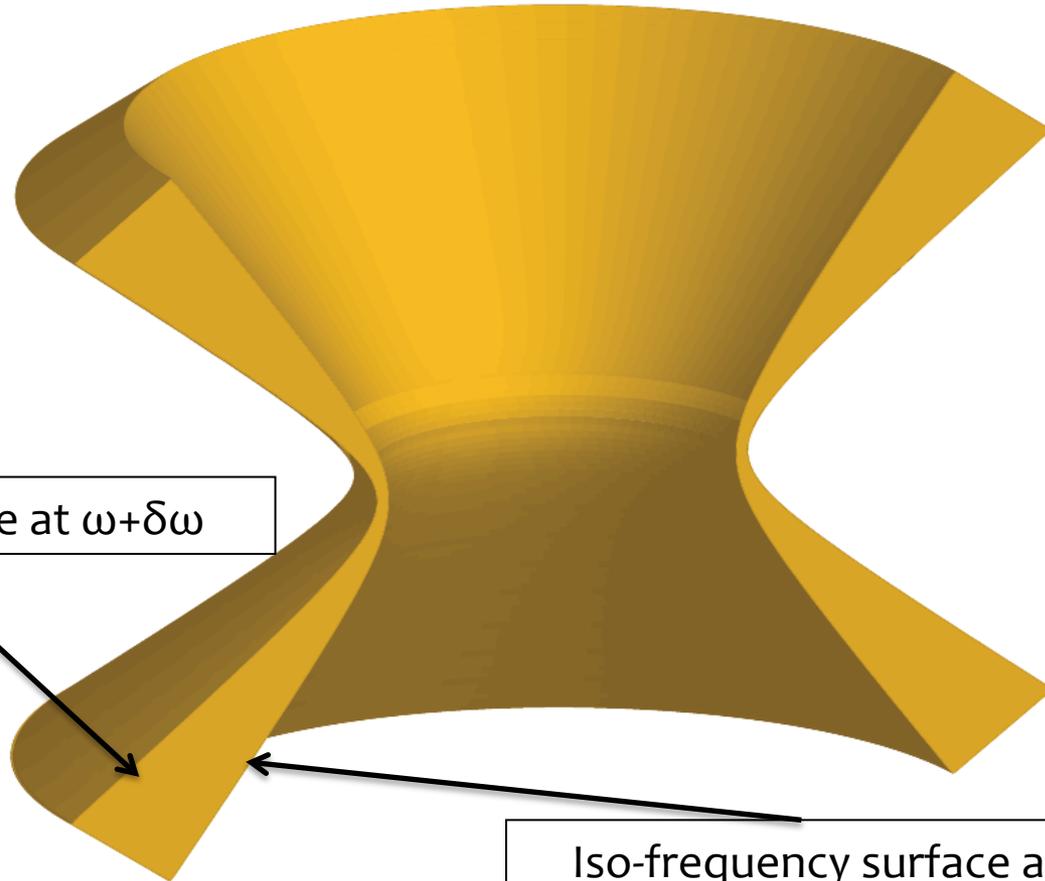


transverse negative (type II)

# PHOTONIC DENSITY OF STATES (PDOS)

Fermi's Golden  
Rule:

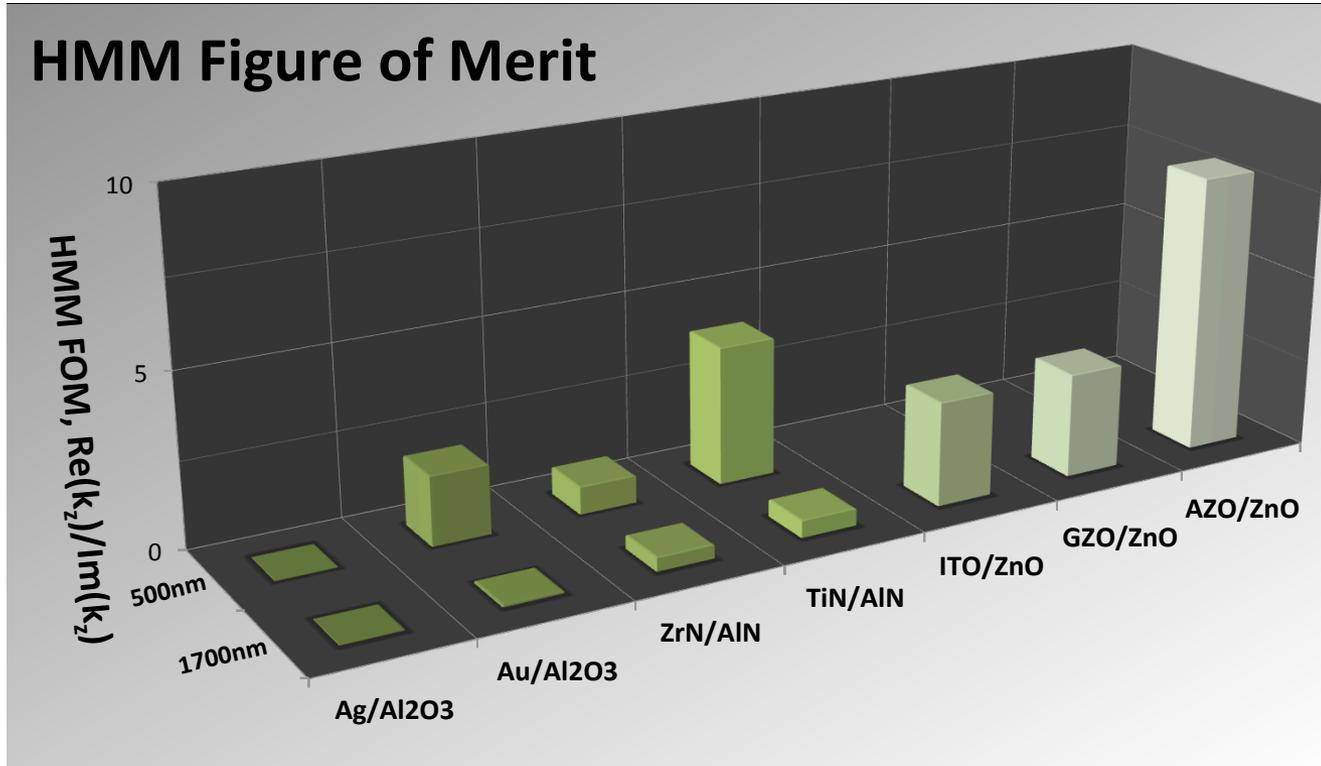
$$\Gamma = \frac{2\pi}{\hbar} \rho(\omega_f) \times (\text{Dipole matrix element})^2$$



unbounded  $|k|$   
**singularity in PDOS**

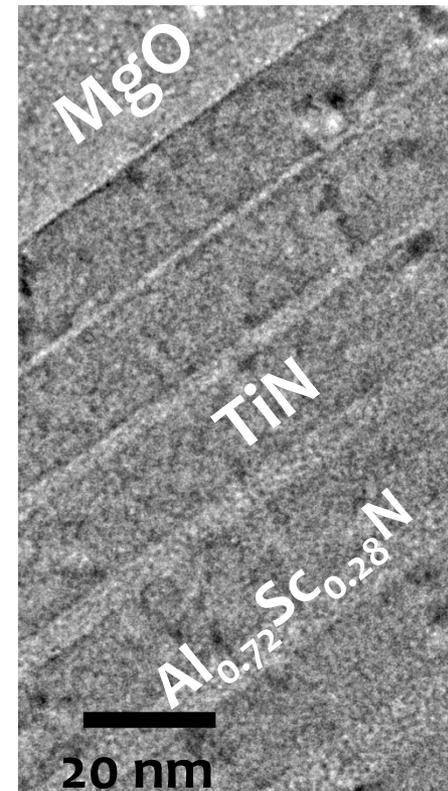
$$\text{DOS} = \infty, \forall \omega !$$

## HMM Figure of Merit



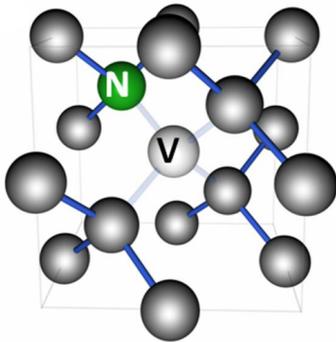
$$\text{Re}(\beta_{\perp})/\text{Im}(\beta_{\perp})$$

Describes the transmission of a low-loss HMM



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

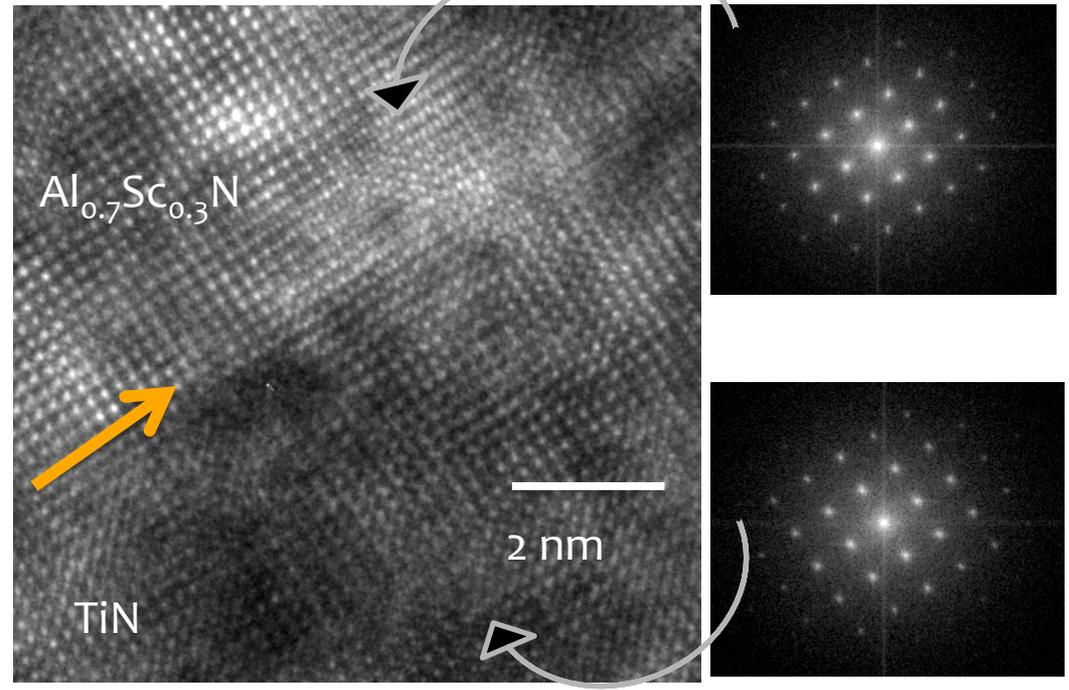
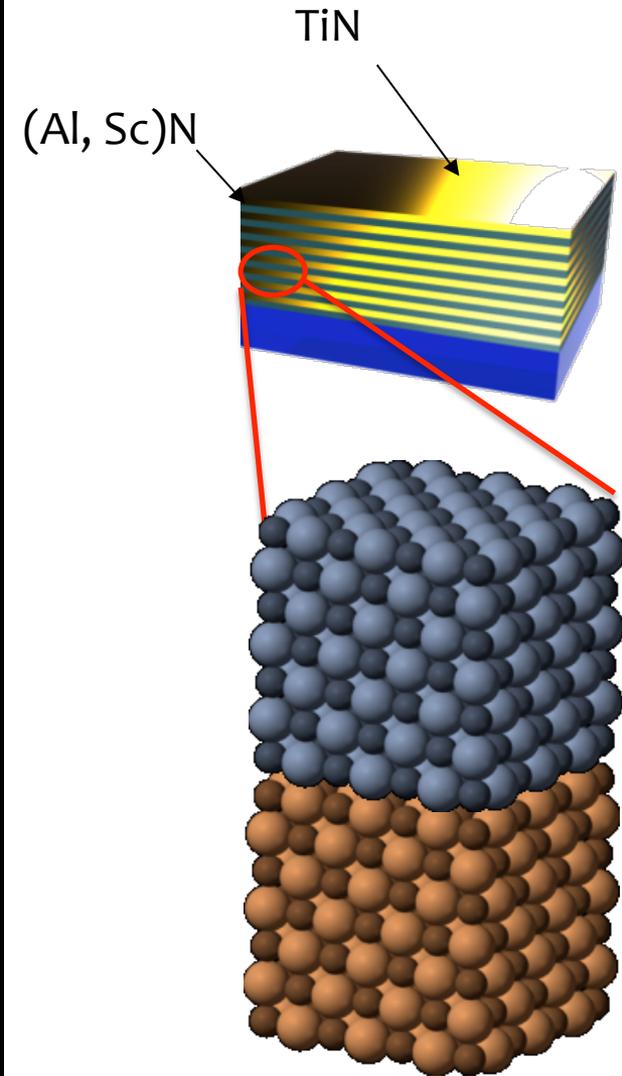
## Nitrogen-vacancy centers in diamond



Color centers in diamond

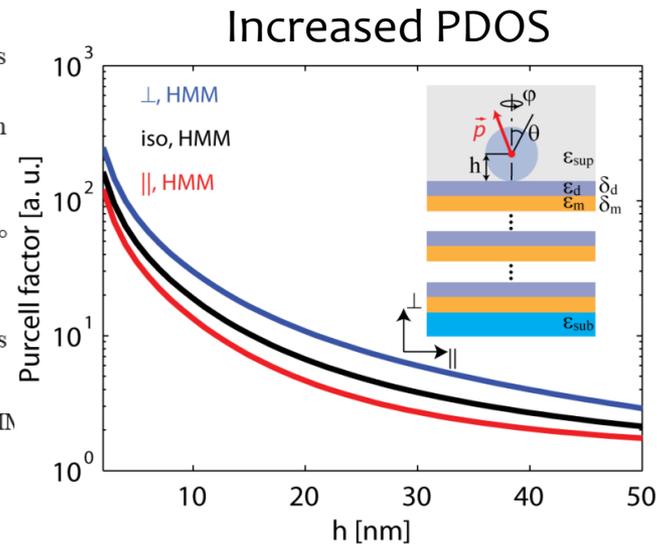
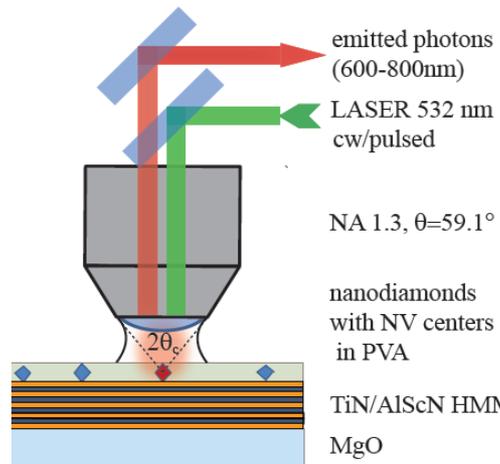
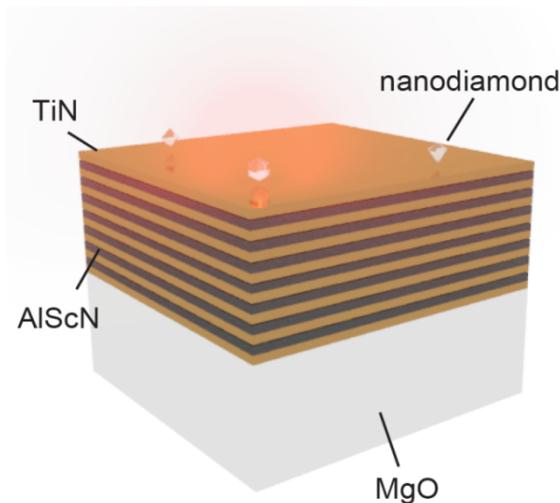
- Photostable source
- Operates at room temperature
- Relatively simple and inexpensive fabrication
- Broadband emission
- Long spin coherence time

# HMM based on CMOS-compatible materials

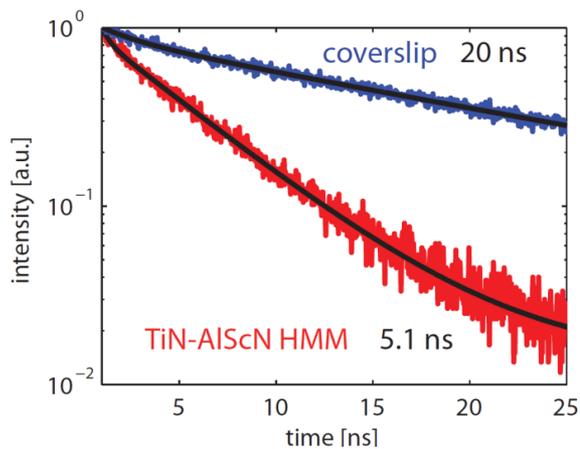


- Extremely high broadband photonic density of states
- 1<sup>st</sup> epitaxial single crystalline metal/semiconductor superlattice
- CMOS-compatible

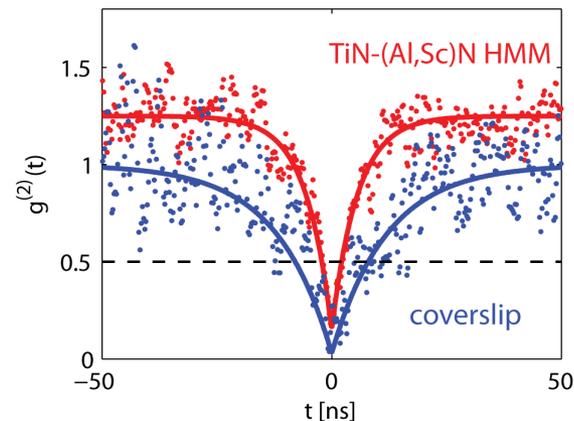
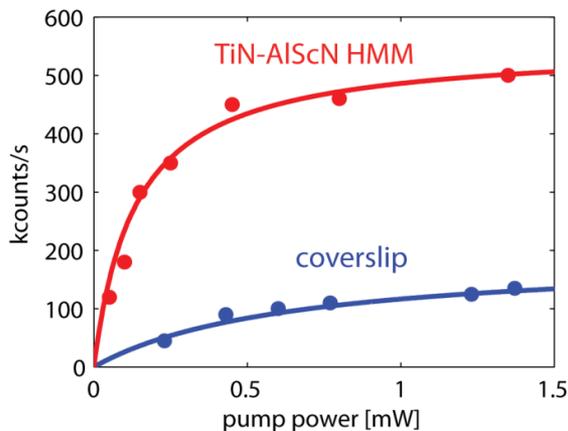
# Single NV centers coupled to TiN HMM



### Fluorescence lifetime



### Collected emission rate Photon anti-bunching statistics



# TEAM AND SUPPORT



Shalaev Group



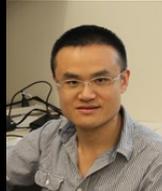
Dr. Marcello Ferrera



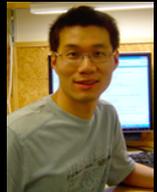
Dr. Simeon Bogdanov



Dr. Urcan Guler



Dr. Xiangeng Meng



Jieran Feng



Rohith Chandrasekar



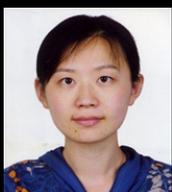
Amr Shaltout



Mikhail Shalaginov



Di Wang



Jingjing Liu



Harsha Eragmareddy



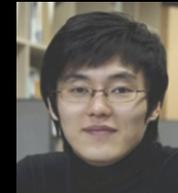
Clayton DeVault



Dewan Woods



Boltasseva Group



Jongbum Kim



Nate Kinsey



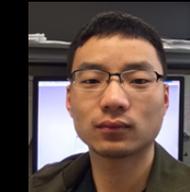
Justus Ndukaife



Aveek Dutta



Krishakali Choudhuri



Zhouxian Wang



Sajid Choudhury



Ikuko Kitamura

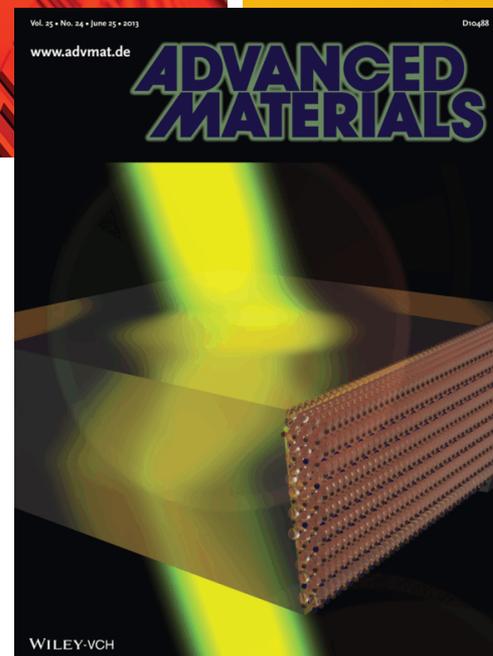
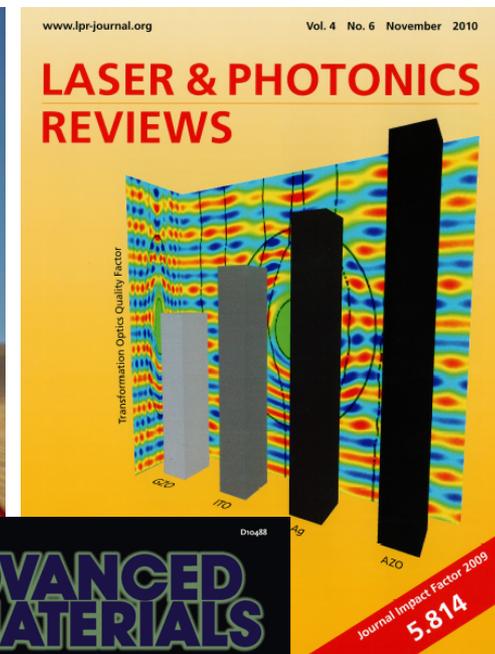
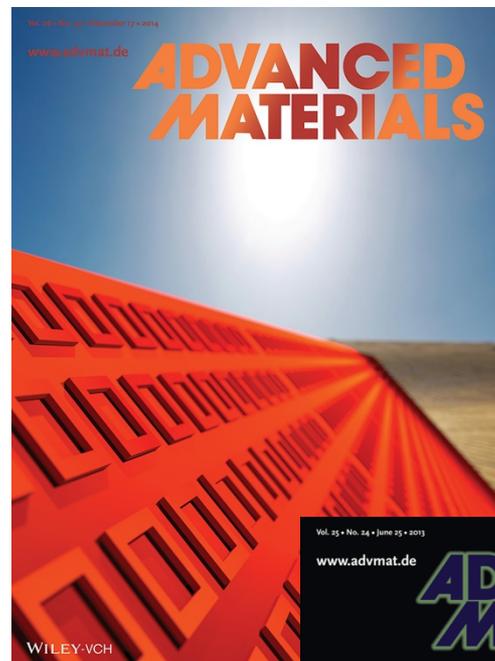
## Collaborations

- Prof. A. Kildishev (Purdue)
- Prof. A. Alu (UTexas Austin)
- Prof. N. Engheta (UPenn)
- Prof. M. Ferrera (Heriot-Watt)

## Former members

- Dr. G. Naik (Stanford)
- Dr. N. Emani (DSI Singapore)

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## Low-Loss Plasmonic Metamaterials

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